CHEMISTRY - ACADEMIC AND CAREER PREPARATION



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Chemistry - Academic and Career Preparation

Adrienne Richards

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TABLE OF CONTENTS

Licensing

1: Nature of Matter

- 1.1: Prelude to Chemistry, Matter, and Measurement
- 1.2: What is Chemistry?
- 1.3: The Classification of Matter
- 1.4: Prelude to Elements, Atoms, and the Periodic Table
- 1.5: Atomic Theory
- 1.6: Dalton's Atomic Theory
- 1.7: Conservation of Mass
- 1.8: Law of Definite Proportions
- 1.9: Law of Multiple Proportions
- 1.10: Classifying Matter According to Its Composition
- 1.11: The Structure of Atoms
- 1.12: Protons
- 1.13: Electrons
- 1.14: Neutrons
- 1.15: Nuclei of Atoms
- 1.16: Atomic Masses

2: Trends and Bonding

- 2.1: The Periodic Table
- 2.2: Periodic Trends- Atomic Radius
- 2.3: Periodic Trends- Ionization Energy
- 2.4: Periodic Trends- Electronegativity
- 2.5: Prelude to Ionic Bonding and Simple Ionic Compounds
- 2.6: Prelude to Covalent Bonding and Simple Molecular Compounds
- 2.7: Lewis Dot and Bonding
- 2.8: Covalent Bonds
- 2.9: Drawing Lewis Structures
- 2.10: Characteristics of Molecules
- 2.11: Exceptions to the Octet Rule

3: Nomenclature

- 3.1: Formulas for Ionic Compounds
- 3.2: Ionic Nomenclature
- 3.3: Covalent Compounds - Formulas and Names
- 3.4: Naming Acids
- 3.5: Names and Formulas of Bases

4: Chemical Calculations 1

- 4.1: Prelude to Introduction to Chemical Reactions
- 4.2: The Law of Conservation of Matter
- 4.3: Chemical Equations

- 4.4: Some Types of Chemical Reactions
- 4.5: Single Replacement Reactions
- 4.6: Activity Series
- 4.7: Double Replacement Reactions
- 4.8: Avogadro's Number
- 4.9: The Mole
- 4.10: Molar Mass
- 4.11: Atomic and Molar Masses
- 4.12: Mole-Mass Conversions
- 4.13: Percent Composition
- 4.14: Percent of Water in a Hydrate

5: Chemical Calculations 2

- 5.1: Everyday Stoichiometry
- 5.2: Mole Ratios
- 5.3: Quantitative Relationships Based on Chemical Equations
- 5.4: Mole-Mole Relationships in Chemical Reactions
- 5.5: Mole-Mass and Mass-Mass Problems
- 5.6: Mass-Volume and Volume-Mass Stoichiometry
- 5.7: Concentration
- 5.8: Limiting Reactant
- 5.9: Determining the Limiting Reactant
- 5.10: Theoretical Yield and Percent Yield
- 5.11: Percent Error

6: Organic Chemistry

- 6.1: Organic Chemistry
- 6.2: Structures and Names of Alkanes
- 6.3: Branched-Chain Alkanes
- 6.4: Condensed Structural and Line-Angle Formulas
- 6.5: IUPAC Nomenclature
- 6.6: Constitutional Isomers
- 6.7: Physical Properties of Alkanes
- 6.8: Chemical Properties of Alkanes
- 6.9: Cycloalkanes
- 6.10: Alkenes- Structures and Names
- 6.11: Physical Properties of Alkenes
- 6.12: Chemical Properties of Alkenes
- 6.13: Polymers
- 6.14: Alkynes
- 6.15: Aromatic Compounds- Benzene
- 6.16: Structure and Nomenclature of Aromatic Compounds

7: Chemistry in the Environment

- 7.1: Prelude to Solids, Liquids, and Gases
- 7.2: Solids and Liquids
- 7.3: Gases and Pressure
- 7.4: Gas Laws

- 7.5: Gay-Lussac's Law
- 7.6: Prelude to Acids and Bases
- 7.7: Arrhenius Definition of Acids and Bases
- 7.8: Brønsted-Lowry Definition of Acids and Bases
- 7.9: Water - Both an Acid and a Base
- 7.10: The Strengths of Acids and Bases
- 7.11: The pOH Concept
- 7.12: Titration Experiment
- 7.13: Titration Calculations
- 7.14: Buffers

8: Electrochemistry

- 8.1: Oxidation-Reduction (Redox) Reactions
- 8.2: Redox Reactions in Organic Chemistry and Biochemistry
- 8.3: Electrolytic Cells
- 8.4: Electrochemical Corrosion

Index

Glossary

Detailed Licensing

Licensing

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

CHAPTER OVERVIEW

1: Nature of Matter

1.1: Prelude to Chemistry, Matter, and Measurement
1.2: What is Chemistry?
1.3: The Classification of Matter
1.4: Prelude to Elements, Atoms, and the Periodic Table
1.5: Atomic Theory
1.6: Dalton's Atomic Theory
1.7: Conservation of Mass
1.8: Law of Definite Proportions
1.9: Law of Multiple Proportions
1.10: Classifying Matter According to Its Composition
1.11: The Structure of Atoms
1.12: Protons
1.13: Electrons
1.14: Neutrons
1.15: Nuclei of Atoms
1.16: Atomic Masses

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1.1: Prelude to Chemistry, Matter, and Measurement

In April 2003, the US Pharmacopeia, a national organization that establishes quality standards for medications, reported a case in which a physician ordered “morphine [a powerful painkiller] 2–3 mg IV [intravenously] every 2–3 hours for pain.” A nurse misread the dose as “23 mg” and thus administered approximately 10 times the proper amount to an 8-year-old boy with a broken leg. The boy stopped breathing but was successfully resuscitated and left the hospital three days later.

Quantities and measurements are as important in our everyday lives as they are in medicine. The posted speed limits on roads and highways, such as 55 miles per hour (mph), are quantities we might encounter all the time. Both parts of a quantity, the amount (55) and the unit (mph), must be properly communicated to prevent potential problems. In chemistry, as in any technical endeavor, the proper expression of quantities is a necessary fundamental skill. As we begin our journey into chemistry, we will learn this skill so that errors—from homework mistakes to traffic tickets to more serious consequences—can be avoided.

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1.2: What is Chemistry?

Learning Objectives

1. Define chemistry in relation to other sciences.
2. Identify the general steps in the scientific method.

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 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 **1.2.1**). 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.

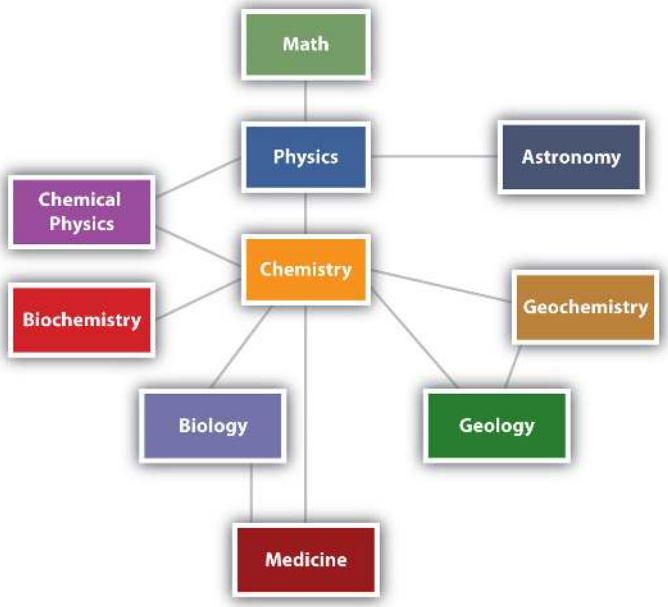


Figure **1.2.1**: The Relationships between Some of the Major Branches of Science. Chemistry lies more or less in the middle, which emphasizes its importance to many branches of science.

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 **1.2.1** shows how many of the individual fields of science are related.

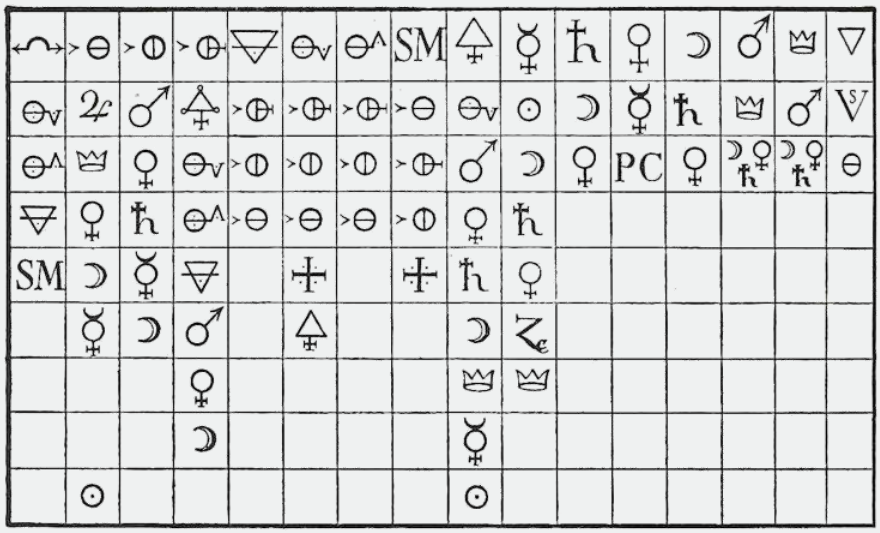
> *There are many other fields of science in addition to the ones listed here.*

Alchemy

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.

Exercise 1.2.1

Which fields of study are branches of science? Explain.

a. sculpture
b. astronomy

Answer a

Sculpture is not considered a science because it is not a study of some aspect of the natural universe.

Answer b

Astronomy is the study of stars and planets, which are part of the natural universe. Astronomy is therefore a field of science.

Exercise 1.2.2

Which fields of study are branches of science?

a. physiology (the study of the function of an animal's or a plant's body)
b. geophysics
c. agriculture
d. politics

Answer

a, b and c only

How do scientists work? Generally, they follow a process called the scientific method. The scientific method is an organized procedure for learning answers to questions and making explanations for observations. To find the answer to a question (for example, “Why do birds fly toward Earth’s equator during the cold months?”), a scientist goes through the following steps, which are also illustrated in Figure **1.2.2**:

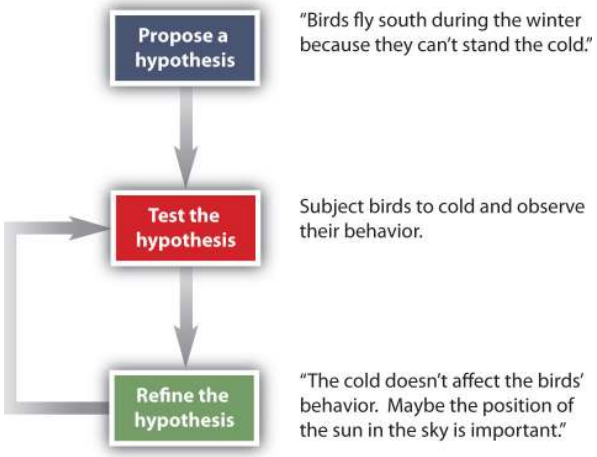


Figure **1.2.2**: The General Steps of the Scientific Method. After an observation is made or a question is identified, a hypothesis is made and experiments are designed to test the hypothesis.

The steps may not be as clear-cut in real life as described here, but most scientific work follows this general outline.

1. **Propose a hypothesis.** A scientist generates a testable idea, or hypothesis, to try to answer a question or explain an observation about how the natural universe works. Some people use the word *theory* in place of hypothesis, but the word hypothesis is the proper word in science. For scientific applications, the word theory is a general statement that describes a large set of observations and data. A theory represents the highest level of scientific understanding.
2. **Test the hypothesis.** A scientist evaluates the hypothesis by devising and carrying out experiments to test it. If the hypothesis passes the test, it may be a proper answer to the question. If the hypothesis does not pass the test, it may not be a good answer.
3. **Refine the hypothesis if necessary.** Depending on the results of experiments, a scientist may want to modify the hypothesis and then test it again. Sometimes the results show the original hypothesis to be completely wrong, in which case a scientist will have to devise a new hypothesis.

Not all scientific investigations are simple enough to be separated into these three discrete steps. But these steps represent the general method by which scientists learn about our natural universe.

1.2.3 Exercise

Define science and chemistry.

Answer

Science is a process by which we learn about the natural universe by observing, testing, and then generating models that explain our observations. Chemistry is the study of matter.

1.2.4 Exercise

Name the steps of the scientific method.

Answer

After identifying the problem or making an observation, propose a hypothesis, test the hypothesis, and refine the hypothesis, if necessary

Key Takeaways

- Chemistry is the study of matter and how it behaves.
- The scientific method is the general process by which we learn about the natural universe.

1. Based on what you know, which fields are branches of science?

    a. meteorology (the study of weather)
    b. astrophysics (the physics of planets and stars)
    c. economics (the study of money and monetary systems)
    d. astrology (the prediction of human events based on planetary and star positions)
    e. political science (the study of politics)

2. Based on what you know, which fields are a branches of science?

    a. history (the study of past events)
    b. ornithology (the study of birds)
    c. paleontology (the study of fossils)
    d. zoology (the study of animals)
    e. phrenology (using the shape of the head to determine personal characteristics)

3. Which of the following are examples of matter?

    a. a baby
    b. an idea
    c. the Empire State Building
    d. an emotion
    e. the air
    f. Alpha Centauri, the closest known star (excluding the sun) to our solar system

4. Which of the following are examples of matter?

    a. your textbook
    b. brain cells
    c. love
    d. a can of soda
    e. breakfast cereal

5. Suggest a name for the science that studies the physics of rocks and the earth.
6. Suggest a name for the study of the physics of living organisms.
7. Engineering is the practical application of scientific principles and discoveries to develop things that make our lives easier. Is medicine science or engineering? Justify your answer.
8. Based on the definition of engineering in Exercise 7, would building a bridge over a river or road be considered science or engineering? Justify your answer.
9. When someone says, “I have a theory that excess salt causes high blood pressure,” does that person really have a theory? If it is not a theory, what is it?
10. When a person says, “My hypothesis is that excess calcium in the diet causes kidney stones,” what does the person need to do to determine if the hypothesis is correct?
11. Some people argue that many scientists accept many scientific principles on faith. Using what you know about the scientific method, how might you argue against that assertion?
12. Most students take multiple English classes in school. Does the study of English use the scientific method?

Answers

1.
   a. science
   b. science
   c. not science
   d. not science
   e. not science

2.
   a. not science
   b. science
   c. science
   d. science
   e. not science

3.
   a. matter
   b. not matter
   c. matter
   d. not matter
   e. matter
   f. matter

4.
   a. matter
   b. matter
   c. not matter
   d. matter
   e. matter

5. geophysics
6. biophysics
7. Medicine is probably closer to a field of engineering than a field of science, but this may be arguable. Ask your doctor.
8. Engineering
9. In scientific terms, this person has a hypothesis.
10. Conduct experiments to determine if kidney stones contain calcium.
11. Science is based on reproducible facts, not blind belief.
12. No.

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1.3: The Classification of Matter

Learning Objectives

- Use physical and chemical properties, including phase, to describe matter.
- Identify a sample of matter as an element, a compound, or a mixture.

Part of understanding matter is being able to describe it. One way chemists describe matter is to assign different kinds of properties to different categories.

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. These characteristics can be observed or measured without changing the *identity* of the matter in question. **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. The observation of chemical properties involves a *chemical change* of the matter in question, resulting in matter with a different *identity* and different physical and chemical properties.



Figure **1.3.1**: (left) Ice Melting is a physical change. When liquid water (H_2O) freezes into a solid state (ice), it appears changed; However, this change is only physical as the the composition of the constituent molecules is the same: 11.19% hydrogen and 88.81% oxygen by mass. (right) Burning of wax to generate water and carbon dioxide is a chemical reaction. (CC-SA-BY-3.0; Andrikkos)

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 called an **element**. Aluminum, which is used in soda cans and is represented by the symbol Al, is an element. A substance that can be broken down into chemically simpler components (because it consists of more than one element) is called a **compound**. Water is a compound composed of the elements hydrogen and oxygen and is described by the chemical formula, H_2O. Today, there are about 118 elements in the known universe. In contrast, scientists have identified tens of millions of different compounds to date.

> Sometimes the word *pure* is used to describe a substance, but this is not absolutely necessary. By definition, any single substance, element or compound 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 of iron atoms that is 1 inch long, you would need approximately 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 two or more 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 viewpoint* of the universe. However, scientists can also describe chemical events on the level of individual atoms or molecules, which is referred to as the *microscopic viewpoint*. We will see examples of both macroscopic and microscopic viewpoints throughout this book (Figure **1.3.2**).

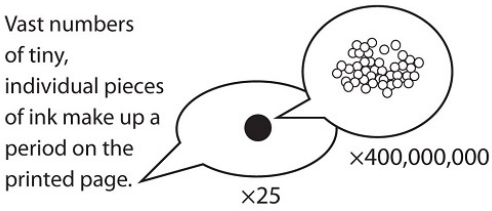


Figure **1.3.2**: How Many Particles Are Needed for a Period in a Sentence? Although we do not notice it from a macroscopic perspective, matter is composed of microscopic particles so tiny that billions of them are needed to make a speck we can see with the naked eye. The ×25 and ×400,000,000 indicate the number of times the image is magnified.

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 or uniform composition throughout are called **homogeneous mixtures** (or solutions). For example, when sugar is dissolved in water to form a liquid solution, the individual properties of the components cannot be distinguished. Other examples or homogenous mixtures include solid solutions, like the metal alloy steel, and gaseous solutions, like air which is a mixture of mainly nitrogen and oxygen.

✔ Example 1.3.1

How would a chemist categorize each example of matter?

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

Answer 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.

Answer b

Soil is composed of small pieces of a variety of materials, so it is a ***h**eterogeneous mixture*.

Answer c

Water is a *substance*; more specifically, because water is composed of hydrogen and oxygen, it is a *compound*.

Answer d

Oxygen, a *substance*, is an *element*.

? Exercise 1.3.2

How would a chemist categorize each example of matter?

a. breakfast coffee
b. hydrogen
c. an egg

Answer a

homogeneous mixture or solution

Answer b

element

Answer c

heterogeneous mixture

Phases or Physical States of Matter

All matter can be further classified by one of three physical **states** or **phases**, solid, liquid or gas. These three descriptions each imply that the matter has certain physical properties when in these states. 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.

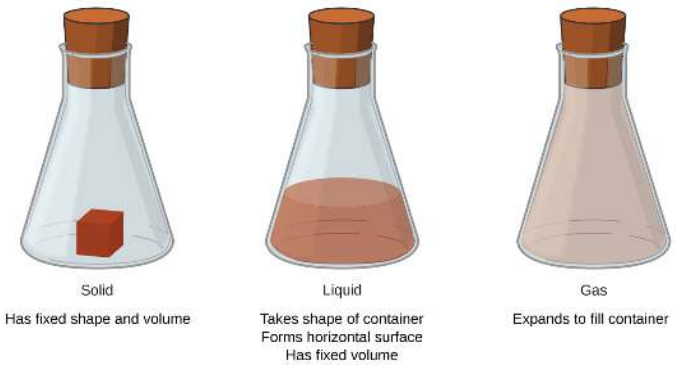


Figure 1.3.3: The three most common states or phases of matter are solid, liquid, and gas. (CC BY-4.0; OpenStax)

A beaker labeled solid contains a cube of red matter and says has fixed shape and volume. A beaker labeled liquid contains a brownish-red colored liquid. This beaker says takes shape of container, forms horizontal surfaces, has fixed volume. The beaker labeled gas is filled with a light brown gas. This beaker says expands to fill container.

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) (Figure 1.3.2).



Figure 1.3.5: Boiling Water. When liquid water boils to make gaseous water, it undergoes a phase change. (CC BY-SA 3.0 Unported; Markus Schweiss via Wikipedia)

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 changes from one phase to another (Figure 1.3.5). Phase changes are identified by particular names depending on what phases are involved, as summarized in Table 1.3.1.

Table 1.3.1: 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

Figure **1.3.3** illustrates the relationships between the different ways matter can be classified.

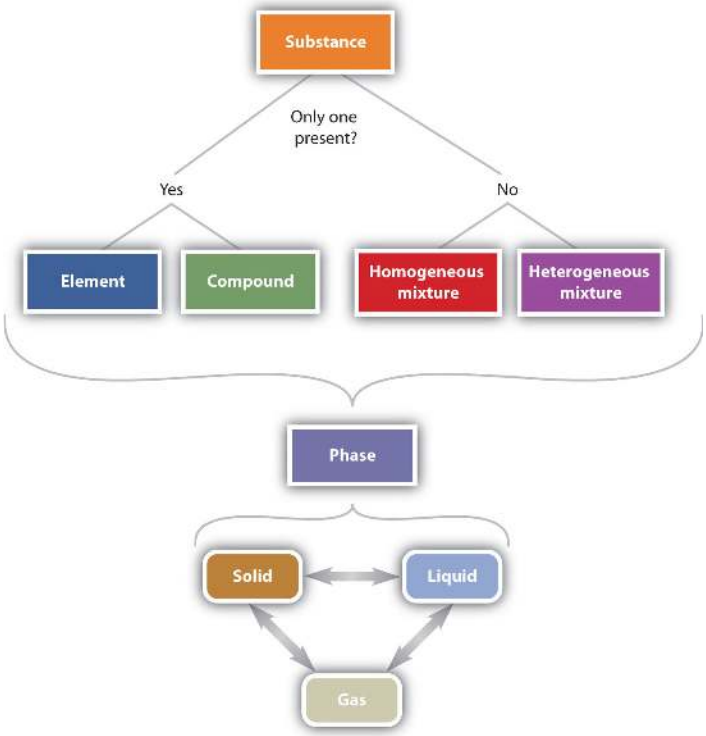


Figure **1.3.6**: The Classification of Matter. Matter can be classified in a variety of ways, depending on its properties.
This table starts with a substance. If there is only one present, it can either be an element or a compound. If there is more than one present, it can either be a homogeneous mixture or a heterogeneous mixture. From these choices, the substance can be in a certain phase. It can either be solid, liquid, or gas, and each phase can go from one to another.

Concept Review Exercises

1. Explain the differences between the physical properties of matter and the chemical properties of matter.
2. What is the difference between a heterogeneous mixture and a homogeneous mixture? Give an example of each.
3. Give at least two examples of a phase change and state the phases involved in each.

Answers

1. Physical properties describe the existence of matter, and chemical properties describe how substances change into other substances.
2. A heterogeneous mixture is obviously a mixture, such as dirt; a homogeneous mixture behaves like a single substance, such as saltwater.
3. solid to liquid (melting) and liquid to gas (boiling) (answers will vary)

Key Takeaways

- Matter can be described with both physical properties and chemical properties.
- Matter can be identified as an element, a compound, or a mixture

Exercise 1.3.3

Does each statement refer to a chemical property or a physical property?

1. Balsa is a very light wood.
2. If held in a flame, magnesium metal burns in air.
3. Mercury has a density of 13.6 g/mL.
4. Human blood is red.

Answer

1. physical property
2. chemical property
3. physical property
4. physical property

Exercise 1.3.4

Does each statement refer to a chemical property or a physical property?

1. The elements sodium and chlorine can combine to make table salt.
2. The metal tungsten does not melt until its temperature exceeds 3,000°C.
3. The ingestion of ethyl alcohol can lead to disorientation and confusion.
4. The boiling point of isopropyl alcohol, which is used to sterilize cuts and scrapes, is lower than the boiling point of water

Answer

1. chemical property
2. physical property
3. chemical property
4. physical property

Exercise 1.3.5

Define *element*. How does it differ from a compound?

Answer

An element is a substance that cannot be broken down into chemically simpler components. Compounds can be broken down into simpler substances.

Exercise 1.3.6

Define *compound*. How does it differ from an element?

Answer

A compound is composed of two or more elements combined in a fixed ratio. An element is the simplest chemical substance.

Exercise 1.3.7

Give two examples of a heterogeneous mixture.

Answer

a salt and pepper mix and a bowl of cereal (answers will vary)

Exercise 1.3.8

Give two examples of a homogeneous mixture.

Answer

vinegar and rubbing alcohol (answers will vary)

Exercise 1.3.9

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

1. xenon, a substance that cannot be broken down into chemically simpler components
2. blood, a substance composed of several types of cells suspended in a salty solution called plasma
3. water, a substance composed of hydrogen and oxygen

Answer

1. element
2. heterogeneous mixture
3. compound

Exercise 1.3.10

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

1. sugar, a substance composed of carbon, hydrogen, and oxygen
2. hydrogen, the simplest chemical substance
3. dirt, a combination of rocks and decaying plant matter

Answer

1. compound
2. element
3. heterogeneous mixture

Exercise 1.3.11

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

1. air, primarily a mixture of nitrogen and oxygen
2. ringer's lactate, a standard fluid used in medicine that contains salt, potassium, and lactate compounds all dissolved in sterile water
3. tartaric acid, a substance composed of carbon, hydrogen, and oxygen

Answer

1. heterogeneous mixture
2. solution
3. compound

Exercise 1.3.12

What word describes each phase change?

1. solid to liquid
2. liquid to gas
3. solid to gas

Answer

1. melting or fusion
2. boiling or evaporation
3. sublimation

Exercise 1.3.13

1. What word describes each phase change?
    1. liquid to solid
    2. gas to liquid
    3. gas to solid

Answer

1. freezing
2. condensation
3. deposition

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1.4: Prelude to Elements, Atoms, and the Periodic Table

The hardest material in the human body is tooth enamel. It has to be hard so that our teeth can serve us for a lifetime of biting and chewing; however, tough as it is, tooth enamel is susceptible to chemical attack. Acids found in some foods or made by bacteria that feed on food residues on our teeth are capable of dissolving enamel. Unprotected by enamel, a tooth will start to decay, thus developing cavities and other dental problems.

In the early 1900s, a dentist in Colorado Springs, Colorado, noted that many people who lived in the area had brown-stained teeth that, while unsightly, were surprisingly resistant to decay. After years of study, excess fluorine compounds in the drinking water were discovered to be the cause of both these effects. Research continued, and in the 1930s, the US Public Health Service found that low levels of fluorine in water would provide the benefit of resisting decay without discoloring teeth.

The protective effects of fluorine have a simple chemical explanation. Tooth enamel consists mostly of a mineral called hydroxyapatite, which is composed of calcium, phosphorus, oxygen, and hydrogen. We know now that fluorine combines with hydroxyapatite to make fluorapatite, which is more resistant to acidic decay than hydroxyapatite is. Currently about 50% of the US population drinks water that has some fluorine added (in the form of sodium fluoride, NaF) to reduce tooth decay. This intentional fluoridation, coupled with the use of fluoride-containing toothpastes and improved oral hygiene, has reduced tooth decay by as much as 60% in children. The nationwide reduction of tooth decay has been cited as an important public health advance in history. (Another important advance was the eradication of polio.)

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1.5: Atomic Theory

Learning Objectives

- Explain how all matter is composed of atoms.
- Describe the modern atomic theory.
- Recognize which elements exist as diatomic molecules.

Take some aluminum foil. Cut it in half. Now you have two smaller pieces of aluminum foil. Cut one of the pieces in half again. Cut one of those smaller pieces in half again. Continue cutting, making smaller and smaller pieces of aluminum foil.

It should be obvious that the pieces are still aluminum foil; they are just becoming smaller and smaller. But how far can you take this exercise, at least in theory? Can you continue cutting the aluminum foil into halves forever, making smaller and smaller pieces? Or is there some limit, some absolute smallest piece of aluminum foil? (Thought experiments like this—and the conclusions based on them—were debated as far back as the fifth century BC.)

The modern atomic theory, proposed about 1803 by the English chemist John Dalton (Figure **1.5.1**), is a fundamental concept that states that all elements are composed of atoms. Previously, we defined an atom as the smallest part of an element that maintains the identity of that element. Individual atoms are extremely small; even the largest atom has an approximate diameter of only 5.4×10^{-10} m. With that size, it takes over 18 million of these atoms, lined up side by side, to equal the width of your little finger (about 1 cm).

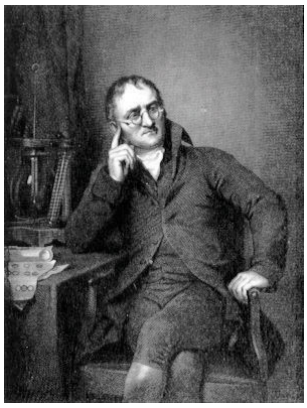


Figure **1.5.1** John Dalton was an English scientist who enunciated the modern atomic theory.

Most elements in their pure form exist as **individual atoms**. For example, a macroscopic chunk of iron (Fe) metal is composed, microscopically, of individual atoms. Some elements, however, exist as groups of atoms called molecules. Several important elements exist as two-atom combinations and are called **diatomic molecules**. In representing a diatomic molecule, we use the symbol of the element and include the ***subscript*** "2" to indicate that two atoms of that element are joined together. The elements that exist as diatomic molecules are hydrogen (H_2), nitrogen (N_2), fluorine (F_2), oxygen (O_2), iodine (I_2), chlorine (Cl_2) and bromine (Br_2). A few other elements can exist as 3-atom molecules like ozone (O_3) and 4-atom molecules like phosphorus (P_4). The most common form of the element sulfur is composed of molecules that consist of eight atoms of sulfur; its molecular formula is S_8 (Figure **1.5.2**).

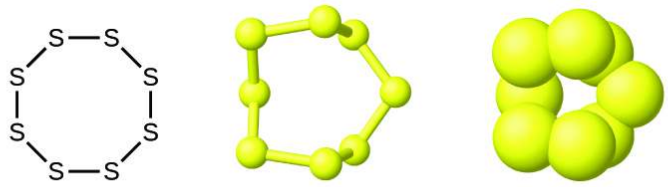


Figure 1.5.2: A molecule of sulfur is composed of eight sulfur atoms and is therefore written as S_8. It can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. Sulfur atoms are represented by yellow spheres.

Figure A shows eight sulfur atoms, symbolized with the letter S, that are bonded to each other to form an octagon. Figure B shows a 3-D, ball-and-stick model of the arrangement of the sulfur atoms. The shape is clearly not octagonal as it is represented in the structural formula. Figure C is a space-filling model that shows each sulfur atom is partially embedded into the sulfur atom it bonds with.

It is important to note that a subscript following a symbol and a number in front of a symbol do not represent the same thing; for example, H_2 and 2H represent distinctly different species. H_2 is a molecular formula; it represents a diatomic molecule of hydrogen, consisting of two atoms of the element that are chemically bonded together. The expression 2H, on the other hand, indicates two separate hydrogen atoms that are **not** combined as a unit. The expression $2H_2$ represents two molecules of diatomic hydrogen (Figure 1.5.3).

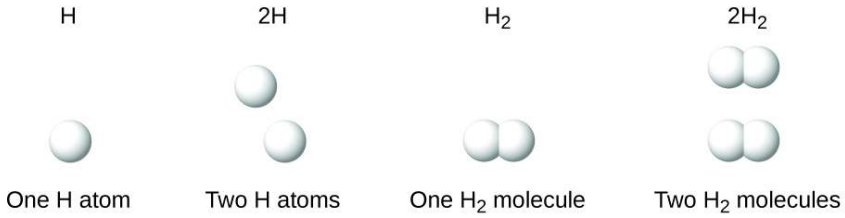


Figure 1.5.3: The symbols H, 2H, H_2, and $2H_2$ represent very different entities.

This figure shows four diagrams. The diagram for H shows a single, white sphere and is labeled one H atom. The diagram for 2 H shows two white spheres that are not bonded together. It is labeled 2 H atoms. The diagram for H subscript 2 shows two white spheres bonded together. It is labeled one H subscript 2 molecule. The diagram for 2 H subscript 2 shows two sets of bonded, white spheres. It is labeled 2 H subscript 2 molecules.

✔ Example 1.5.1

Write the chemical formula of the following elements:

a. oxygen
b. carbon
c. potassium

Solution

Memorizing the diatomic molecules is worthwhile for our future endeavors. A mnemonic device to help in the memorization of the diatomic elements is as follows: **H**ave **N**o **F**ear **O**f **I**ce **C**old **B**eer. (hydrogen, nitrogen, fluorine, oxygen, iodine, chlorine and bromine).

a. Oxygen is one of the seven diatomic molecular elements. Its chemical formula is O_2.
b. Carbon is monatomic, hence its formula is C.
c. Potassium is monatomic hence its formula is K.

1.5.1 Exercise

Write the chemical formula of the following elements:

a. hydrogen
b. nitrogen
c. neon

Answer a

Hydrogen is one of the seven diatomic molecular elements. Its chemical formula is H_2.

Answer b

Nitrogen is one of the seven diatomic molecular elements. Its chemical formula is N_2.

Answer c

Neon is a monatomic element, hence its formula is Ne.

Looking Closer: Atomic Theory

Dalton's ideas are called the *modern* atomic theory because the concept of atoms is very old. The Greek philosophers Leucippus and Democritus originally introduced atomic concepts in the fifth century BC. (The word *atom* comes from the Greek word *atomos*, which means "indivisible" or "uncuttable.") Dalton had something that the ancient Greek philosophers didn't have, however; he had experimental evidence, such as the formulas of simple chemicals and the behavior of gases. In the 150 years or so before Dalton, natural philosophy had been maturing into modern science, and the scientific method was being used to study nature. So when Dalton announced a modern atomic theory, he was proposing a fundamental theory to describe many previous observations of the natural world; he was not just participating in a philosophical discussion.

Concept Review Exercises

1. What is the modern atomic theory?
2. What are atoms?

Answers

1. The modern atomic theory states that all matter is composed of atoms.
2. Atoms are the smallest parts of an element that maintain the identity of that element.

Key Takeaways

- **Atoms** are the ultimate building blocks of all matter.
- The modern atomic theory establishes the concepts of **atoms** and how they compose matter.
- The **diatomic** elements are hydrogen, nitrogen, fluorine, oxygen, iodine, chlorine and bromine.

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1.6: Dalton's Atomic Theory



Figure **1.6.1** (Public Domain; Luca della Robbia, photographed by Jastrow via Wikipedia)

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

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

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

John Dalton

While it must be assumed that many more scientists, philosophers, and others studied the composition of matter after Democritus, a major leap forward in our understanding of the composition of matter took place in the 1800s with the work of the British scientist John Dalton. He started teaching school at age twelve, and was primarily known as a teacher. In his twenties, he moved to the growing city of Manchester, where he was able to pursue some scientific studies. His work in several areas of science brought him a number of honors. When he died, over 40,000 people in Manchester marched at his funeral.

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



Figure **1.6.2**: John Dalton. (Public Domain; Henry Roscoe (author), William Henry Worthington (engraver), and Joseph Allen (painter) via Wikipedia)

Dalton's Atomic Theory (1804)

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

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

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

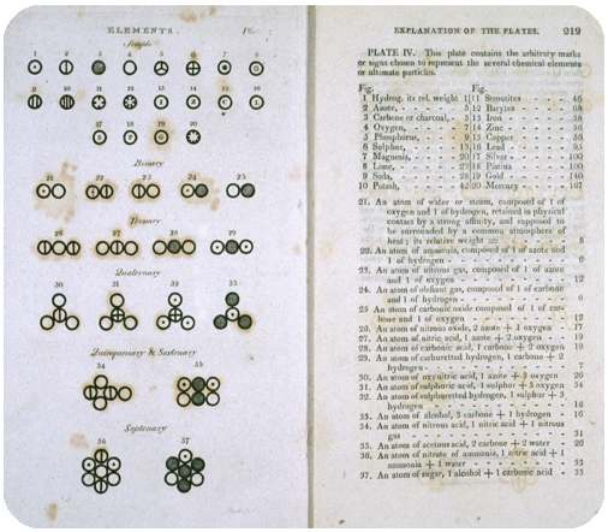


Figure **1.6.3**: Dalton's symbols. (Public Domain; John Dalton via Wikipedia)



Summary

- Dalton proposed his atomic theory in 1804.
- The general tenets of this theory are:
  - All matter is composed of extremely small particles called atoms
  - Atoms cannot be subdivided, created, or destroyed.
  - 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 of different elements can combine in whole number ratios to form chemical compounds;
  - In chemical reaction, atoms are rearranged, combined, or separated.

Review

1. Did Dalton believe that atoms could be created or destroyed?
2. According to Dalton's theory, all atoms of the same _____ are identical in size, mass, and other properties.
3. What parts of the theory are not considered valid any more?

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1.7: Conservation of Mass



Figure **1.7.1** (CC BY 2.0; Douglas Heriot via Flickr)

Have you ever lost a screw?

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

Law of Conservation of Mass

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

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

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



Summary

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

Review

1. The law of conservation of mass states that, during a chemical reaction, the total _____ of the products must be equal to the total _____ of the reactants.
2. Describe an example of the law of conservation of mass.

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1.8: Law of Definite Proportions



Figure 1.8.1 (Public Domain; Staff Sgt. Christopher Flurry, U.S. Marine Corps via Commons Wikimedia, File:USMC-110609-M-FK922-004.jpg [commons.wikimedia.org])

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

Law of Definite Proportions

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



Figure 1.8.2: Water. (CC BY 2.0; Jenn Durfey via Flickr Photos, Water Faucet [www.flickr.com])

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



Figure 1.8.3: Carbon dioxide is produced during the burning process. (Public Domain; Patsy Lynch, FEMA via Commons Wikimedia, FEMA Photograph by Patsy Lynch taken on 04-17-2006 in Missouri [commons.wikimedia.org])

Summary

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

Review

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

Explore More

Use the resource below to answer the questions that follow.



1. How many hydrogen atoms are there in a molecule of water?
2. How many oxygen atoms are there in a molecule of water?
3. What is the mass ratio of hydrogen to oxygen in a molecule of water?
4. Will the mass ratio of hydrogen to oxygen change depending on the size of the sample? For example if the sample size was 10 L or 10,000 L.

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1.9: Law of Multiple Proportions

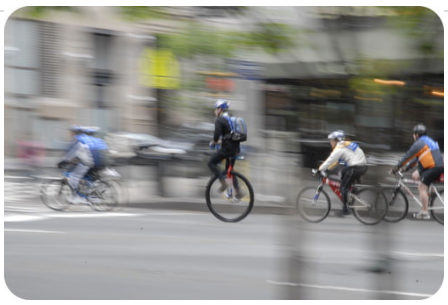


Figure 1.9.1 (CC by 2.0; Flickr: Sutibu via Commons WIkimedia, Five Boro Bike Tour Unicycle [commons.wikimedia.org])

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

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

Law of Multiple Proportions

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

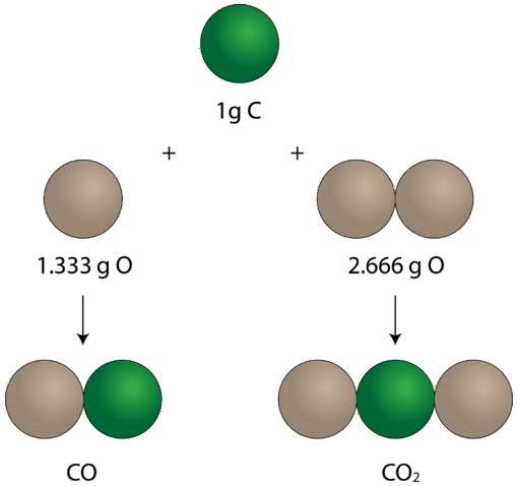


Figure 1.9.2: Carbon can form two different compounds with oxygen. (CC BY-NC-SA 3.0; Christopher Auyeung via CK-12 Foundation)

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

The difference between carbon monoxide and carbon dioxide is significant. Carbon monoxide is a deadly gas, formed from the incomplete combustion of some carbon-containing materials (such as wood and gasoline). This compound will attach to hemoglobin in the red blood cells and block the binding of oxygen to those cells. If oxygen does not bind, it cannot be carried to

the cells of the body where it is needed, and death can occur. Carbon dioxide, on the other hand, is not toxic like carbon monoxide is. However, it can displace oxygen in systems since it is heavier. Carbon dioxide fire extinguishers cut off the flow of oxygen in a fire, putting out the fire.



Summary

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

Review

1. State the law of multiple proportions.
2. In carbon dioxide (CO_2), how many grams of oxygen (O) would there be if there are 24 grams of carbon (C)?
3. How many grams of carbon (C) would be present in carbon monoxide (CO) that contains 2.666 grams of oxygen (O)?

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1.10: Classifying Matter According to Its Composition

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Learning Objectives

- Explain the difference between a pure substance and a mixture.
- Explain the difference between an element and a compound.
- Explain the difference between a homogeneous mixture and a heterogeneous mixture.

One useful way of organizing our understanding of matter is to think of a hierarchy that extends down from the most general and complex to the simplest and most fundamental (Figure **1.10.1**). Matter can be classified into two broad categories: pure substances and mixtures. A **pure substance** is a form of matter that has a constant composition (meaning it's the same everywhere) and properties that are constant throughout the sample (meaning there is only one set of properties such as melting point, color, boiling point, etc. throughout the matter). A material composed of two or more substances is a **mixture**. Elements and compounds are both examples of pure 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**. For example, water is a compound composed of the elements hydrogen and oxygen. Today, there are about 118 elements in the known universe. In contrast, scientists have identified tens of millions of different compounds to date.

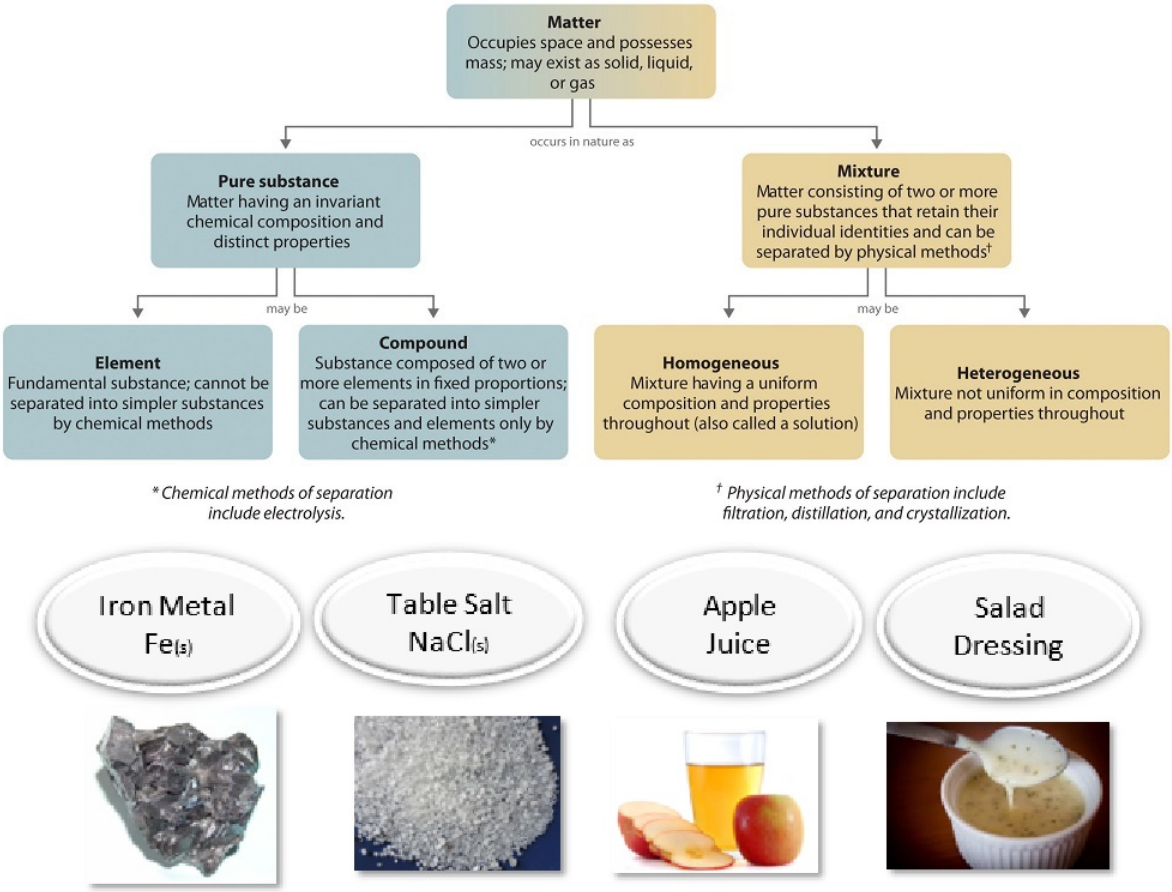


Figure **1.10.1**: *Relationships between the Types of Matter and the Methods Used to Separate Mixtures*

Ordinary table salt is called sodium chloride. It is considered a **substance** because it has a uniform and definite composition. All samples of sodium chloride are chemically identical. Water is also a pure substance. Salt easily dissolves in water, but salt water cannot be classified as a substance because its composition can vary. You may dissolve a small amount of salt or a large amount

into a given amount of water. A mixture is a physical blend of two or more components, each of which retains its own identity and properties in the **mixture**. Only the form of the salt is changed when it is dissolved into water. It retains its composition and properties.

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

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

Phase

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

Example 1.10.1

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

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

Given: a chemical substance

Asked for: its classification

Strategy:

A. Decide whether a substance is chemically pure. If it is pure, the substance is either an element or a compound. If a substance can be separated into its elements, it is a compound.
B. If a substance is not chemically pure, it is either a heterogeneous mixture or a homogeneous mixture. If its composition is uniform throughout, it is a homogeneous mixture.

Solution:

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

Exercise 1.10.1

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

a. white wine

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

Answer a:
homogeneous mixture (solution)

Answer b:
element

Answer c:
heterogeneous mixture

Answer d:
compound

Example 1.10.2

How would a chemist categorize each example 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 1.10.2

How would a chemist categorize each example of matter?

a. coffee
b. hydrogen
c. an egg

Answer a:
a homogeneous mixture (solution), assume it'd filtered coffee

Answer b:
element

Answer c:
heterogeneous mixture.

Summary

Matter can be classified into two broad categories: pure substances and mixtures. A pure substance is a form of matter that has a constant composition and properties that are constant throughout the sample. Mixtures are physical combinations of two or more elements and/or compounds. Mixtures can be classified as homogeneous or heterogeneous. Elements and compounds are both examples of pure substances. Compounds are substances that are made up of more than one type of atom. Elements are the simplest substances made up of only one type of atom.

Vocabulary

- Element: A substance that is made up of only one type of atom.
- Compound: A substance that is made up of more than one type of atom bonded together.
- Mixture: A combination of two or more elements or compounds which have not reacted to bond together; each part in the mixture retains its own properties.

Contributors and Attributions

-
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1.11: The Structure of Atoms

Learning Objectives

- Describe the three main subatomic particles.
- State how the subatomic particles are arranged in atoms.

There have been several minor but important modifications to Dalton's atomic theory. For one thing, Dalton considered atoms to be indivisible. We know now that atoms not only can be divided but also are composed of three different kinds of particle, *subatomic particles*, with their own properties that are different from the chemical properties of atoms.

Subatomic Particles

The first subatomic particle was identified in 1897 and called the electron. It is an extremely tiny particle, with a mass of about 9.109×10^{-31} kg. Experiments with magnetic fields showed that the electron has a negative electrical charge. By 1920, experimental evidence indicated the existence of a second particle. A proton has the same amount of charge as an electron, but its charge is positive, not negative. Another major difference between a proton and an electron is mass. Although still incredibly small, the mass of a proton is 1.673×10^{-27} kg, which is almost 2,000 times greater than the mass of an electron. Because opposite charges attract each other (while like charges repel each other), protons attract electrons (and vice versa).

Finally, additional experiments pointed to the existence of a third particle. Evidence produced in 1932 established the existence of the neutron, a particle with about the same mass as a proton but with no electrical charge, it is *neutral*. We understand now that all atoms can be broken down into subatomic particles: protons, neutrons, and electrons. Table **1.11.1** lists some of their important characteristics and the symbols used to represent each particle.

Table **1.11.1**: Properties of the Subatomic Particles

Particle	Symbol	Mass (kg)	Relative Mass (proton = 1)	Relative Charge
proton	p^+	1.673×10^{-27}	1	+1
neutron	n^0	1.675×10^{-27}	1	0
electron	e^-	9.109×10^{-31}	0.00055	−1

The Nucleus

How are these subatomic particles arranged? Between 1909 and 1911, Ernest Rutherford, a Cambridge physicist, and his associates Hans Geiger and Ernest Marsden performed experiments that provided strong evidence concerning the internal structure of an atom. They took a very thin metal foil, such as gold or platinum, and aimed a beam of positively charged particles (called alpha particles, which are combinations of two protons and two neutrons) from a radioactive source toward the foil. Surrounding the foil was a detector—either a scintillator (a material that glows when hit by such particles) or some unexposed film (which is exposed where the particles hit it). The detector allowed the scientists to determine the distribution of the alpha particles after they interacted with the foil. Figure **1.11.1** shows a diagram of the experimental setup.

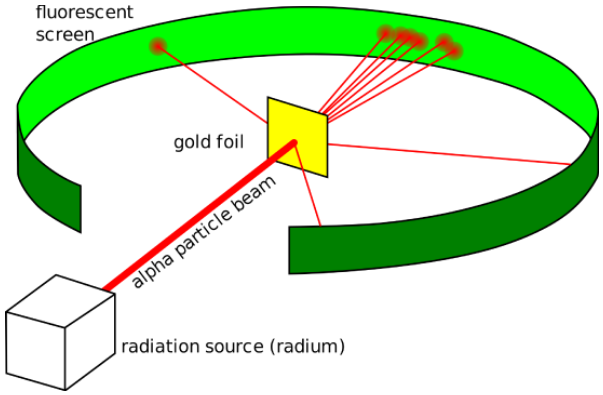


Figure 1.11.1: The Geiger-Marsden Experimental Setup. Experiments using this setup were used to investigate the structure of atoms. In this experiment, most of the particles traveled straight through the foil, but some alpha particles were deflected off to one side. Some were even deflected back toward the source. This was unexpected. Rutherford once said, "It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you." (CC SA-BY 3.0; Kurzon).

Rutherford proposed the following model to explain these experimental results. Protons and neutrons are concentrated in a central region he called the nucleus (plural, *nuclei*) of the atom. Electrons are outside the nucleus and orbit about it because they are attracted to the positive charge in the nucleus. Most of the mass of an atom is in the nucleus, while the orbiting electrons account for an atom's size. As a result, an atom consists largely of empty space. Rutherford called his description the "planetary model" of the atom. Figure 1.11.2 shows how this model explains the experimental results.

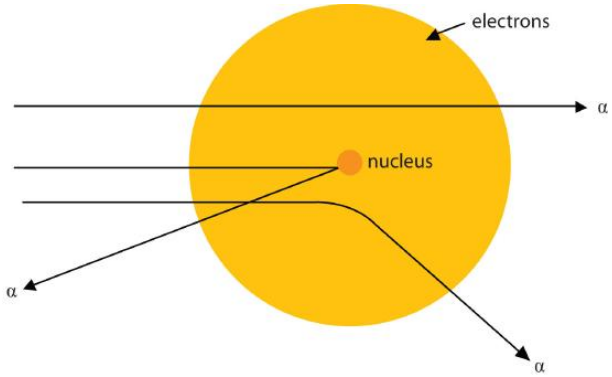


Figure 1.11.2: Rutherford's Metal Foil Experiments. Rutherford explained the results of the metal foil experiments by proposing that most of the mass and the positive charge of an atom are located in its nucleus, while the relatively low-mass electrons orbit about the nucleus. Most alpha particles go straight through the empty space, a few particles are deflected, and fewer still ricochet back toward the source. The nucleus is much smaller proportionately than depicted here.

> *The planetary model of the atom replaced the plum pudding model, which had electrons floating around aimlessly like plums in a "pudding" of positive charge.*

Rutherford's model is essentially the same model that we use today to describe atoms but with one important modification. The planetary model suggests that electrons occupy certain specific, circular orbits about the nucleus. We know now that this model is overly simplistic. A better description is that electrons form fuzzy clouds around nuclei. Figure 1.11.3 shows a more modern version of our understanding of atomic structure.

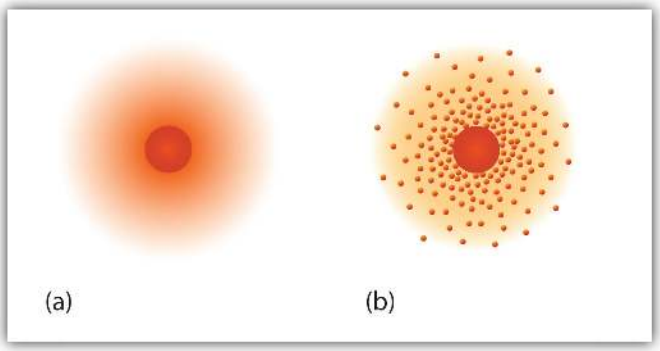


Figure **1.11.3**: A Modern Depiction of Atomic Structure. A more modern understanding of atoms, reflected in these representations of the electron in a hydrogen atom, is that electrons occupy regions of space about the nucleus; they are not in discrete orbits like planets around the sun. (a) The darker the color, the higher the probability that an electron will be at that point. (b) In a two-dimensional cross section of the electron in a hydrogen atom, the more crowded the dots, the higher the probability that an electron will be at that point. In both (a) and (b), the nucleus is in the center of the diagram.

Concept Review Exercises

1. What are the charges and the relative masses of the three subatomic particles?
2. Describe the structure of an atom in terms of its protons, neutrons, and electrons.

Answers

1. proton: +1, large; neutron: 0, large; electron: −1, small
2. Protons and neutrons are located in a central nucleus, while electrons orbit about the nucleus.

Key Takeaways

- Atoms are composed of three main subatomic particles: protons, neutrons, and electrons.
- Protons and neutrons are grouped together in the nucleus of an atom, while electrons orbit about the nucleus.

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1.12: Protons



Figure **1.12.1** (Public Domain; Adrian Pingstone (User:Arpingstone/Wikimedia Commons) via Wikipedia)

Can you name this car?

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

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

Putting the Puzzle Pieces Together

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

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

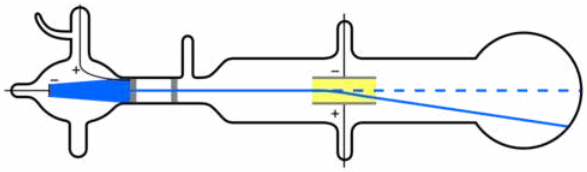


Figure **1.12.2**: JJ Thomson's experiment with cathode rays. (Public Domain; User:Kurzon/Wikimedia Commons via Wikipedia)

If cathode rays are electrons that are given off by the metal atoms of the cathode, then what remains of the atoms that have lost those electrons? We know several basic things about electrical charges. They are carried by particles of matter. Millikan's experiment showed that they exist as whole-number multiples of a single basic unit. Atoms have no overall electrical charge, meaning that each and every atom contains an exactly equal number of positively and negatively charged particles. A hydrogen atom is the simplest kind of atom with only one electron. When that electron is removed, a positively charged particle should remain.

Discovery of the Proton

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



Summary

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

Review

1. Why is it easy to describe things we can see?
2. Why did researchers believe that the particle left after electrons were emitted as cathode rays had to be positive?
3. Atoms, which are always neutral in electric charge, contain electrons as well as protons and neutrons. An electron has an electrical charge of -1. If an atom has three electrons, infer how many protons it has.
4. How many electrons does it take to weight the same as one proton?

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1.13: Electrons

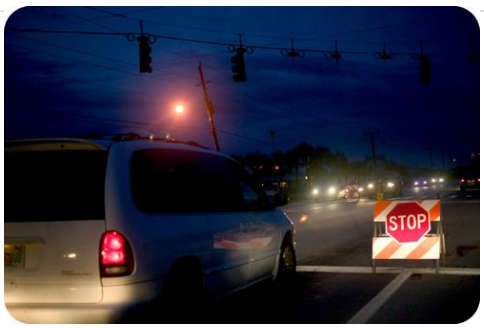


Figure 1.13.1 (Public Domain; Andrea Booher, FEMA via Wikipedia)

What causes a power outage?

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

Is There Anything Inside an Atom?

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

The Electron

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

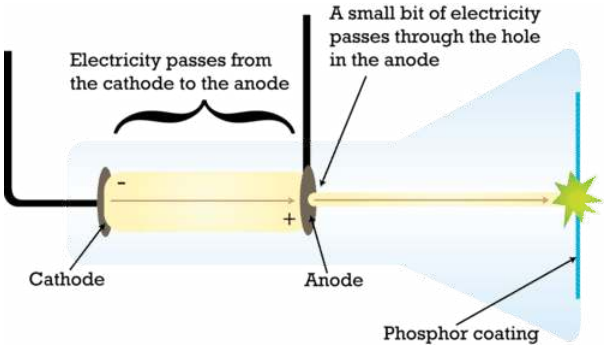


Figure 1.13.2 (CC BY-NC 3.0; Christopher Auyeung via CK-12 Foundation)

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

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

attributed it to pressure by these particles on the wheel. Thomson correctly surmised that these particles were producing heat, which caused the wheel to turn.

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

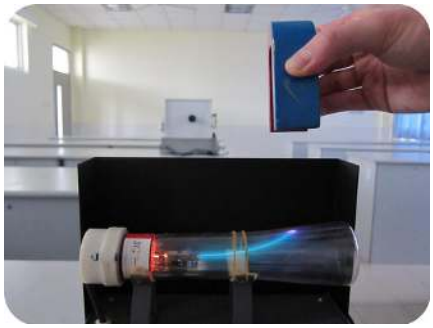


Figure **1.13.3** (CC BY 2.0; Micah Sittig via Flickr)

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

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



Summary

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

Review

1. What subatomic particle creates electric power, and how does it do it?
2. Whose work did Thomson repeat and revise?
3. What experiment did Thomson perform that showed cathode rays to be particles?
4. How did he show that these particles had a charge on them?
5. Did the cathode ray have positive or negative charge?

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1.14: Neutrons



Figure **1.14.1** (Public Domain; Sidney Paget via Wikipedia)

Was Sherlock Holmes real or the product of someone's imagination?

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

The Quest for the Neutron

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

Research had shown the properties of the electron and the proton. Scientists learned that approximately 1,837 electrons weighed the same as one proton. There was evidence to suggest that electrons went around the heavy nucleus composed of protons. Charge was balanced with equal numbers of electrons and protons which made up an electrically neutral atom. But there was a problem with this model – the atomic number (number of protons) did not match the atomic weight. In fact, the atomic number was usually about half the atomic weight. This indicated that something else must be present. That something must weigh about the same as a proton, but could not have a charge – this new particle had to be electrically neutral.

In 1920, Ernest Rutherford tried to explain this phenomenon through the presence of another particle in the nucleus. He proposed that the "extra" particles were protons and electrons that had combined into a new particle in the nucleus (this did not turn out to be the case). These new particles would have a mass very similar to a proton, but would be electrically neutral since the positive charge of the proton and the negative charge of the electron would cancel each other out.

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

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



Neutron Applications

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

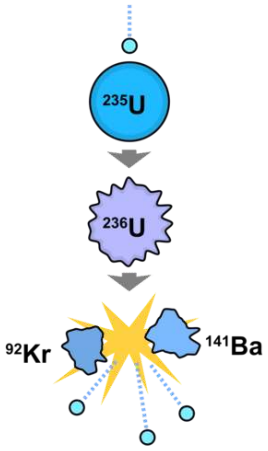


Figure **1.14.2**: A neutron collides with a large atom, splitting it into smaller atoms. (Public Domain; User:Fastfission/Wikimedia Commons via Wikipedia)

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

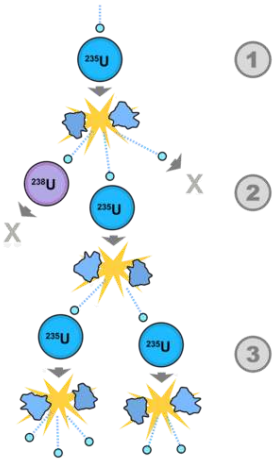


Figure **1.14.3**: How nuclear fission produces new isotopes. (Public Domain; User: Fastfission/Wikimedia Commons via Wikipedia)

Summary

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

Review

1. How did Rutherford try to explain the differences between the number of protons in the nucleus and the atomic weight?
2. What did German researchers find when they bombarded beryllium with alpha particles?
3. What did Chadwick determine about these new particle (observed by the German scientist and the Curies)?

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1.15: Nuclei of Atoms

Learning Objectives

- Define and differentiate between the atomic number and the mass number of an element.
- Explain how isotopes differ from one another.

Now that we know how atoms are generally constructed, what do atoms of any particular element look like? How many protons, neutrons, and electrons are in a specific kind of atom? First, if an atom is electrically neutral overall, then the number of protons equals the number of electrons. Because these particles have the same but opposite charges, equal numbers cancel out, producing a neutral atom.

Atomic Number

In the 1910s, experiments with x-rays led to this 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 called the atomic number (Z).

For example, hydrogen has the atomic number 1; all hydrogen atoms have 1 proton in their nuclei. Helium has the atomic number 2; all helium atoms have 2 protons in their nuclei. There is no such thing as a hydrogen atom with 2 protons in its nucleus; a nucleus with 2 protons would be a helium atom. The atomic number *defines* an element. Table **1.15.1** lists some common elements and their atomic numbers. Based on its **atomic number**, you can determine the **number of protons in the nucleus** of an atom. The largest atoms have over 100 protons in their nuclei.

Example 1.15.1

What is the number of protons in the nucleus of each element?

a. aluminum
b. iron
c. carbon

Answer a

According to Table 2.4.1, aluminum has an atomic number of 13. Therefore, every aluminum atom has 13 protons in its nucleus.

Answer b

Iron has an atomic number of 26. Therefore, every iron atom has 26 protons in its nucleus.

Answer c

Carbon has an atomic number of 6. Therefore, every carbon atom has 6 protons in its nucleus.

Exercise 1.15.1

What is the number of protons in the nucleus of each element? Use Table 2.4.1.

a. sodium
b. oxygen
c. chlorine

Answer a

Sodium has 11 protons in its nucleus.

Answer b

Oxygen has 8 protons in its nucleus.

Answer c

Chlorine has 17 protons in its nucleus

How many electrons are in an atom? Previously we said that for an electrically neutral atom, the **number of electrons equals the number of protons**, so the total opposite charges cancel. Thus, the **atomic number** of an element also gives the **number of electrons** in an atom of that element. (Later we will find that some elements may gain or lose electrons from their atoms, so those atoms will no longer be electrically neutral. Thus we will need a way to differentiate the number of electrons for those elements.)

Example 1.15.2

How many electrons are present in the atoms of each element?

a. sulfur
b. tungsten
c. argon

Answer a

The atomic number of sulfur is 16. Therefore, in a neutral atom of sulfur, there are 16 electrons.

Answer b

The atomic number of tungsten is 74. Therefore, in a neutral atom of tungsten, there are 74 electrons.

Answer c

The atomic number of argon is 18. Therefore, in a neutral atom of argon, there are 18 electrons.

Exercise 1.15.2

How many electrons are present in the atoms of each element?

a. magnesium
b. potassium
c. iodine

Answer a

Mg has 12 electrons.

Answer b

K has 19 electrons.

Answer c

I has 53 electrons.

Table 1.15.1: Some Common Elements and Their Atomic Numbers

Element	Atomic Number	Element	Atomic Nmbers
aluminum (Al)	13	magnesium (Mg)	12
americium (Am)	95	manganese (Mn)	25
argon (Ar)	18	mercury (Hg)	80
barium (Ba)	56	neon (Ne)	10
beryllium (Be)	4	nickel (Ni)	28
bromine (Br)	35	nitrogen (N)	7
calcium (Ca)	20	oxygen (O)	8
carbon (C)	6	phosphorus (P)	15
chlorine (Cl)	17	platinum (Pt)	78
chromium (Cr)	24	potassium (K)	19
cesium (Cs)	55	radon (Rn)	86
fluorine (F)	9	silver (Ag)	47
gallium (Ga)	31	sodium (Na)	11
gold (Au)	79	strontium (Sr)	38
helium (He)	2	sulfur (S)	16
hydrogen (H)	1	titanium (Ti)	22
iron (Fe)	26	tungsten (W)	74
iodine (I)	53	uranium (U)	92
lead (Pb)	82	zinc (Zn)	30
lithium (Li)	3	zirconium (Zr)	40

Isotopes

How many neutrons are in atoms of a particular element? At first it was thought that the number of neutrons in a nucleus was also characteristic of an element. However, it was found that atoms of the same element can have *different* numbers of neutrons. Atoms of the same element (i.e., same atomic number, Z) that have different numbers of neutrons are called isotopes. For example, 99% of the carbon atoms on Earth have 6 neutrons and 6 protons in their nuclei; about 1% of the carbon atoms have 7 neutrons in their nuclei. Naturally occurring carbon on Earth, therefore, is actually a mixture of isotopes, albeit a mixture that is 99% carbon with 6 neutrons in each nucleus.

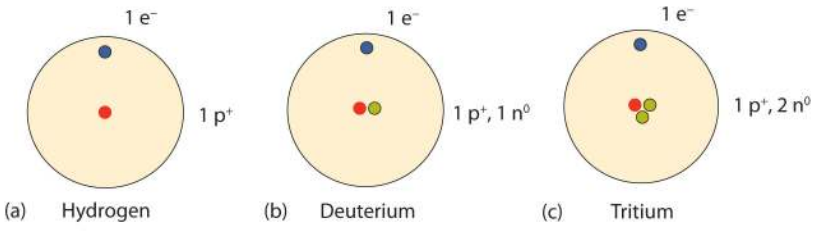


Figure **1.15.1**: Isotopes of Hydrogen. Most hydrogen atoms have only a proton in the nucleus (a). A small amount of hydrogen exists as the isotope deuterium, which has one proton and one neutron in its nucleus (b). A tiny amount of the hydrogen isotope tritium, with one proton and two neutrons in its nucleus, also exists on Earth (c). The nuclei and electrons are proportionately much smaller than depicted here.

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 **1.15.1** compares the three isotopes of hydrogen.

> 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.

Most elements exist as mixtures of isotopes. In fact, 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. The *mass number* (A) of an atom is the sum of the numbers of protons and neutrons in the nucleus. Given the mass number for a nucleus (and knowing the atomic number of that particular atom), you can determine the number of neutrons by subtracting the atomic number from the mass number.

A simple way of indicating the mass number of a particular isotope is to list it as a superscript on the left side of an element's symbol. Atomic numbers are often listed as a subscript on the left side of an element's symbol. Thus, we might see

$$\begin{matrix}\text{mass number}\longrightarrow 56\\ \text{atomic number}\longrightarrow 26\end{matrix}\mathrm{Fe} \tag{1.15.1}$$

which indicates a particular isotope of iron. The 26 is the atomic number (which is the same for all iron atoms), while the 56 is the mass number of the isotope. To determine the number of neutrons in this isotope, we subtract 26 from 56: 56 − 26 = 30, so there are 30 neutrons in this atom.

✔ Example 1.15.3

How many protons and neutrons are in each atom?

a. $^{35}_{17}\mathrm{Cl}$
b. $^{127}_{53}\mathrm{I}$

Answer a

In $^{35}_{17}\mathrm{Cl}$ there are 17 protons, and 35 − 17 = 18 neutrons in each nucleus.

Answer b

In $^{127}_{53}\mathrm{I}$ there are 53 protons, and 127 − 53 = 74 neutrons in each nucleus.

? Exercise 1.15.3

How many protons and neutrons are in each atom?

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

Answer a

In $^{197}_{79}\mathrm{Au}$ there are 79 protons, and 197 − 79 = 118 neutrons in each nucleus.

Answer b

In $^{23}_{11}\mathrm{Na}$ there are 11 protons, and 23 − 11 = 12 neutrons in each nucleus.

It is not absolutely necessary to indicate the atomic number as a subscript because each element has its own unique atomic number. Many isotopes are indicated with a superscript only, such as $^{13}\mathrm{C}$ or $^{235}\mathrm{U}$. You may also see isotopes represented in print as, for example, carbon-13 or uranium-235.

Summary

The atom consists of discrete particles that govern its chemical and physical behavior. Each atom of an element contains the same number of protons, which is the **atomic number (Z)**. Neutral atoms have the same number of electrons and protons. Atoms of an element that contain different numbers of neutrons are called **isotopes**. Each isotope of a given element has the same atomic number but a different **mass number (A)**, which is the **sum of the numbers of protons and neutrons**.

Almost all of the mass of an atom is from the total protons and neutrons contained within a tiny (and therefore very dense) nucleus. The majority of the volume of an atom is the surrounding space in which the electrons reside. A representation of a carbon-12 atom is shown below in Figure 1.15.2.

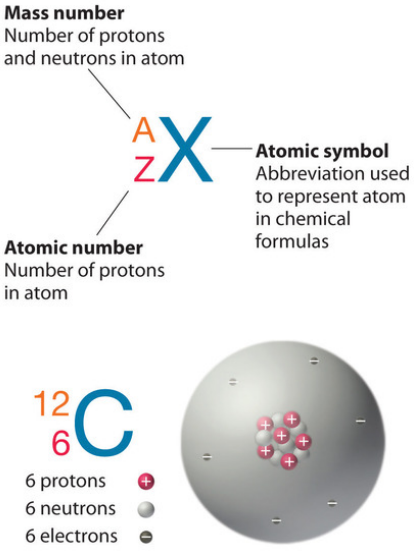


Figure 1.15.2: Formalism used for identifying specific nuclide (any particular kind of nucleus)

The atomic symbol, X, is the abbreviation used to represent an atom in chemical formulas. The mass number, A, is the number of protons and neutrons in the atom, which is to the left of the X. The atomic number, Z, is the number of protons in the atom, which is to the left of the X and below the A.

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?

Answers

1. The atomic number defines the identity of an element. It describes the number of protons in the nucleus.
2. In an electrically neutral atom, the number of protons equals the number of electrons.
3. Isotopes of an element have the same number of protons but 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.

Key Takeaways

- Each element is identified by its atomic number. The atomic number provides the element's location on the periodic table
- The isotopes of an element have different masses and are identified by their mass numbers.

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1.16: Atomic Masses

Learning Objectives

- Define atomic mass and atomic mass unit.
- Calculate atomic mass.

Even though atoms are very tiny pieces of matter, they have mass. Their masses are so small, however, that chemists often use a unit other than grams to express them—the atomic mass unit.

Atomic Mass Unit

The atomic mass unit (abbreviated u, although amu is also used) is defined as 1/12 of the mass of a ^{12}C atom:

$$1\ \text{u} = \frac{1}{12}\ \text{the mass of}\ ^{12}\text{C atom} \tag{1.16.1}$$

It is equal to 1.661×10^{-24} g.

Masses of other atoms are expressed with respect to the atomic mass unit. For example, the mass of an atom of ^{1}H is 1.008 u, the mass of an atom of ^{16}O is 15.995 u, and the mass of an atom of ^{32}S is 31.97 u. Note, however, that these masses are for particular isotopes of each element. Because most elements exist in nature as a mixture of isotopes, any sample of an element will actually be a mixture of atoms having slightly different masses (because neutrons have a significant effect on an atom's mass). How, then, do we describe the mass of a given element? By calculating an average of an element's atomic masses, weighted by the natural abundance of each isotope, we obtain a weighted average mass called the atomic mass (also commonly referred to as the *atomic weight*) of an element.

Atomic Mass is the Weighted Average Mass of Isotopes

As stated above, most elements occur naturally as a mixture of two or more isotopes. Listed below (Table 1.16.1) are the naturally occurring isotopes of selected elements along with the percent natural abundance of each.

Table 1.16.1: Atomic Masses and Percent Abundances of Some Natural Isotopes

Element	Isotope (Symbol)	Percent Natural Abundance	Atomic Mass (amu)	Average Atomic Mass (amu)
Hydrogen	$^{1}_{1}H$	99.985	1.0078	1.0079
	$^{2}_{1}H$	0.015	2.0141	
	$^{3}_{1}H$	negligible	3.0160	
Carbon	$^{12}_{6}C$	98.89	12.000	12.011
	$^{13}_{6}C$	1.11	13.003	
	$^{14}_{6}C$	trace	14.003	
Oxygen	$^{16}_{8}O$	99.759	15.995	15.999
	$^{17}_{8}O$	0.037	16.995	
	$^{18}_{8}O$	0.204	17.999	
Chlorine	$^{35}_{17}Cl$	75.77	34.969	35.453
	$^{38}_{17}Cl$	24.23	36.966	
Copper	$^{63}_{29}Cu$	69.17	62.930	63.546
	$^{65}_{29}Cu$	30.83	64.928	

For some elements, one particular isotope is much more abundant than any other isotopes. For example, naturally occurring hydrogen is nearly all hydrogen-1, and naturally occurring oxygen is nearly all oxygen-16. For many other elements, however, more than one isotope may exist in substantial quantities. Chlorine (atomic number 17) is yellowish-green toxic gas. About three quarters of all chlorine atoms have 18 neutrons, giving those atoms a mass number of 35. About one quarter of all chlorine atoms have 20 neutrons, giving those atoms a mass number of 37. Were you to simply calculate the arithmetic average of the precise atomic masses, you would get approximately 36.

$$\frac{34.969\,u + 36.966\,u}{2} = 35.968\,u$$

As you can see, the average atomic mass given in the last column of the table above (35.453) is significantly lower. Why? The reason is that we need to take into account the natural abundance percentages of each isotope in order to calculate what is called the **weighted average**. The atomic mass *of an element is the weighted average of the atomic masses of the naturally occurring isotopes of that element.*

$$0.7577\,(34.969\,u) + 0.2423\,(36.966\,u) = 35.453\,u$$

The weighted average is determined by multiplying the percent of natural abundance by the actual mass of the isotope. This is repeated until there is a term for each isotope. For chlorine, there are only two naturally occurring isotopes so there are only two terms.

Atomic mass = (%1)(mass 1) + (%2)(mass 2) + ⋯

Another example: oxygen exists as a mixture that is 99.759% ^{16}O, 0.037% ^{17}O and 0.204% ^{18}O. The atomic mass of oxygen (use percent natural abundance data from Table 2.5.1) would be calculated as follows:

Atomic mass = (%1)(mass 1) + (%2)(mass 2) + (%3)(mass 3)

$$0.99759\,(15.995u) + 0.00037\,(16.995u) + 0.00204\,(17.999u) = 15.999u$$

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

Example 1.16.1

Calculate the atomic mass of oxygen. Oxygen exists as a mixture of 3 isotopes. Their respective masses and natural abundance are shown below.

- ^{16}O: 15.995 u (99.759%)
- ^{17}O: 16.995 u (0.037%)
- ^{18}O: 17.999 u (0.204%)

Solution

Multiply the isotope abundance by the actual mass of the isotope, and then sum up the products.

$$0.99759\,(15.995\,u) + 0.00037\,(16.995\,u) + 0.00204\,(17.999\,u) = 15.999\,u$$

1.16.1 Exercise

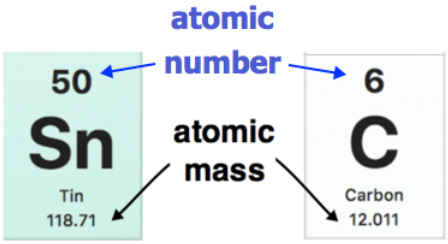
Calculate the atomic mass of copper. Copper exists as a mixture of 2 isotopes. Their respective masses and natural abundance are shown below.

- ^{63}Cu: 62.930 u (69.17%)
- ^{65}Cu: 64.928 u (30.83%)

Answer

63.546 u

The **atomic mass** of each element is found under the element symbol in the **periodic table.** Examples are shown below. The atomic mass of tin (Sn) is 118.71 u while the atomic mass of carbon (C) is 12.011 u. On the other hand, the **atomic number (Z)** of each element is found **above** the atomic symbol.



Atomic mass indicated on entries of the Periodic Table. (public Domain; Pubchem)

The **periodic table** is found in this link:

https://pubchem.ncbi.nlm.nih.gov/periodic-table/png/Periodic_Table_of_Elements_w_Atomic_Mass_PubChem.png

Example 1.16.2: Mass of Carbon

What is the average mass of a carbon atom in grams? The atomic mass is found in the Periodic Table. Please use two decimal places.

Solution

This is a simple one-step conversion, similar to conversions we did in Chapter 1. We use the fact that 1 u = 1.661×10^{-24} g:

$$12.01\ \cancel{u} \times \frac{1.661 \times 10^{-24}\ g}{1\ \cancel{u}} = 1.995 \times 10^{-23}\ g$$

This is an extremely small mass, which illustrates just how small individual atoms are.

? Exercise 1.16.2: Mass of Tin

What is the average mass of a tin atom in grams? The average atomic mass is found in the Periodic Table. Please use two decimal places.

Answer

$$118.71 \cancel{u} \times \frac{1.661 \times 10^{-24}\ \text{g}}{1\ \cancel{u}} = 1.972 \times 10^{-22}\ \text{g}$$

Concept Review Exercises

1. Define atomic mass. Why is it considered a weighted average?
2. What is an atomic mass unit?

Answers

1. The atomic mass is an average of an element's atomic masses, weighted by the natural abundance of each isotope of that element. It is a weighted average because different isotopes have different masses.
2. An atomic mass unit is 1/12th of the mass of a ^{12}C atom.

Key Takeaway

- Atoms have a mass that is based largely on the number of protons and neutrons in their nucleus.
- The atomic mass of each element in the Periodic Table is the weighted average of the mass of all its isotopes.

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CHAPTER OVERVIEW

2: Trends and Bonding

2.1: The Periodic Table
2.2: Periodic Trends- Atomic Radius
2.3: Periodic Trends- Ionization Energy
2.4: Periodic Trends- Electronegativity
2.5: Prelude to Ionic Bonding and Simple Ionic Compounds
2.6: Prelude to Covalent Bonding and Simple Molecular Compounds
2.7: Lewis Dot and Bonding
2.8: Covalent Bonds
2.9: Drawing Lewis Structures
2.10: Characteristics of Molecules
2.11: Exceptions to the Octet Rule

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2.1: The Periodic Table

Learning Objectives

- Explain how elements are organized into the periodic table.
- Describe how some characteristics of elements relate to their positions on the periodic table.

In the 19th century, many previously unknown elements were discovered, and scientists noted that certain sets of elements had similar chemical properties. For example, chlorine, bromine, and iodine react with other elements (such as sodium) to make similar compounds. Likewise, lithium, sodium, and potassium react with other elements (such as oxygen) to make similar compounds. Why is this so?

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 later 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 on a regular basis throughout the table (that is, they are periodic), it became known as the periodic table.

> *Mendeleev had to list some elements out of the order of their atomic masses to group them with other elements that had similar properties.*

The periodic table is one of the cornerstones of chemistry because it organizes all the known elements on the basis of their chemical properties. A modern version is shown in Figure **2.1.1**. Most periodic tables provide additional data (such as atomic mass) in a box that contains each element's symbol. The elements are listed in order of atomic number.

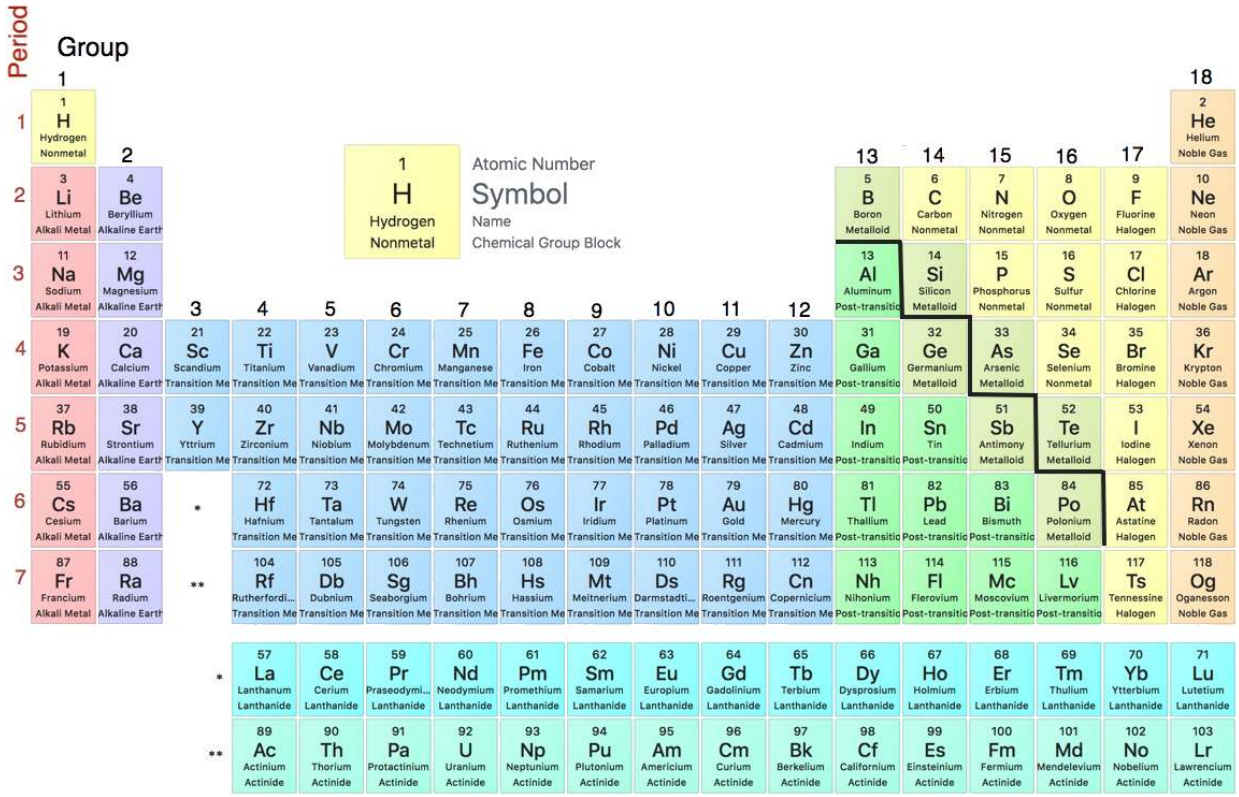


Figure **2.1.1**: Modern Periodic Table. (Public Domain; PubChem modified Leticia Colmenares).

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).

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.

Metals, Nonmetals and Metalloids

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 semimetal, as shown in Figure **2.1.2**. 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 **2.1.2**, **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 **semimetals** (or **metalloids**). Elements adjacent to the **bold zigzag** line in the right-hand portion of the periodic table have semimetal properties.

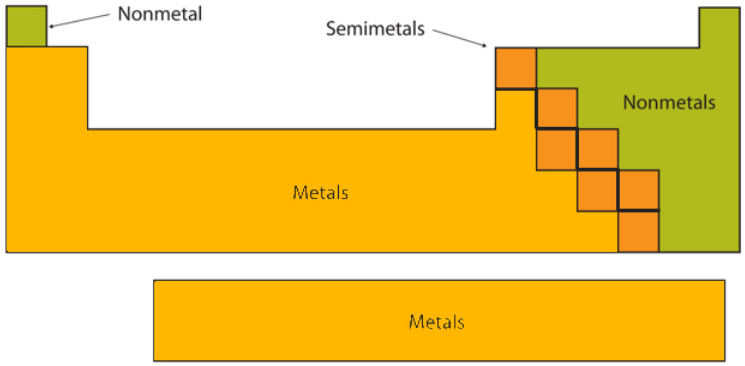


Figure **2.1.2**: Types of Elements. Elements are either metals, nonmetals, or semimetals. Each group is located in a different part of the periodic table.

Example 2.1.1

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

Solution

The atomic number of selenium is 34, which places it in period 4 and group 16. In Figure 2.7.1, selenium lies above and to the right of the diagonal line marking the boundary between metals and nonmetals, so it should be a nonmetal. Note, however, that because selenium is close to the metal-nonmetal dividing line, it would not be surprising if selenium were similar to a semimetal in some of its properties.

2.1.1 Exercise

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

Answer

metal

Representative, Transition and Inner-transition

Another way to categorize the elements of the periodic table is shown in Figure **2.1.3**. The first two columns on the left and the last six columns on the right are called the **main group** or **representative** elements. The ten-column block between these columns contains the **transition metals**. The two rows beneath the main body of the periodic table contain the inner transition metals. The elements in these two rows are also referred to as, respectively, the **lanthanide metals** and the **actinide metals**.

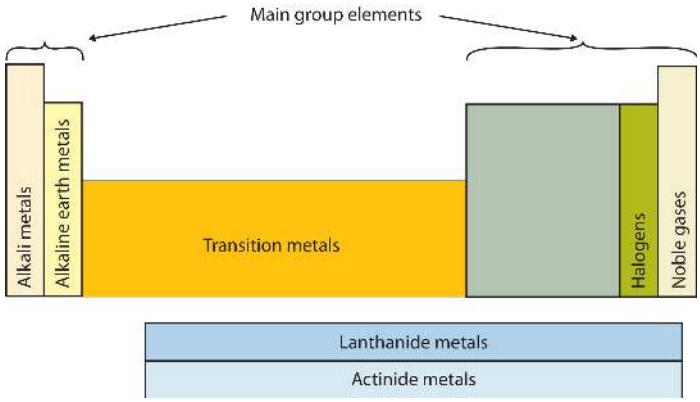


Figure **2.1.3**: Special Names for Sections of the Periodic Table. Some sections of the periodic table have special names. The elements lithium, sodium, potassium, rubidium, cesium, and francium are collectively known as alkali metals.

Alkali metals are the first column. Alkaline earth metals are the second. Halogens are the second to last column. Noble gases are the last column.

To Your Health: Transition Metals in the Body

Most of the elemental composition of the human body consists of main group elements. The first element appearing on the list that is not a main group element is iron, at 0.006 percentage by mass. Because iron has relatively massive atoms, it would appear even lower on a list organized in terms of percent by *atoms* rather than percent by mass.

Iron is a transition metal. Transition metals have interesting chemical properties, partially because some of their electrons are in *d* subshells. The chemistry of iron makes it a key component in the proper functioning of red blood cells.

Red blood cells are cells that transport oxygen from the lungs to cells of the body and then transport carbon dioxide from the cells to the lungs. Without red blood cells, animal respiration as we know it would not exist. The critical part of the red blood cell is a protein called *hemoglobin*. Hemoglobin combines with oxygen and carbon dioxide, transporting these gases from one location to another in the body. Hemoglobin is a relatively large molecule, with a mass of about 65,000 u.

The crucial atom in the hemoglobin protein is iron. Each hemoglobin molecule has four iron atoms, which act as binding sites for oxygen. It is the presence of this particular transition metal in your red blood cells that allows you to use the oxygen you inhale.

Other transition metals have important functions in the body, despite being present in low amounts. Zinc is needed for the body's immune system to function properly, as well as for protein synthesis and tissue and cell growth. Copper is also needed for several proteins to function properly in the body. Manganese is needed for the body to metabolize oxygen properly. Cobalt is a necessary component of vitamin B-12, a vital nutrient. These last three metals are not listed explicitly in Table 2.1.2, so they are present in the body in very small quantities. However, even these small quantities are required for the body to function properly.

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. For example, the elements of Group 1 are known as the alkali metals, Group 2 are the alkaline earth metals, Group 17 are the halogens, and Group 18 are the noble gases.

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

Group 18: The Noble Gases

The noble gases are helium, neon, argon, krypton, xenon, and radon. Because the noble gases are composed of only single atoms, they are 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 the noble gases were prepared in 1962. Although the noble gases are relatively minor constituents of the atmosphere, natural gas contains substantial amounts of helium. Because of its low reactivity, argon is often used as an unreactive (inert) atmosphere for welding and in light bulbs. The red light emitted by neon in a gas discharge tube is used in neon lights.

To Your Health: Radon

Radon is an invisible, odorless noble gas that is slowly released from the ground, particularly from rocks and soils whose uranium content is high. Because it is a noble gas, radon is not chemically reactive. Unfortunately, it is radioactive, and increased exposure to it has been correlated with an increased lung cancer risk.

Because radon comes from the ground, we cannot avoid it entirely. Moreover, because it is denser than air, radon tends to accumulate in basements, which if improperly ventilated can be hazardous to a building's inhabitants. Fortunately, specialized ventilation minimizes the amount of radon that might collect. Special fan-and-vent systems are available that draw air from below the basement floor, before it can enter the living space, and vent it above the roof of a house.

After smoking, radon is thought to be the second-biggest *preventable* cause of lung cancer in the United States. The American Cancer Society estimates that 10% of all lung cancers are related to radon exposure. There is uncertainty regarding what levels of exposure cause cancer, as well as what the exact causal agent might be (either radon or one of its breakdown products, many of which are also radioactive and, unlike radon, not gases). The US Environmental Protection Agency recommends testing every floor below the third floor for radon levels to guard against long-term health effects.

Why do elements in a given group have similar properties?

The periodic table is organized on the basis of similarities in elemental properties, but what explains these similarities? It turns out that the shape of the periodic table reflects the filling of subshells with electrons, as shown in Figure **2.1.4**. Starting with the first

period and going from left to right, the table reproduces the order of filling of the electron subshells in atoms. Furthermore, elements in the same *group* share the same valence shell electron configuration. For example, all elements in the first column have a single *s* electron in their valence shells, so their electron configurations can be described as ns^1 (where *n* represents the shell number). This last observation is crucial. Chemistry is largely the result of interactions between the valence electrons of different atoms. Thus, atoms that have **the same valence shell electron configuration** will have **similar chemistry.**

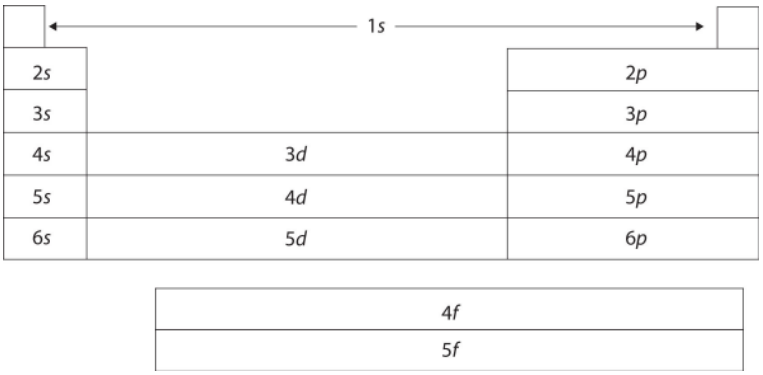


Figure **2.1.4** The Shape of the Periodic Table. The shape of the periodic table reflects the order in which electron shells and subshells fill with electrons.

Example 2.1.1

Using the variable *n* to represent the number of the valence electron shell, write the valence shell electron configuration for each group.

a. the alkaline earth metals
b. the column of elements headed by carbon

Answer a

The alkaline earth metals are in the second column of the periodic table. This column corresponds to the *s* subshell being filled with 2 electrons. Therefore, the valence shell electron configuration is ns^2.

Answer b

The electron configuration of carbon is $1s^22s^22p^2$. Its valence shell electron configuration is $2s^22p^2$. Every element in the same column should have a similar valence shell electron configuration, which we can represent as ns^2np^2.

Exercise 2.1.1

Using the variable *n* to represent the number of the valence electron shell, write the valence shell electron configuration for each group.

a. the halogens
b. the column of elements headed by oxygen

Answer a

The halogens are in the 17th column (or Group 7A) of the periodic table. This column corresponds to the *p* subshell being filled with 5 electrons. Therefore, the valence shell electron configuration is ns^2np^5.

Answer b

The column headed by O is the 16th column (or Group 6A). This column corresponds to the *p* subshell being filled with 4 electrons. Therefore, the valence shell electron configuration is ns^2np^4.

Valence Electrons and Group Number

The number of valence electrons of an element can be determined by the periodic table group (vertical column) in which the element is categorized. With the exception of groups 3–12 (the transition metals), the units digit of the group number identifies how many valence electrons are associated with a neutral atom of an element listed under that particular column.

Table **2.1.1**. The Group number and the number of valence electrons.

Periodic table group	Valence electrons
Group 1 (I) (alkali metals)	1
Group 2 (II) (alkaline earth metals)	2
Groups 3-12 (transition metals)	2*
Group 13 (III) (boron group)	3
Group 14 (IV) (carbon group)	4
Group 15 (V) (pnictogens)	5
Group 16 (VI) (chalcogens)	6
Group 17 (VII) (halogens)	7
Group 18 (VIII or 0) (noble gases)	8**

** The general method for counting valence electrons is generally not useful for transition metals.*

*** Except for helium, which has only two valence electrons.*

Atomic Radius

The periodic table is useful for understanding atomic properties that show periodic trends. One such property is the atomic radius (Figure **2.1.5**). The atomic radius is defined as one-half the distance between the nuclei of identical atoms that are bonded together. The units for atomic radii are picometers, equal to 10^{-12} meters. As an example, the internuclear distance between the two hydrogen atoms in an $\mathbf{H_2}$ molecule is measured to be $\mathbf{74\ pm}$. Therefore, the atomic radius of a hydrogen atom is $\frac{74}{2} = \mathbf{37\ pm}$.

As mentioned earlier, the higher the shell number, the farther from the nucleus the electrons in that shell are likely to be. In other words, the size of an atom is generally determined by the number of the valence electron shell. Therefore, as we go down a column on the periodic table, the atomic radius increases. As we go *across* a period on the periodic table, however, electrons are being added to the *same* valence shell; meanwhile, more protons are being added to the nucleus, so the positive charge of the nucleus is increasing. The increasing positive charge attracts the electrons more strongly, pulling them closer to the nucleus. Consequently, as we go across a period, from left to right, the atomic radius decreases. These trends are seen clearly in Figure **2.1.5**

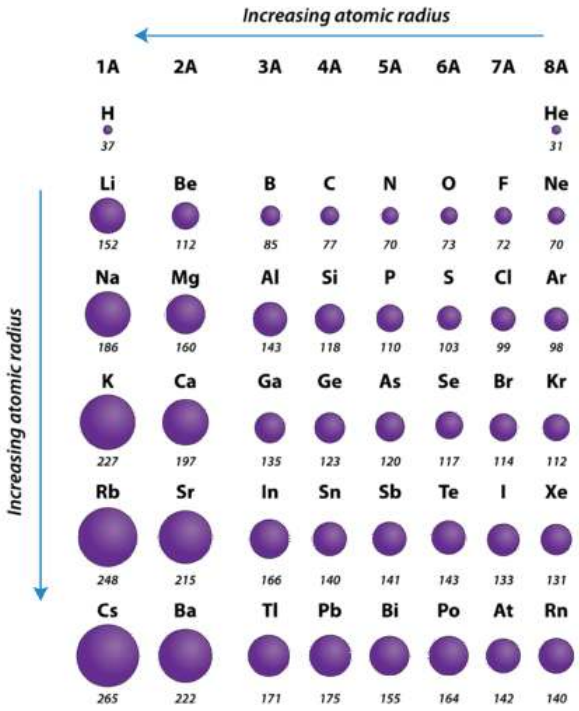


Figure **2.1.5** Trends on the Periodic Table. Atomic radii of the representative elements measured in picometers. The relative sizes of the atoms show several trends with regard to the structure of the periodic table. Atoms become larger going down a group and going from right to left across a period.

✔ Example 2.1.2

Using the periodic table (rather than Figure **2.1.5**), which atom is larger?

a. N or Bi
b. Mg or Cl

Answer a

Bi is below N in Group 5A in the periodic table and has electrons in higher-numbered shells, hence we expect that Bi atoms are larger than N atoms.

Answer b

Both Mg and Cl are in period 3 of the periodic table, but Cl lies farther to the right. Therefore we expect Mg atoms to be larger than Cl atoms.

? Exercise 2.1.2

Using the periodic table (rather than Figure **2.1.5**), which atom is larger?

a. Li or F
b. Na or K

Answer a

Li and F are on the same period, but F lies farther to the right. Therefore, we expect Li to be larger than F atoms.

Answer b

K lies below Na in Group 1A, hence has more electron shells, making it larger than Na.

Career Focus: Clinical Chemist

Clinical chemistry is the area of chemistry concerned with the analysis of body fluids to determine the health status of the human body. Clinical chemists measure a variety of substances, ranging from simple elements such as sodium and potassium to complex molecules such as proteins and enzymes, in blood, urine, and other body fluids. The absence or presence, or abnormally low or high amounts, of a substance can be a sign of some disease or an indication of health. Many clinical chemists use sophisticated equipment and complex chemical reactions in their work, so they not only need to understand basic chemistry, but also be familiar with special instrumentation and how to interpret test results.

Concept Review Exercises

1. How are the elements organized into the periodic table?
2. Looking at the periodic table, where do the following elements appear?
    a. the metals
    b. the nonmetals
    c. the halogens
    d. the transition metals
    e. the noble gases
3. Describe the trends in atomic radii as related to an element's position on the periodic table.

Answers

1. Elements are organized in order of increasing atomic number.
2. a. the left three-quarters of the periodic table (to the left of the zigzag band)
    b. the right quarter of the periodic table (to the right of the zigzag band)
    c. the next-to-last column of the periodic table
    d. the middle section of the periodic table
    e. the last column of the periodic table
3. As you go across the periodic table, atomic radii decrease; as you go down the periodic table, atomic radii increase.

Key Takeaways

- The chemical elements are arranged in a chart called the periodic table.
- Some characteristics of the elements are related to their position on the periodic table.
- The number of valence electrons of an element can be determined by the group (vertical column) number in the Periodic Table. Elements with the same number of valence electrons have similar chemical properties.

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2.2: Periodic Trends- Atomic Radius



Figure 2.2.1 (CC by 2.0; James Cridland via Flickr)

How can all of these people fit in such a small space?

Events draw large numbers of people to them. Even an outdoor event can fill up so that there is no room for more people. The crowd capacity depends on the amount of space in the venue, and the amount of space depends on the size of the objects filling it. We can get more people into a given space than can elephants, because elephants are larger than people. We can get more squirrels into that same space than we can people for the same reason. Knowing the sizes of objects to be dealt with can be important in deciding how much space is needed.

Atomic Radius

The size of atoms is important to explanations of the behavior of atoms or compounds. One way to express the size of atoms is by use of **atomic radius**. This data helps us understand why some molecules fit together and why other molecules have parts that get too crowded under certain conditions.

The size of an atom is defined by the edge of its orbital. However, orbital boundaries are fuzzy, and variable under different conditions. In order to standardize the measurement of atomic radii, the distance between the nuclei of two identical atoms bonded together is measured. The atomic radius is defined as one-half the distance between the nuclei of identical atoms that are bonded together.

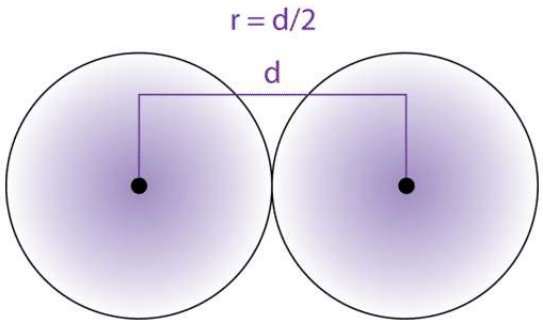


Figure 2.2.2: The atomic radius (r) of an atom can be defined as one half the distance (d) between two nuclei in a diatomic molecule. (CC BY-NC 3.0; Christopher Auyeung via CK-12 Foundation)

Atomic radii have been measured for elements. The units for atomic radii are picometers, equal to 10^{-12} meters. As an example, the internuclear distance between the two hydrogen atoms in an H_2 molecule is measured to be $74\ \text{pm}$. Therefore, the atomic radius of a hydrogen atom is $\frac{74}{2} = 37\ \text{pm}$.

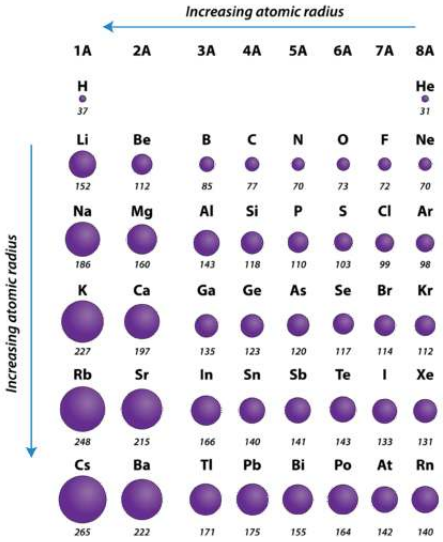


Figure **2.2.3**: Atomic radii of the representative elements measured in picometers. (CC BY-NC 3.0; Christopher Auyeung via CK-12 Foundation)

Periodic Trend

The atomic radius of atoms generally decreases from left to right across a period. There are some small exceptions, such as the oxygen radius being slightly greater than the nitrogen radius. Within a period, protons are added to the nucleus as electrons are being added to the same principal energy level. These electrons are gradually pulled closer to the nucleus because of its increased positive charge. Since the force of attraction between nuclei and electrons increases, the size of the atoms decreases. The effect lessens as one moves further to the right in a period, because of electron-electron repulsions that would otherwise cause the atom's size to increase.

Group Trend

The atomic radius of atoms generally increases from top to bottom within a group. As the atomic number increases down a group, there is again an increase in the positive nuclear charge. However, there is also an increase in the number of occupied principal energy levels. Higher principal energy levels consist of orbitals which are larger in size than the orbitals from lower energy levels. The effect of the greater number of principal energy levels outweighs the increase in nuclear charge, and so atomic radius increases down a group.

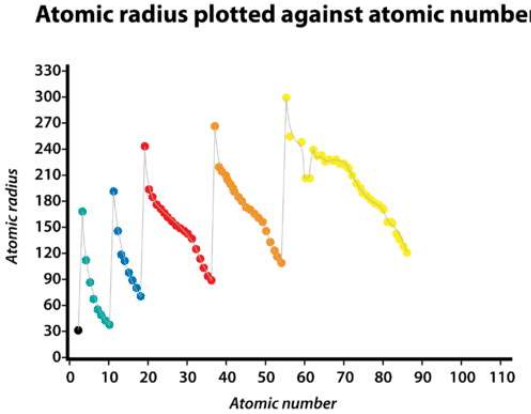
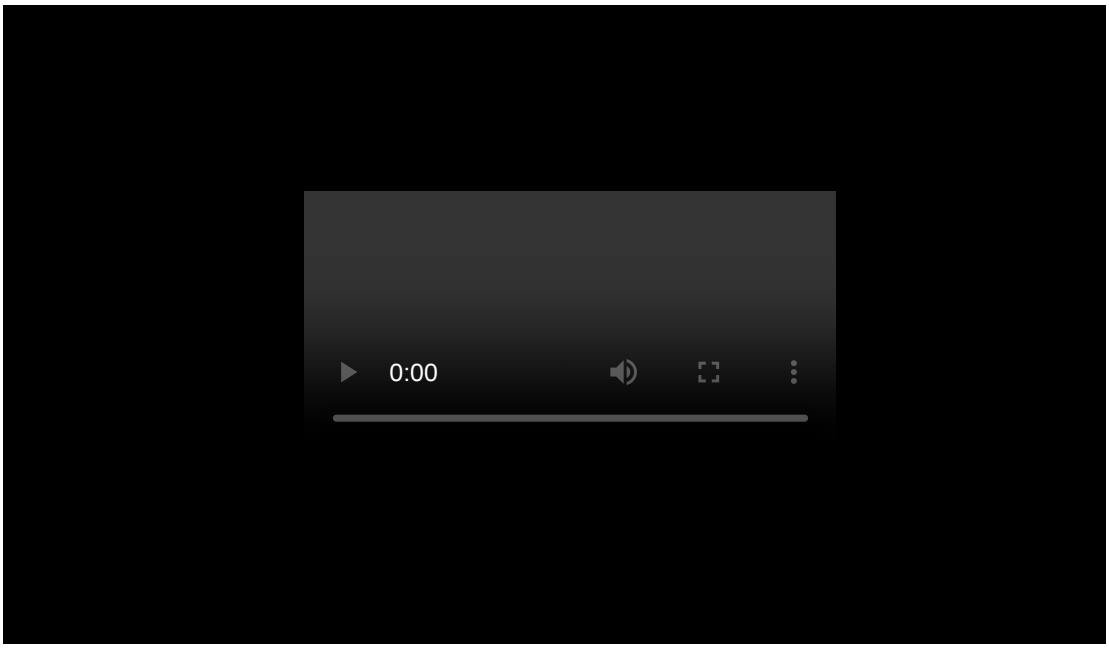


Figure **2.2.4**: A graph of atomic radius plotted versus atomic number. Each successive period is shown in a different color. As the atomic number increases within a period, the atomic radius decreases. (CC BY-NC 3.0; Christopher Auyeung via CK-12 Foundation)



Summary

- Atomic radius is determined as half the distance between the nuclei of two identical atoms bonded together.
- The atomic radius of atoms generally decreases from left to right across a period.
- The atomic radius of atoms generally increases from top to bottom within a group.

Review

1. Define “atomic radius.”
2. What are the units of measurement for atomic radius?
3. How does the atomic radius of different elements change across a period?
4. How does atomic radius change from top to bottom within a group?
5. Explain why the atomic radius of hydrogen is so much smaller than the atomic radius of potassium.

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2.3: Periodic Trends- Ionization Energy



Figure **2.3.1** (CC by 2.0; Nick Russill via Flickr, Northern Lights, Greenland [www.flickr.com])

The incredible green lights in this cold northern sky consist of charged particles known as ions. Their swirling pattern is caused by the pull of Earth's magnetic field. Called the northern lights, this phenomenon of nature shows that ions respond to a magnetic field. Do you know what ions are? Read on to find out.

Atoms Are Neutral

The northern lights aren't caused by atoms, because atoms are not charged particles. An atom always has the same number of electrons as protons. Electrons have an electric charge of -1 and protons have an electric charge of +1. Therefore, the charges of an atom's electrons and protons "cancel out." This explains why atoms are neutral in electric charge.

Q: What would happen to an atom's charge if it were to gain extra electrons?

A: If an atom were to gain extra electrons, it would have more electrons than protons. This would give it a negative charge, so it would no longer be neutral.

Atoms to Ions

Atoms cannot only gain extra electrons. They can also lose electrons. In either case, they become **ions**. Ions are atoms that have a positive or negative charge because they have unequal numbers of protons and electrons. If atoms lose electrons, they become positive ions, or cations. If atoms gain electrons, they become negative ions, or anions. Consider the example of fluorine (see figure below). A fluorine atom has nine protons and nine electrons, so it is electrically neutral. If a fluorine atom gains an electron, it becomes a fluoride ion with an electric charge of -1.

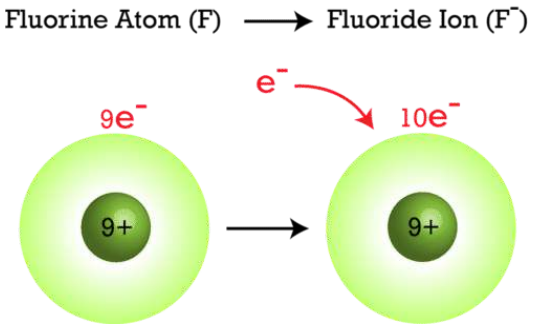


Figure **2.3.2** (CC BY-NC 3.0; Christopher AuYeung via CK-12 Foundation)

Names and Symbols

Like fluoride, other negative ions usually have names ending in *–ide*. Positive ions, on the other hand, are just given the element name followed by the word *ion*. For example, when a sodium atom loses an electron, it becomes a positive sodium ion. The charge of an ion is indicated by a plus (+) or minus sign (-), which is written to the right of and just above the ion's chemical symbol. For example, the fluoride ion is represented by the symbol F^-, and the sodium ion is represented by the symbol Na^+. If the charge is greater than one, a number is used to indicate it. For example, iron (Fe) may lose two electrons to form an ion with a charge of plus

two. This ion would be represented by the symbol Fe^{2+}. This and some other common ions are listed with their symbols in the table below.

Table *PageIndex*1: Some Common Ions

Cations		Anions	
Name of Ion	Chemical Symbol	Name of Ion	Chemical Symbol
Calcium ion	Ca^{2+}	Chloride	Cl^-
Hydrogen ion	H^+	Fluoride	F^-
Iron(II) ion	Fe^{2+}	Bromide	Br^-
Iron(III) ion	Fe^{3+}	Oxide	O^{2-}

Q: How does the iron(III) ion differ from the iron(II) ion?

A: The iron(III) ion has a charge of +3, so it has one less electron than the iron(II) ion, which has a charge of +2.

Q: What is the charge of an oxide ion? How does its number of electrons compare to its number of protons?

A: An oxide ion has a charge of -2. It has two more electrons than protons.

How Ions Form

The process in which an atom becomes an ion is called ionization. It may occur when atoms are exposed to high levels of radiation. The radiation may give their outer electrons enough energy to escape from the attraction of the positive nucleus. However, most ions form when atoms transfer electrons to or from other atoms or molecules. For example, sodium atoms may transfer electrons to chlorine atoms. This forms positive sodium ions (Na^+) and negative chloride ions (Cl^-).



Q: Why do you think atoms lose electrons to, or gain electrons from, other atoms?

A: Atoms form ions by losing or gaining electrons because it makes them more stable and this state takes less energy to maintain. The most stable state for an atom is to have its outermost energy level filled with the maximum possible number of electrons. In the case of metals such as lithium, with just one electron in the outermost energy level, a more stable state can be achieved by losing that one outer electron. In the case of nonmetals such as fluorine, which has seven electrons in the outermost energy level, a more stable state can be achieved by gaining one electron and filling up the outer energy level.



Properties of Ions

Ions are highly reactive, especially as gases. They usually react with ions of opposite charge to form neutral compounds. For example, positive sodium ions and negative chloride ions react to form the neutral compound sodium chloride, commonly known as table salt. This occurs because oppositely charged ions attract each other. Ions with the same charge, on the other hand, repel each other. Ions are also deflected by a magnetic field, as you saw in the opening image of the northern lights.

Summary

- Atoms have equal numbers of positive protons and negative electrons, so they are neutral in electric charge.
- Atoms can gain or lose electrons and become ions, which are atoms that have a positive or negative charge because they have unequal numbers of protons and electrons.
- The process in which an atom becomes an ion is called ionization. It may occur when atoms are exposed to high levels of radiation or when atoms transfer electrons to or from other atoms.
- Ions are reactive, attracted or repulsed by other charged particles, and deflected by a magnetic field.

Review

1. Why are atoms neutral in electric charge?
2. Define ion.
3. Compare and contrast cations and anions, and give an example of each.
4. Describe how ions form.
5. List properties of ions.
6. The model in the illustration below represents an atom of lithium (Li). If the lithium atom becomes an ion, which type of ion will it be, a cation or an anion? What will be the electric charge of this ion? What will the ion be named? What symbol will be used to represent it?

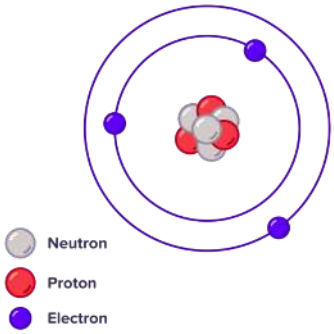


Figure **2.3.3** (CC BY-NC 3.0; CK-12 Foundation Employee via CK-12 Foundation)

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2.4: Periodic Trends- Electronegativity



Figure 2.4.1 (Used under licenses from Shutterstock.com; (left) Image copyright Pressmaster, 2013; (right) Image copyright cdrin, 2013 via http://www.shutterstock.com; http://www.shutterstock.com)

Is it easy or hard for you to make new friends?

Have you ever noticed how some people attract others to them? Whether it be their personality, attractiveness, or athletic skills—something pulls people toward them; while others have a smaller group of friends and acquaintances. Atoms do the same thing. One atom may pull electrons strongly to it, while a second type of atom has much less "pulling power".

Electronegativity

Valence electrons of both atoms are always involved when those two atoms come together to form a chemical bond. Chemical bonds are the basis for how elements combine with one another to form compounds. When these chemical bonds form, atoms of some elements have a greater ability to attract the valence electrons involved in the bond than other elements.

Electronegativity is a measure of the ability of an atom to attract the electrons when the atom is part of a compound. Electronegativity differs from electron affinity because electron affinity is the actual energy released when an atom gains an electron. Electronegativity is not measured in energy units, but instead a relative scale. All elements are compared to one another, with the most electronegative element, fluorine, being assigned an electronegativity value of 3.98. Fluorine attracts electrons better than any other element. The table below shows the electronegativity values for the elements.

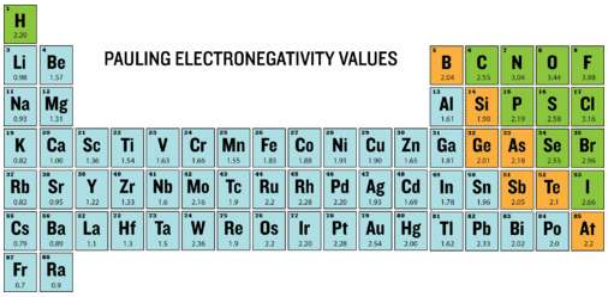


Figure 2.4.2: The electronegativity scale was developed by Nobel Prize winning American chemist Linus Pauling. The largest electronegativity (3.98) is assigned to fluorine and all other electronegativity measurements are on a relative scale. (CC BY-NC 3.0; Christopher Auyeung via CK-12 Foundation)

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

Trends

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

Of the main group elements, fluorine has the highest electronegativity (EN $= 4.0$) and cesium the lowest (EN $= 0.79$). This indicates that fluorine has a high tendency to gain electrons from other elements with lower electronegativities. We can use these values to predict what happens when certain elements combine.

When the difference between atom electronegativities is greater than ~1.7, then a complete exchange of electrons occurs. Typically this exchange is between a metal and a nonmetal. For instance, sodium and chlorine will typically combine to form a new compound and each ion becomes isoelectronic with its nearest noble gas. When we compare the EN values, we see that the electronegativity for $\mathbf{Na}$ is 0.93 and the value for $\mathbf{Cl}$ is 3.2. The absolute difference between ENs is $|0.93 - 3.2| = 2.27$. This value is greater than 1.7, and therefore indicates the occurence of a complete electron exchange.

Summary

- Electronegativity is a measure of the ability of an atom to attract the electrons when the atom is part of a compound.
- Electronegativity values generally increase from left to right across the periodic table.
- Electronegativities generally decrease from the top to bottom of a group.
- The highest electronegativity value is for fluorine.

Review

1. Define “electronegativity.”
2. How does electronegativity differ from electron affinity?
3. Why are the electronegativity values of metals generally low?
4. Describe the trend in electronegativities across the periodic table.
5. Describe the trends in electronegativities in a group of the periodic table.

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2.5: Prelude to Ionic Bonding and Simple Ionic Compounds

We will see that the word salt has a specific meaning in chemistry, but to most people, this word refers to table salt. This kind of salt is used as a condiment throughout the world, but it was not always so abundant. Two thousand years ago, Roman soldiers received part of their pay as salt, which explains why the words salt and salary come from the same Latin root (salarium). Today, table salt is either mined or obtained from the evaporation of saltwater.

Table salt is sodium chloride (NaCl), which is a simple compound of two elements that are necessary for the human body to function properly. Sodium, for example, is important for nerve conduction and fluid balance. In fact, human blood is about a 0.9% sodium chloride solution, and a solution called normal saline is commonly administered intravenously in hospitals.

Although some salt in our diets is necessary to replenish the sodium and chloride ions that we excrete in urine and sweat, too much is unhealthy, and many people may be ingesting more salt than their bodies need. The RDI of sodium is 2,400 mg—the amount in about 1 teaspoon of salt—but the average intake of sodium in the United States is between 4,000 mg and 5,000 mg, partly because salt is a common additive in many prepared foods. Previously, the high ingestion of salt was thought to be associated with high blood pressure, but current research does not support this link. Even so, some doctors still recommend a low-salt diet (never a “no-salt” diet) for patients with high blood pressure, which may include using a salt substitute. Most salt substitutes use potassium instead of sodium, but some people complain that the potassium imparts a slightly bitter taste.

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2.6: Prelude to Covalent Bonding and Simple Molecular Compounds

Cholesterol ($C_{27}H_{46}O$), a compound that is sometimes in the news, is a white, waxy solid produced in the liver of every animal, including humans. It is important for building cell membranes and in producing certain hormones (chemicals that regulate cellular activity in the body). As such, it is necessary for life, but why is cholesterol the object of attention?

Besides producing cholesterol, we also ingest some whenever we eat meat or other animal-based food products. People who eat such products in large quantities, or whose metabolisms are unable to handle excess amounts, may experience an unhealthy buildup of cholesterol in their blood. Deposits of cholesterol, called plaque, may form on blood vessel walls, eventually blocking the arteries and preventing the delivery of oxygen to body tissues. Heart attacks, strokes, and other circulatory problems can result.

Most medical professionals recommend diets that minimize the amount of ingested cholesterol as a way of preventing heart attacks and strokes. Tests are available to measure cholesterol in the blood, and there are several drugs capable of lowering cholesterol levels.

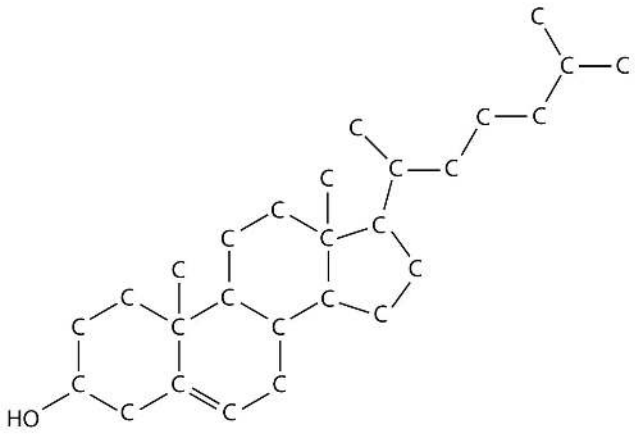


Figure 2.6.1: A Molecular Model of Cholesterol

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2.7: Lewis Dot and Bonding

Learning Objectives

- Realize that valence electrons can be represented by dots.
- Know that there are two types of bonding: ionic and covalent.
- Know that ionic bonding involves a metal and a nonmetal with a transfer of electrons.
- Know that covalent bonding involves two nonmetals or a metalloid with a nonmetal sharing electrons.

Bonding (Ionic and Covalent Basics)

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 stabile 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. A few examples of real-world ionic compounds would be NaCl (table salt) and NaF (active ingredient in toothpaste).



Figure **2.7.1**: NaCl crystals. Image used with permission (Public Domain; NASA).

If two nonmetals interact, then a covalent bond will result. The connection that forms is due to each atom sharing it(s) valence electron(s). In this type of bonding, each atom (except for H, B, and Be) obtains an octet and becomes stable. Metalloids and nonmetals can bond to form covalent compounds as well. Solid covalent compound are not crystalline in texture. Unlike ionic compounds. covalent compounds can be liquids or even gases.



Figure **2.7.2**: Covalent compounds NO_2 and N_2O_4 contained in glass bottles. Image taken from: https://commons.wikimedia.org/wiki/File:NO2-N2O4.jpg

***Table* 2.7.1:** *Comparing ionic and covalent compounds*

Ionic Bonding	Covalent Bonding
Metal/nonmetal combination	nonmetal/nonmetal or metalloid/nonmetal combination
Metal loses valence electrons and nonmetal gains up to eight.	Both elements share valence electrons to achieve stability
Individual species have cation/anion charges	No charges are present in these compounds
All ionic compounds are solids	Covalent compounds can be solid, liquid, or gas.
Examples could include: Li_2CO_3, Fe_2O_3, and $MgSO_4$	Examples include: CO_2, H_2O, and CH_3CH_2OH

Lewis Symbols

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. Each Lewis dot symbol consists of the chemical symbol for an element surrounded by dots that represent its valence electrons. Lewis knew that incorporating models into his teaching would enable students to visualize chemical bonding easier. Gilbert Lewis was known for his interactive teaching methods and his interest in student success. Unfortunately, his nervous personality limited his ability to lecture in front of large groups of people.

Regarding his research, Lewis constructed his own theory to explain the nature of acids and bases. He was the first to synthesize D_2O (heavy water) and wrote numerous textbooks for his courses. In World War I, he served as a Major in the Gas Service unit of the American Army. He trained over 200 soldiers a week on how to adequately protect themselves from gas warfare. From these efforts, he helped reduce fatalities due to chemical gas exposures and was awarded the Distinguish Service Medal in 1922.

Lewis was nominated over thirty times for the Nobel Prize. He never received this award and does not have an element named in honor of him. For more on Gilbert Lewis, click on this link.

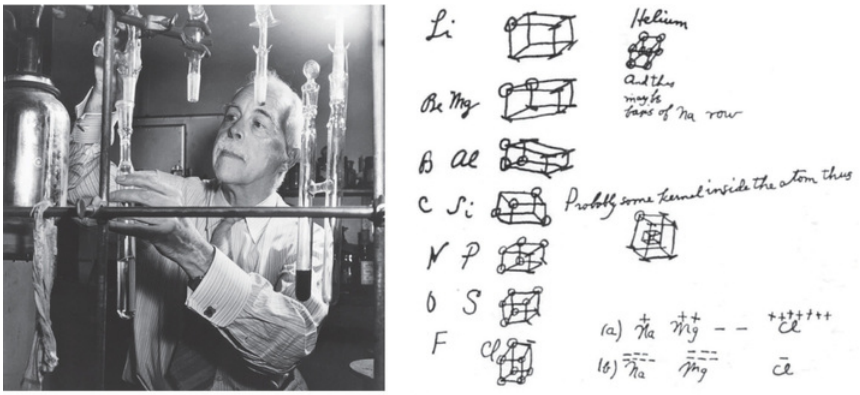


Figure **2.7.3**: G. N. Lewis and the Octet Rule. (a) Lewis is working in the laboratory. (b) In Lewis's original sketch for the octet rule, he initially placed the electrons at the corners of a cube rather than placing them as we do now.

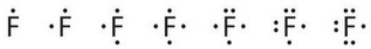
Lewis Dot symbols

- convenient representation of valence electrons
- allows scientists to keep track of valence electrons during bond formation
- consists of the chemical 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:



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



The number of dots in the Lewis dot symbol is the same as the number of valence electrons, which is the same as the last digit of the element's group number in the periodic table. Lewis dot symbols and electron configurations (not a topic for this course) for the elements in period 2 are given in Table **2.7.2**.

***Table* 2.7.2:** *Lewis Dot Symbols for the Elements in Period 2*

Group	1	2	13	14	15	16	17	18
Electron Configuration	$[He]2s^1$	$[He]2s^2$	$[He]2s^2 2p^1$	$[He]2s^2 2p^2$	$[He]2s^2 2p^3$	$[He]2s^2 2p^4$	$[He]2s^2 2p^5$	$[He]2s^2 2p^6$
Lewis Dot Symbol	Li ·	·Be·	· B ·	· C ·	· N ·	: O ·	: F ·	:Ne:

Ionic compounds are produced when a metal bonds with a nonmetal. Stability is achieved for both atoms once the transfer of electrons has occurred. The image below shows how sodium and chlorine bond to form the compound sodium chloride. Unlike a sodium atom, the resulting compound is not explosive and less corrosive than chlorine. Ionic bonding can be viewed by noting the donation of valence electrons from a metal atom to a nonmetal atom by using the Bohr model. From this theory, we will move on the Lewis structure with an understanding that metals will always lose valence electrons and nonmetals will gain up to eight in order to form stable compounds.

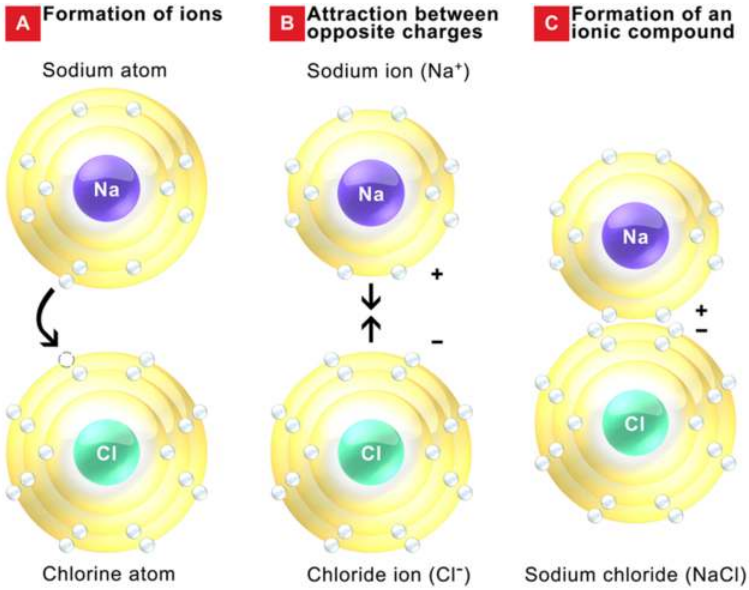


Figure **2.7.4**: Formation of an ionic bond between sodium and chlorine. Image courtesy of By BruceBlaus - Own work, CC BY-SA 4.0, https://commons.wikimedia.org/w/inde...curid=44968540

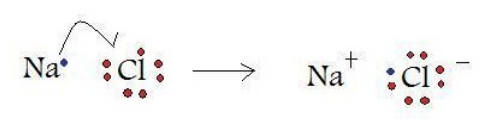
Rules for Drawing IOnic Lewis structures

When drawing Lewis structures for compounds formed from the combination of a metal/nonmetal, use the list of rules shown below:

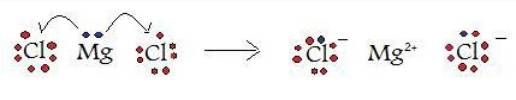
a. Locate the elements of interest and recall how many valence electrons each species has.
b. Draw dots around each element individually.
c. To obtain successful octets, the metal must transfer all of its valence electrons to the nonmetal.
d. At this point, the metal should have no electrons around it. In addition, the nonmetal will have an octet. If this does not occur, then refer to step e.
e. Additional atoms of the same two elements may be brought in to accomplish rules a-c.
f. **Cation and anion charges must be on Lewis structure to receive full credit (this is an ionic compound).**

g. To check structure, quickly write a formula for the ionic compound. This involves crossing down the charges diagonally and losing signs. You must reduce subscripts if they are divisible by a factor.

Example 2.7.1: Chloride Salts



In this example, 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. Only one atom of each element is needed to obtain a stable compound.



In this example, the magnesium atom is donating both of its valence electrons to chlorine atoms. Each chlorine atom can only accept 1 electron before it can achieve an octet; therefore, 2 atoms of chlorine are required to accept the 2 electrons donated by the magnesium. Notice that the net charge of the compound is 0. This Lewis structure requires two anions per one cation to produce a stable compound.

For more rigorous examples, access the CHM101 Furman moodle page (chapter 4 documents), to view a lightboard video of your instructor.

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2.8: Covalent Bonds

Learning Objectives

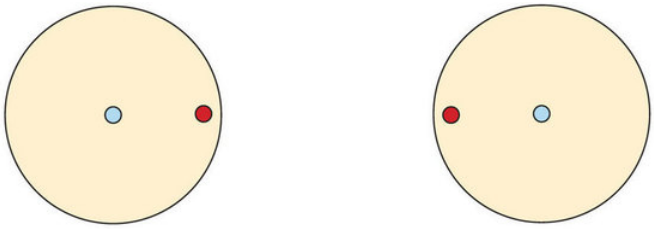
- To describe how a covalent bond forms.
- To apply the octet rule to covalent compounds

You have already seen examples of substances that contain covalent bonds. One substance mentioned previously was water (H_2O). You can tell from its formula that it is not an ionic compound; it is not composed of a metal and a nonmetal. Consequently, its properties are different from those of ionic compounds.

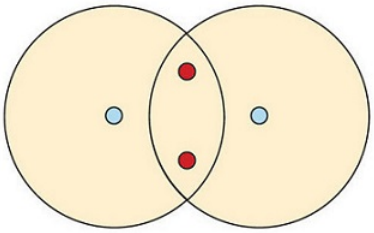
Electron Sharing

Previously, we discussed ionic bonding where electrons can be transferred from one atom to another so that both atoms have an energy-stable outer electron shell. Because most filled electron shells have eight electrons in them, chemists called this tendency the octet rule. However, there is another way an atom can achieve a full valence shell: atoms can *share* electrons.

This concept can be illustrated by using two hydrogen atoms, each of which has a single electron in its valence shell. (For small atoms such as hydrogen atoms, the valence shell will be the first shell, which holds only two electrons.) We can represent the two individual hydrogen atoms as follows:



In contrast, when two hydrogen atoms get close enough together to share their electrons, they can be represented as follows:



By sharing their valence electrons, both hydrogen atoms now have two electrons in their respective valence shells. Because each valence shell is now filled, this arrangement is more stable than when the two atoms are separate. The sharing of electrons between atoms is called a covalent bond, and the two electrons that join atoms in a covalent bond are called a bonding pair of electrons. A discrete group of atoms connected by covalent bonds is called a molecule—the smallest part of a compound that retains the chemical identity of that compound.

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:



This depiction of molecules is simplified further by using a dash to represent a covalent bond. The hydrogen molecule is then represented as follows:



Remember that the dash, also referred to as a single bond, represents a *pair* of electrons.

The bond in a hydrogen molecule, measured as the distance between the two nuclei, is about 7.4×10^{-11} m, or 74 picometers (pm; 1 pm = 1×10^{-12} m). This particular bond length represents a balance between several forces: the attractions between oppositely charged electrons and nuclei, the repulsion between two negatively charged electrons, and the repulsion between two positively charged nuclei. If the nuclei were closer together, they would repel each other more strongly; if the nuclei were farther apart, there would be less attraction between the positive and negative particles.

Fluorine is another element whose atoms bond together in pairs to form *diatomic* (two-atom) molecules. Two separate fluorine atoms have the following electron dot diagrams:

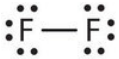


Each fluorine atom contributes one valence electron, making a single bond and giving each atom a complete valence shell, which fulfills the **octet** rule:



Two F's with two dots in between them, and two dots on the top, left/right side, and bottoms of each F.

The circles show that each fluorine atom has eight electrons around it. As with hydrogen, we can represent the fluorine molecule with a dash in place of the bonding electrons:



Two F's with a long dash in between them, and two dots on the top, left/right side, and bottoms of each F.

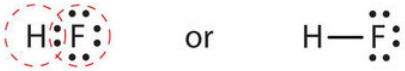
Each fluorine atom has six electrons, or three pairs of electrons, that are not participating in the covalent bond. Rather than being shared, they are considered to belong to a single atom. These are called nonbonding pairs (or lone pairs) of electrons.

Covalent Bonds between Different Atoms

Now that we have looked at electron sharing between atoms of the same element, let us look at covalent bond formation between atoms of different elements. Consider a molecule composed of one hydrogen atom and one fluorine atom:



Each atom needs one additional electron to complete its valence shell. By each contributing one electron, they make the following molecule:



An H and F connected by two dots, and the F has 2 dots on the top, right, and bottom. It also shows the same combination but with a long dash in between the H and F rather than two dots.

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 2.8.1

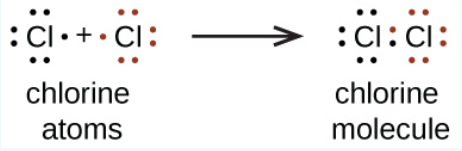
Use Lewis diagrams to indicate the formation of the following:

a. Cl_2
b. HBr

Solution

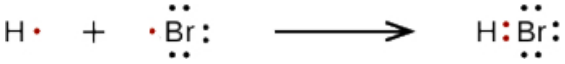
a. When two chlorine atoms form a chlorine molecule, they share one pair of electrons. In Cl_2 molecule, each chlorine atom is surrounded by an **octet** number of electrons.

The Lewis diagram for a Cl_2 molecule is similar to the one for F_2 (shown above).



Cl with 7 dots surrounding it plus Cl with 7 dots surrounding it means they are chlorine atoms. To turn into a chlorine molecule, have two dots in between each Cl and 6 dots surrounding each Cl on the sides that aren't connected.

b. When a hydrogen atom and a bromine atom form HBr, they share one pair of electrons. In the HBr molecule, H achieves a full valence of two electrons (**duet**) while Br achieves an **octet**. The Lewis diagram for HBr is similar to that for HF shown above.



H with one dot plus Br with 7 dots turns into H connected to Br by two dots, with 6 other dots surrounding Br.

? Exercise 2.8.1

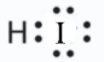
Draw the Lewis diagram for each compound.

a. a molecule composed of one chlorine atom and one fluorine atom
b. a molecule composed of one hydrogen atom and one iodine atom

Answer a:

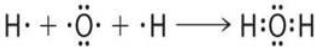


Answer b:



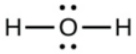
Covalent Bonds in Larger Molecules

The formation of a water molecule from two hydrogen atoms and an oxygen atom can be illustrated using Lewis dot symbols (shown below).



H with one dot + O with 6 dots + H with one dot turns into H connected to O with two dots connected to H with two dots. O also has two dots on top and top dots on bottom.

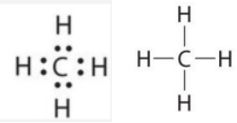
The structure on the right is the *Lewis electron structure*, or *Lewis structure*, for H_2O. With two bonding pairs and two lone pairs, the oxygen atom has now completed its **octet**. Moreover, by sharing a bonding pair with oxygen, each hydrogen atom now has a full valence shell of two electrons. Chemists usually indicate a bonding pair by a single line, as shown (below).



Water

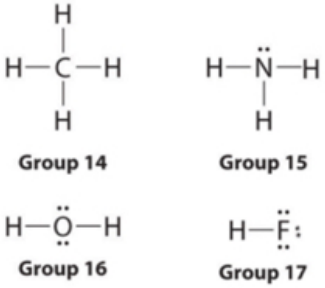
Other large molecules are constructed in a similar fashion, with some atoms participating in more than one covalent bond. For example, methane (CH_4), the central carbon atom bonded to four hydrogen atoms, can be represented using either of the Lewis

structures below. Again, sharing electrons between C and H atoms results in C achieving and octet while H achieving a duet number of electrons.



How Many Covalent Bonds Are Formed?

The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons). In the Lewis structure, the number of bonds formed by an element in a neutral compound is the same as the number of unpaired electrons it must share with other atoms to complete its octet of electrons. For example, each atom of a **group 4A** (14) element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming **four covalent bonds**, as illustrated here for carbon in CH_4 (methane). **Group 5A** (15) elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form **three covalent bonds**, as in NH_3 (ammonia). Oxygen and other atoms in **group 6A** (16) obtain an octet by forming **two covalent bonds**. Fluorine and the other halogens in **group 7A** (17) have seven valence electrons and can obtain an octet by forming **one covalent bond**.



Typically, the atoms of group 4A form 4 covalent bonds; group 5A form 3 bonds; group 6A form 2 bonds; and group 7A form one bond. The number of electrons required to obtain an octet determines the number of covalent bonds an atom can form. This is summarized in the table below. In each case, the sum of the number of bonds and the number of lone pairs is 4, which is equivalent to eight (octet) electrons.

This table shows atoms and their group numbers, and how many bonds and lone pairs each has.

Atom (Group number)	Number of Bonds	Number of Lone Pairs
Carbon (Group 14 or 4A)	4	0
Nitrogen (Group 15 or 5A)	3	1
Oxygen (Group 16 or 6A)	2	2
Fluorine (Group 17 or 7A)	1	3

Because hydrogen only needs two electrons to fill its valence shell, it follows the duet rule. It is an **exception to the octet rule.** Hydrogen only needs to form one bond. This is the reason why H is always a terminal atom and never a central atom. Figure **2.8.1** shows the number of covalent bonds various atoms typically form.

The transition elements and inner transition elements also do not follow the octet rule since they have d and f electrons involved in their valence shells.

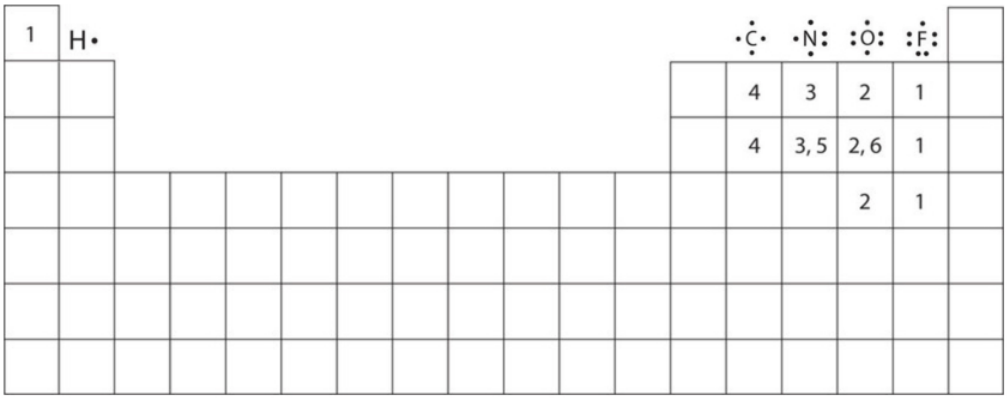
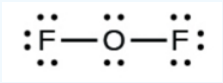


Figure **2.8.1**: How Many Covalent Bonds Are Formed? In molecules, there is a pattern to the number of covalent bonds that different atoms can form. Each block with a number indicates the number of covalent bonds formed by that atom in neutral compounds.

Example 2.8.2

Examine the Lewis structure of OF_2 below. Count the number of bonds formed by each element. Based on the element's location in the periodic table, does it correspond to the expected number of bonds shown in Table 4.1? Does the Lewis structure below follow the octet rule?



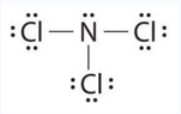
F surrounded by 6 dots, connected to O with a long dash. O surrounded by 4 dots and connects to another F with a long dash. F surrounded by 6 dots.

Solution

Yes. F (group 7A) forms one bond and O (group 6A) forms 2 bonds. Each atom is surrounded by 8 electrons. This structure satisfies the octet rule.

2.8.2Exercise

Examine the Lewis structure of NCl_3 below. Count the number of bonds formed by each element. Based on the element's location in the periodic table, does it correspond to the expected number of bonds shown in Table 4.1? Does the Lewis structure below follow the octet rule?



Answer

Both Cl and N form the expected number of bonds. Cl (group 7A) has one bond and 3 lone pairs. The central atom N (group 5A) has 3 bonds and one lone pair. Yes, the Lewis structure of NCl_3 follows the octet rule.

Key Takeaways

- A covalent bond is formed between two atoms by sharing electrons.
- The number of bonds an element forms in a covalent compound is determined by the number of electrons it needs to reach octet.
- Hydrogen is an exception to the octet rule. H forms only one bond because it needs only two electrons.

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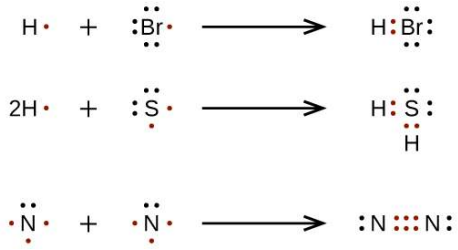
2.9: Drawing Lewis Structures

Learning Objectives

- To draw Lewis structures.
- To recognize molecules that are likely to have multiple covalent bonds.

DRAWING LEWIS STRUCTURES

For very simple molecules and molecular ions, we can write the Lewis structures by merely pairing up the unpaired electrons on the constituent atoms. See these examples:



For more complicated molecules and molecular ions, it is helpful to follow the step-by-step procedure outlined here:

1. Determine the total number of valence (outer shell) electrons among all the atoms. For cations, subtract one electron for each positive charge. For anions, add one electron for each negative charge.
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom. (Generally, the least electronegative element should be placed in the center.) Connect each atom to the central atom with a single bond (one electron pair).
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen), completing an octet around each atom.
4. Place all remaining electrons on the central atom.
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

Let us determine the Lewis structures of OF_2 and HCN as examples in following this procedure:

1. Determine the total number of valence (outer shell) electrons in the molecule or ion. For a molecule, we add the number of valence electrons (use the main group number) on each atom in the molecule. This is the total number of electrons that must be used in the Lewis structure.

$$O + 2\,(F) = OF_2$$

$$6e^- + (2 \times 7e^-) = 20e^-$$

$$H + C + N = HCN$$

$$1e^- + 4e^- + 5e^- = 10e^-$$

2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond. Note that H and F can only form one bond, and are always on the periphery rather than the central atom.

F—O—F H—C—N

3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.

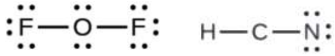
- In OF_2, six electrons are placed on each F.

- In HCN, six electrons placed on N



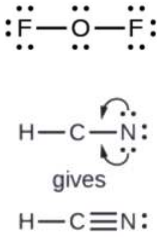
4. Place all remaining electrons on the central atom.

- In OF_2, 4 electrons are placed on O.
- In HCN: no electrons remain (the total valence of $10e^-$ is reached) so nothing changes.



5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

- In OF_2, each atom has an octet as drawn, so nothing changes.
- In HCN, form two more C–N bonds

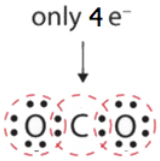


H dash C dash N with 6 dots around the N. 4 of the dots are pointing to the dash connecting the C and the N. This turns the formula into H dash C and three lines connecting the C and N together, with two dots on the outside of the N.

Finally, check to see if the total number of valence electrons are present in the Lewis structure. And then, inspect if the H atom has 2 electrons surrounding it and if each of the main group atoms is surrounded by 8 electrons.

MULTIPLE BONDS

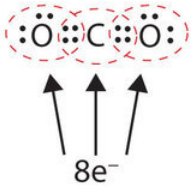
In many molecules, the octet rule would not be satisfied if each pair of bonded atoms shares only two electrons. Review HCN in Step 5 above. Another example is carbon dioxide (CO_2). CO_2 has a total valence of $4e^- + (2 \times 6e^-) = 16e^-$. Following steps 1 to 4, we draw the following:



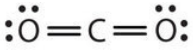
This does not give the carbon atom a complete octet; only four electrons are in its valence shell. This arrangement of shared electrons is far from satisfactory.



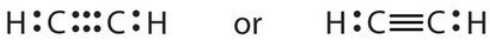
In this case, more than one pair of electrons must be shared between two atoms for both atoms to have an octet. A second electron pair from each oxygen atom must be shared with the central carbon atom shown by the arrows above. A lone pair from each O must be converted into a bonding pair of electrons.



In this arrangement, the carbon atom shares four electrons (two pairs) with the oxygen atom on the left and four electrons with the oxygen atom on the right. There are now eight electrons around each atom. Two pairs of electrons shared between two atoms make a double bond between the atoms, which is represented by a double dash:



Some molecules contain triple bonds (like HCN, shown above). Triple bonds are covalent bonds in which *three* pairs of electrons are shared by two atoms. Another compound that has a triple bond is acetylene (C_2H_2), whose Lewis diagram is as follows:



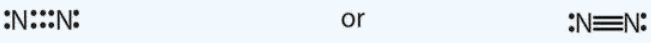
Example 2.9.1

Draw the Lewis diagram for each molecule.

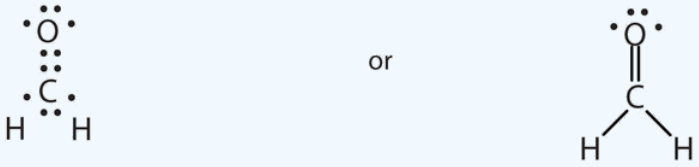
1. $\mathbf{N_2}$
2. $\mathbf{CH_2O}$ (The carbon atom is the central atom.) One application of CH_2O, also called formaldehyde, is the preservation of biological specimens. Aqueous solutions of CH_2O are called formalin and have a sharp, characteristic (pungent) odor.

Solution

1. The total number of electrons is 2 x 5 = 10 electrons. The bond between the two nitrogen atoms is a triple bond. The Lewis diagram for $N_2$is as follows:



2. The total number of electrons is 4 x 2(1) + 6 = 12 electrons. In CH_2O, the central atom is surrounded by two different types of atoms. The Lewis diagram that fills each atom's valence electron shell is as follows:

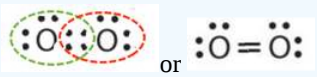


Exercise 2.9.1

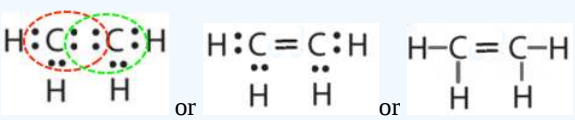
Draw the Lewis diagram for each molecule.

a. $\mathbf{O_2}$
b. $\mathbf{C_2H_4}$

Answer a:

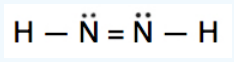


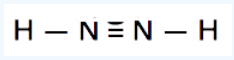
Answer b:

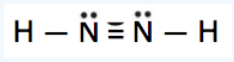


Example 2.9.2

Which is the correct Lewis structure for N_2H_2?

A. 

B. 

C. 

Solution

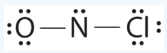
Lewis structure A is the correct answer. It has a total of (2 x $5e^-$) + (2 x $1e^-$) = $12e^-$. Each of the N atoms satisfy the octet requirement and the H atoms follow the duet rule.

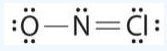
Structure B is electron deficient. It has only $10e^-$ instead of 12.

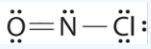
Structure C has 14 (2 extra) electrons. The N atoms do not satisfy the octet.

2.9.2 Exercise

Which is the correct Lewis structure for NOCl?

A. 

B. 

C. 

Answer

Structure A violates the octet rule; N is surrounded by only $6e^-$.

Structure B violates the octet rule; Cl has $10e^-$ around it. Furthermore, there are a total of $20e^-$ instead of $18e^-$.

Structure C is the correct structure. It has a total of $6e^-$ + $5e^-$ + $7e^-$ = $18e^-$. Each atom is surrounded by 8 electrons (octet rule).

Key Takeaways

- A Lewis structure shows the bonding and nonbonding electrons around individual atoms in a molecule.
- Some molecules must have multiple covalent bonds between atoms to satisfy the octet rule.
- A double bond contains four electrons and a triple bond contains six electrons.

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2.10: Characteristics of Molecules

Learning Objectives

- Determine the molecular mass of a molecule.
- Predict the general shape of a simple covalent molecule.
- Predict the polarity of the molecule.
- Compare the properties of ionic and molecular compounds.

Unlike the ions in ionic compounds, which are arranged in lattices called crystals, molecules of covalent compounds exist as discrete units with a characteristic mass and a certain three-dimensional shape.

Molecular Mass

The mass of a molecule—the molecular mass (sometimes called the molecular weight)—is simply the sum of the masses of its atoms. As with formula masses, it is important that you keep track of the number of atoms of each element in the molecular formula to obtain the correct molecular mass.

Example 2.10.1

What is the molecular mass of each covalent compound?

a. H_2O
b. C_6H_6
c. NO_2
d. N_2O_5

Solution

Use the atomic masses from the Periodic Table in Section 2.7.

The molecular formula H_2O indicates that there are two hydrogen atoms and one oxygen atom in each molecule. Summing the masses of these atoms,

This table finds the mass of atoms.

2 H:	2 × 1.01 =	2.02 amu
1 O:		+ 16.00 amu
Total:		18.02 amu

The molecular mass of H_2O is **18.02** amu.

This table finds the mass of atoms.

6 C:	6 × 12.01 =	72.06 amu
6 H:	6 × 1.01 =	+ 6.06 amu
Total:		78.12 amu

The molecular mass of C_6H_6 is **78.12** amu.

This table finds the mass of atoms.

1 N:		14.01 amu
2 O:	2 × 16.00 =	+ 32.00 amu
Total:		46.01 amu

The molecular mass of NO_2 is **46.01** amu.

This table finds the mass of atoms.

2 N:	2 × 14.01 =	28.02 amu
5 O:	5 × 16.00 =	+ 80.00 amu
Total:		108.02 amu

The molecular mass of N_2O_5 is **108.02** amu.

Note that the two different nitrogen and oxygen compounds in these examples have different molecular masses.

? Exercise 2.10.1

What is the molecular mass of each covalent compound?

a. C_2H_2
b. CO
c. CO_2
d. BF_3

Answer a:

26.04 amu

Answer b:

28.01 amu

Answer c:

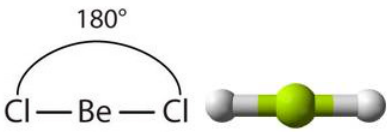
44.01 amu

Answer d:

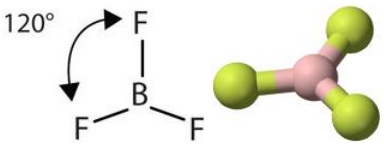
67.81 amu

Molecular Shape: VSEPR Theory

Unlike ionic compounds, with their extended crystal lattices, covalent molecules are discrete units with specific three-dimensional shapes. The shape of a molecule is determined by the fact that covalent bonds, which are composed of negatively charged electrons, tend to repel one another. This concept is called the **valence shell electron pair repulsion (VSEPR) theory**. For example, the two covalent bonds in $BeCl_2$ **stay as far from each other** as possible, ending up 180° apart from each other. The result is a ***linear*** molecule:



The three covalent bonds in BF_3 repel each other to form 120° angles in a plane, in a shape called ***trigonal planar***:



The molecules $BeCl_2$ and BF_3 actually violate the octet rule; however, such exceptions are rare and will not be discussed in this text.

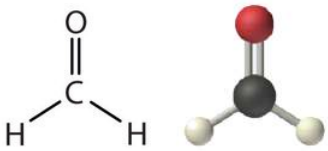
> Try sticking three toothpicks into a marshmallow or a gumdrop and see if you can find different positions where your "bonds" are farther apart than the planar 120° orientation.

The four covalent bonds in CCl_4 arrange themselves three dimensionally, pointing toward the corner of a tetrahedron and making bond angles of 109.5°. CCl_4 is said to have a ***tetrahedral*** shape:

Table describes how to use the number of atoms around the central atom to determine the geometry of a molecule, as well as examples.

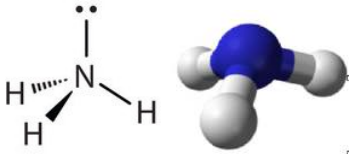
Atoms Around Central Atom	Geometry	Example
2 $\mathbf{AB_2}$	Linear	$\mathbf{BeCl_2}$
3 $\mathbf{AB_3}$	Trigonal Planar	$\mathbf{BF_3}$
4 $\mathbf{AB_4}$	Tetrahedral	$\mathbf{CCl_4}$

In determining the shapes of molecules, it is useful to first determine the Lewis diagram for a molecule. The shapes of molecules with multiple bonds are determined by treating the multiple bonds as one bond. Thus, formaldehyde (CH_2O) has a shape similar to that of BF_3. It is ***trigonal planar***.

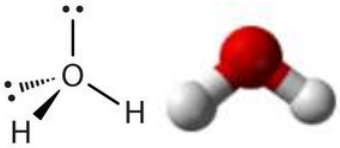


Molecules With Lone Pairs Around Central Atom

Molecules with lone electron pairs around the central atom have a shape based on the position of the atoms, not the electron pairs. For example, NH_3 has **one lone electron pair** and **three bonded electron pairs**. These four electron pairs repel each other and adopt a tetrahedral arrangement. However, the shape of the molecule is described in terms of the positions of the atoms, not the lone electron pairs. Thus, NH_3 is said to have a ***trigonal pyramidal*** shape, not a tetrahedral one.



Similarly, H_2O has **two lone pairs** of electrons around the central oxygen atom and **two bonded electron pairs**. Although the four electron pairs adopt a tetrahedral arrangement, the shape of the molecule is described by the positions of the atoms only. The shape of H_2O is ***bent*** with an approximate 109.5° angle.

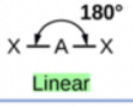
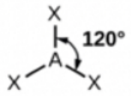
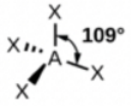


In summary, to determine the molecular geometry:

Step 1: Draw the Lewis structure.

Step 2: Count the number of bonds (a double/triple bond counts as one) and lone pairs around the **central atom**.

Step 3: Use Table 4.5.1 to determine the molecular geometry.

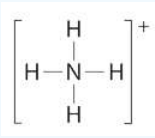
Number of bonds and lone pairs	Number of bonds 0 lone pair	1 lone pair	2 lone pairs
2	 Linear		
3	 Trigonal planar	 Bent or angular	Lone Pair
4	 Tetrahedral	 Trigonal pyramid	 Bent or angular

If a molecule has 2 bonds and 0 lone pairs, it is linear. If a molecule has 3 bonds and 0 lone pairs, it is trigonal planar. If a molecule has 3 bonds and 1 lone pair, it is bent or angular. If a molecule has 4 bonds and 0 lone pairs, it is tetrahedral. If a molecule has 4 bonds and 1 lone pair, it is trigonal pyramid. If a molecule has 4 bonds and 2 lone pairs, it is bent or angular.

Table 4.5.1: *The molecular geometry depends on the number of bonds and lone pairs around the* **central atom, A.**

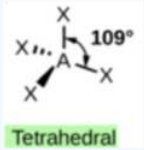
Example 2.10.1

What is the geometry of the ammonium ion, NH_4^+? Its Lewis structure is shown below. How is this different from ammonia, NH_3?

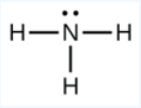


Solution

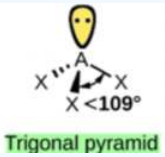
In ammonium ion, the central atom N has 4 bonds and no lone pair. It is equivalent to the below in Table 4.5.1. Hence, this is *tetrahedral*.



In ammonia (NH_3), shown below, N has 3 bonds and one lone pair.

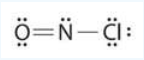


It is equivalent to the below in Table 4.5.1. Hence, the shape of this molecule is *trigonal pyramid*.



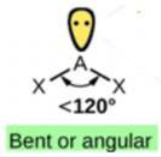
2.10.1 Exercise

What is the molecular shape of nitrosyl chloride, a highly corrosive, reddish-orange gas? Its Lewis structure is shown below.



Answer

Focus on the central atom, N. It has a double bond to O, count this as one bond. It also has a single bond to Cl. Thus, N has 2 bonds and one lone pair. These 3 electron pairs will spread out 120 degrees from each other. But, since the shape is defined by the arrangement of the atoms only, the shape is bent or angular. If you consult Table 4.5.1, this molecule is equivalent to the below. Hence, two bonds and one lone pair has a *bent or angular* shape.



Molecular Polarity

In general, a molecule is nonpolar if all its bonds are nonpolar. Examples are I_2, O_2, H_2, CH_4, C_2H_6 and C_3H_8.

In general, a molecule is polar if it contains polar bonds EXCEPT when the bond polarities cancel each other. As mentioned in Section 4.4, the shape of the CO_2 molecule (linear) orients the two C=O polar bonds **directly opposite** each other, thus **cancelling** each other's effect. **Carbon dioxide** (CO_2) is a ***nonpolar*** molecule.

On the other hand, water (as discussed above) is a bent molecule because of the two lone pairs on the central oxygen atom. Because of the bent shape, the dipoles do not cancel each other out and the water molecule is ***polar***. In the figure below, the individual H-O polar bonds represented by the two red arrows are not directly opposite each other. These two dipoles don't cancel each other out. In fact, the net dipole (blue arrow) points upward. There is a resultant partial positive charge at one end (between the two H atoms) and a partial negative charge on the other end (where O is located). The uneven distribution of charge or the overall dipole is shown by the blue arrow below (Figure 4.5.1). Hence, **water is *polar*** (has + and - poles) while **carbon dioxide is *nonpolar***.

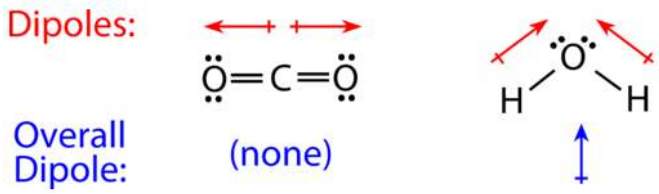


Figure 4.5.1: The molecular geometry of a molecule (linear vs. bent) affects its polarity.

Similarly, in BF_3 (trigonal planar), the effect of a B-F bond is cancelled by the sum of the other two B-F bonds (see video). Hence, a trigonal planar molecule (BF_3) is nonpolar because the bond polarities cancel each other, but a trigonal pyramidal molecule (NH_3) is polar.

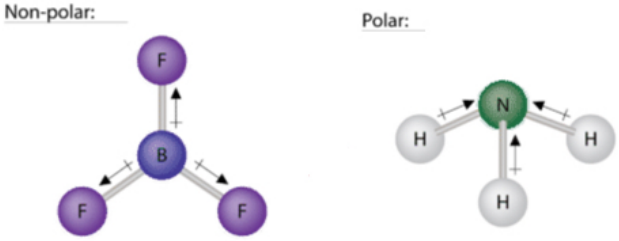


Figure 4.5.2: The molecular geometry of a molecule (trigonal planar vs. trigonal pyramid) affects its polarity.

Some other molecules are shown in the figure below. Notice that a tetrahedral molecule such as CCl_4 is ***nonpolar***. However, if the peripheral atoms are not of the same electronegativity, the bond polarities don't cancel and the molecule becomes ***polar***, as in CH_3Cl.

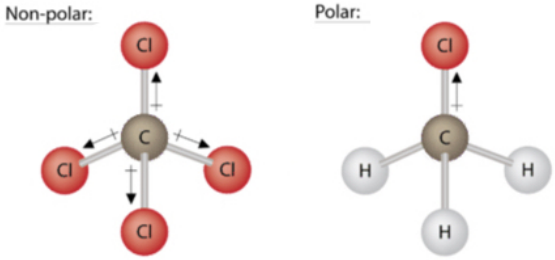


Figure 4.5.3: *The same molecular geometry but peripheral bonds are of different electronegativity. CCl_4 is nonpolar but CH_3Cl is polar.*

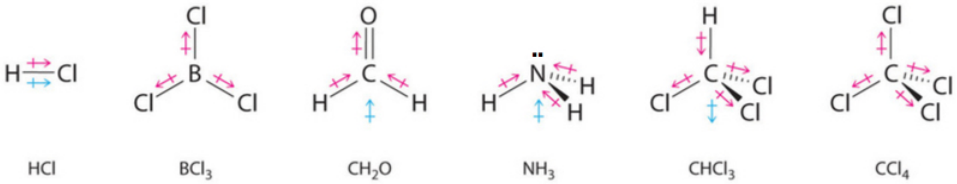


Figure **2.10.4**: Molecules with Polar Bonds. Individual bond dipole moments are indicated in red. Due to their different three-dimensional geometry, some molecules with polar bonds have a net dipole moment (HCl, CH_2O, NH_3, and $CHCl_3$), indicated in blue, whereas others do not because the bond dipoles cancel due to symmetry (BCl_3 and CCl_4).

Physical Properties of Molecular Compounds

The physical state and properties of a particular compound depend in large part on the type of chemical bonding it displays. **Molecular compounds**, sometimes called covalent compounds, display a wide range of physical properties due to the different types of intermolecular attractions such as different kinds of polar interactions. The melting and boiling points of molecular compounds are generally quite low compared to those of **ionic compounds**. This is because the energy required to disrupt the **intermolecular forces** (discussed in Section 8.1) between molecules is far less than the energy required to break the ionic bonds in a crystalline ionic compound. Since molecular compounds are composed of neutral molecules, their electrical conductivity is generally quite poor, whether in the solid or liquid state. Ionic compounds do not conduct electricity in the solid state because of their rigid structure, but conduct well when either molten or dissolved into a solution. The water solubility of molecular compounds is variable and depends primarily on the type of intermolecular forces involved. Substances that exhibit hydrogen bonding or dipole-dipole forces are generally water soluble, whereas those that exhibit only London dispersion forces are generally insoluble. Most, but not all, ionic compounds are quite soluble in water. The table below summarizes some of the differences between ionic and molecular compounds.

Table 4.5.2: Comparison of Ionic and Molecular Compounds

Property	Ionic Compounds	Molecular Compounds
Type of elements	Metal and nonmetal	Nonmetals only
Bonding	Ionic - transfer of electron(s) between atoms	Covalent - sharing of pair(s) of electrons between atoms
Representative unit	Formula unit	Molecule
Physical state at room temperature	Solid	Gas, liquid, or solid
Water solubility	Usually high	Variable
Melting and boiling temperatures	Generally high	Generally low
Electrical conductivity	Good when molten or in solution	Poor

In summary, covalent compounds are softer, have lower boiling and melting points, are more flammable, are less soluble in water and do not conduct electricity compared to ionic compounds. The individual melting and boiling points, solubility and other physical properties of molecular compounds depend on molecular polarity.

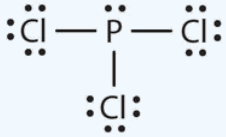
Example 2.10.2

Describe the shape of each molecule. Is it polar or nonpolar?

a. PCl_3
b. CO_2

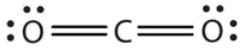
Solution

a. The Lewis diagram for PCl_3 is as follows:



Focus on the central atom, P that has 3 bonds and one lone pair. The four electron pairs arrange themselves tetrahedrally, but the lone electron pair is not considered in describing the molecular shape. Like NH_3, this molecule is *pyramidal*. The 3 P-Cl bonds don't cancel each other. This is *polar.*

- The Lewis diagram for CO_2 is as follows:



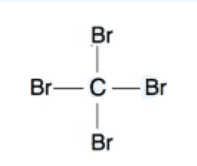
Focus on the central atom, C. The multiple bonds are treated as one group, hence C has 2 bonds and zero lone pair. CO_2 has only two groups of electrons that repel each other. They will direct themselves 180° apart from each other, so CO_2 molecules are *linear*. This is highly symmetrical, with the two opposite dipoles cancelling each other. The CO_2 molecule is *nonpolar*.

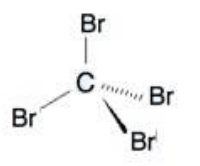
Exercise 2.10.2

Describe the shape of each molecule. Is it polar or nonpolar?

a. CBr_4
b. BCl_3

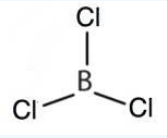
Answer a:



or


The Lewis structure shows 4 groups attached to the central atom, hence *tetrahedral*. All the 4 groups are identical and the shape is symmetrical. Hence, it is *nonpolar.*

Answer b:



The Lewis diagram shows 3 groups attached to the central atom, hence *trigonal planar*. All the 3 groups are identical and shape is symmetrical, hence, it is *nonpolar.*

Key Takeaways

- A molecule has a certain mass, called the molecular mass.
- Simple molecules have geometries that can be determined from VSEPR theory.
- Polar molecules result from differences in electronegativity of the atoms in the molecule.
- Dipoles that are directly opposite one another cancel each other out.

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2.11: Exceptions to the Octet Rule



Figure **2.11.1** (Public Domain; the US Internal Revenue Service via Wikipedia)

Are rules always followed?

Every spring, millions of Americans file their income tax forms. The different rules determine how much tax a person pays. There are also exceptions to the rules. You pay less tax if you are married and/or have children. There are certain limits on how much money you can make before paying taxes. The rule is that you pay taxes, but there are also exceptions based on your personal situation. The bonding rules for molecules are generally applicable, but there are some exceptions allowed.

Exceptions to the Octet Rule

As the saying goes, all rules are made to be broken. When it comes to the octet rule, this is true. Exceptions to the octet rule fall into one of three categories: (1) an **incomplete octet**, (2) **odd-electron molecules**, and (3) an **expanded octet**.

Incomplete Octet

In some compounds, the number of electrons surrounding the central atom in a stable molecule is fewer than eight. Beryllium is an alkaline earth metal and so may be expected to form ionic bonds. However, its very small size and somewhat higher ionization energy compared to other metals actually leads beryllium to form primarily molecular compounds. Since beryllium only has two valence electrons, it does not typically attain an octet through sharing of electrons. The Lewis structure of gaseous beryllium hydride (BeH_2) consists of two single covalent bonds between **Be** and **H** (see figure below).

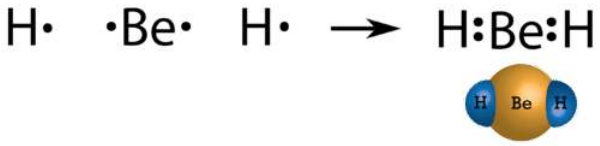


Figure **2.11.2**: Beryllium hydride. (CC BY-NC 3.0; Christopher Auyeung, Joy Sheng via CK-12 Foundation)

Boron and aluminum, with three valence electrons, also tend to form covalent compounds with an incomplete octet. The central boron atom in boron trichloride (BCl_3) has six valence electrons, as shown in the figure below.

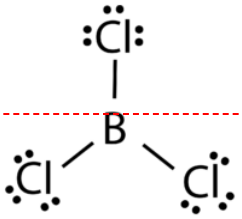


Figure **2.11.3**: Boron trichloride. (CC BY-NC 3.0; Joy Sheng via CK-12 Foundation)

Odd-Electron Molecules

There are a number of molecules whose total number of valence electrons is an odd number. It is not possible for all of the atoms in such a molecule to satisfy the octet rule. An example is nitrogen dioxide (NO_2). Each oxygen atom contributes six valence electrons and the nitrogen atom contributes five for a total of seventeen. The Lewis structure for NO_2 appears in the figure below.

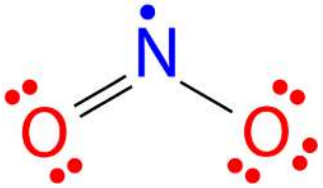


Figure **2.11.4**: The Lewis structure for nitrogen dioxide, an odd electron molecule. (CC BY-NC-SA; Todd Helmenstine via about.com)

Expanded Octets

Atoms of the second period cannot have more than eight valence electrons around the central atom. However, atoms of the third period and beyond are capable of exceeding the octet rule by having more than eight electrons around the central atom. Starting with the third period, the ***d*** sublevel becomes available, so it is possible to use these orbitals in bonding, resulting in an expanded octet.

Phosphorus and sulfur are two elements that react with halogen elements and make stable compounds with expanded octets. In phosphorus pentachloride, the central phosphorus atom makes five single bonds to chlorine atoms and, as a result, has ten electrons surrounding it (see figure below). In sulfur hexafluoride, the central sulfur atom has twelve electrons from its six bonds to fluorine atoms (see figure below).

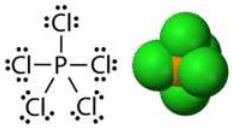


Figure **2.11.5**: Phosphorus pentachloride. Left image: Lewis structure. Right image: molecular model. (CC BY-NC 3.0; Molecule Public Domain; CK-12 Foundation - Joy Sheng, using 3D molecular structure by Ben Mills (Wikimedia: Benjah-bmm27) via Molecular structure: http://commons.wikimedia.org/wiki/File:Phosphorus-pentachloride-3D-vdW.png)

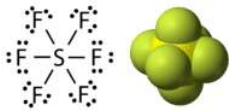


Figure **2.11.6**: Sulfur hexafluoride. Left image: Lewis structure. Right image: molecular model. (CC BY-NC 3.0; Molecule Public Domain; CK-12 Foundation - Joy Sheng, using 3D molecular structure by Ben Mills (Wikimedia: Benjah-bmm27) via Molecular structure: http://commons.wikimedia.org/wiki/File:Sulfur-hexafluoride-3D-vdW.png)



Summary

- Exceptions exist to the rules for covalent bonding
- These exceptions apply to atoms whose electrons will not accommodate the normal octet rule.

Review

1. What is an incomplete octet?
2. What is an odd-electron molecule?
3. Why are there extra electrons in the expanded octet?

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CHAPTER OVERVIEW

3: Nomenclature

3.1: Formulas for Ionic Compounds

3.2: Ionic Nomenclature

3.3: Covalent Compounds - Formulas and Names

3.4: Naming Acids

3.5: Names and Formulas of Bases

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3.1: Formulas for Ionic Compounds

Learning Objectives

- Write the chemical formula for a simple ionic compound.
- Recognize polyatomic ions in chemical formulas.

We have already encountered some chemical formulas for simple ionic compounds. A chemical formula is a concise list of the elements in a compound and the ratios of these elements. To better understand what a chemical formula means, we must consider how an ionic compound is constructed from its ions.

Ionic compounds exist as alternating positive and negative ions in regular, three-dimensional arrays called crystals (Figure **3.1.1**). As you can see, there are no individual **NaCl** "particles" in the array; instead, there is a continuous lattice of alternating sodium and chloride ions. However, we can use the ratio of sodium ions to chloride ions, expressed in the lowest possible whole numbers, as a way of describing the compound. In the case of sodium chloride, the ratio of sodium ions to chloride ions, expressed in lowest whole numbers, is 1:1, so we use **NaCl** (one **Na** symbol and one **Cl** symbol) to represent the compound. Thus, **NaCl** is the chemical formula for sodium chloride, which is a concise way of describing the relative number of different ions in the compound. A macroscopic sample is composed of myriads of NaCl pairs; each individual pair called a **formula unit**. Although it is convenient to think that **NaCl** crystals are composed of individual **NaCl** units, Figure **3.1.1** shows that no single ion is exclusively associated with any other single ion. Each ion is surrounded by ions of opposite charge.

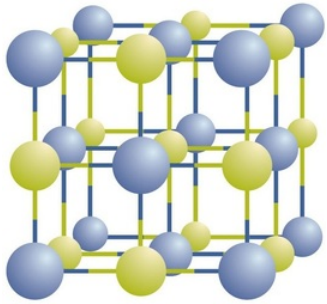


Figure **3.1.1**: A Sodium Chloride Crystal. A crystal contains a three-dimensional array of alternating positive and negative ions. The precise pattern depends on the compound. A crystal of sodium chloride, shown here, is a collection of alternating sodium and chlorine ions.

The formula for an ionic compound follows several conventions. First, the **cation** is written **before** the **anion**. Because most metals form cations and most nonmetals form anions, formulas typically list the metal first and then the nonmetal. Second, **charges** are **not written** in a formula. Remember that in an ionic compound, the component species are ions, not neutral atoms, even though the formula does not contain charges. Finally, the proper formula for an ionic compound always has ***a net zero charge,*** meaning the total positive charge must equal the total negative charge. To determine the proper formula of any combination of ions, determine how many of each ion is needed to balance the total positive and negative charges in the compound.

> *This rule is ultimately based on the fact that matter is, overall, electrically neutral.*

By convention, assume that there is only one atom if a subscript is not present. We do not use 1 as a subscript.

If we look at the ionic compound consisting of lithium ions and bromide ions, we see that the lithium ion has a 1+ charge and the bromide ion has a 1− charge. Only one ion of each is needed to balance these charges. The formula for lithium bromide is **LiBr**.

When an ionic compound is formed from magnesium and oxygen, the magnesium ion has a 2+ charge, and the oxygen atom has a 2− charge. Although both of these ions have higher charges than the ions in lithium bromide, they still balance each other in a one-to-one ratio. Therefore, the proper formula for this ionic compound is **MgO**.

Now consider the ionic compound formed by magnesium and chlorine. A magnesium ion has a 2+ charge, while a chlorine ion has a 1− charge:

$$Mg^{2+}Cl^{-}$$

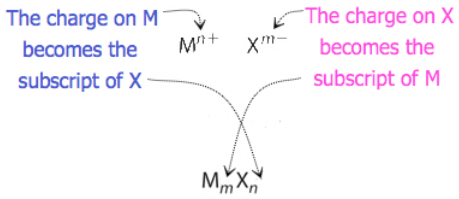
Combining one ion of each does not completely balance the positive and negative charges. The easiest way to balance these charges is to assume the presence of *two* chloride ions for each magnesium ion:

$$Mg^{2+}\ Cl^{-}\ Cl^{-}$$

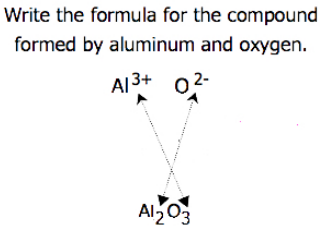
Now the positive and negative charges are balanced. We could write the chemical formula for this ionic compound as **MgClCl**, but the convention is to use a numerical subscript when there is more than one ion of a given type—**$MgCl_2$**. This chemical formula says that there are one magnesium ion and *two* chloride ions in this formula. (Do not read the "Cl_2" part of the formula as a molecule of the diatomic elemental chlorine. Chlorine does not exist as a diatomic element in this compound. Rather, it exists as two individual chloride ions.) By convention, the **lowest whole number ratio** is used in the formulas of ionic compounds. The formula **Mg_2Cl_4** has balanced charges with the ions in a 1:2 ratio, but it is not the lowest whole number ratio.

> By convention, the lowest whole-number ratio of the ions is used in ionic formulas. There are exceptions for certain ions, such as **Hg_2^{2+}**.

For compounds in which the ratio of ions is not as obvious, the subscripts in the formula can be obtained by **crossing charges**: use the absolute value of the charge on one ion as the subscript for the other ion. This method is shown schematically in Figure 3.3.2.



The image shows M with a charge of n+ and X with a charge of m-. The charge on the M becomes the subscript of X, and the charge on X becomes the subscript of M, making the final product M subscript m X subscript n.



The image asks to write the formula for the compound formed by aluminum and oxygen. It shows Al with a charge of 3+ and O with a charge of 2-. By crossing charges, the final result is Al subscript 2 O subscript 3.

Figure **3.1.2**: Crossing charges. One method for obtaining subscripts in the empirical formula is by crossing charges.

When crossing charges, it is sometimes necessary to reduce the subscripts to their simplest ratio to write the empirical formula. Consider, for example, the compound formed by Pb^{4+} and O^{2-}. Using the absolute values of the charges on the ions as subscripts gives the formula Pb_2O_4. This simplifies to its correct empirical formula **PbO_2**. The empirical formula has one Pb^{4+} ion and two O^{2-} ions.

✔ Example 3.1.1

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

a. the sodium ion and the sulfur ion
b. the aluminum ion and the fluoride ion
c. the 3+ iron ion and the oxygen ion

Solution

a. To obtain a valence shell octet, sodium forms an ion with a 1+ charge, while the sulfur ion has a 2− charge. Two sodium 1+ ions are needed to balance the 2− charge on the sulfur ion. Rather than writing the formula as $\mathbf{NaNaS}$, we shorten it by convention to $\mathbf{Na_2S}$.

b. The aluminum ion has a 3+ charge, while the fluoride ion formed by fluorine has a 1− charge. Three fluorine 1− ions are needed to balance the 3+ charge on the aluminum ion. This combination is written as $\mathbf{AlF_3}$.

c. Iron can form two possible ions, but the ion with a 3+ charge is specified here. The oxygen atom has a 2− charge as an ion. To balance the positive and negative charges, we look to the least common multiple—6: two iron 3+ ions will give 6+, while three 2− oxygen ions will give 6−, thereby balancing the overall positive and negative charges. Thus, the formula for this ionic compound is $\mathbf{Fe_2O_3}$. Alternatively, use the crossing charges method shown in Figure 3.3.2.

? Exercise 3.1.1

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:

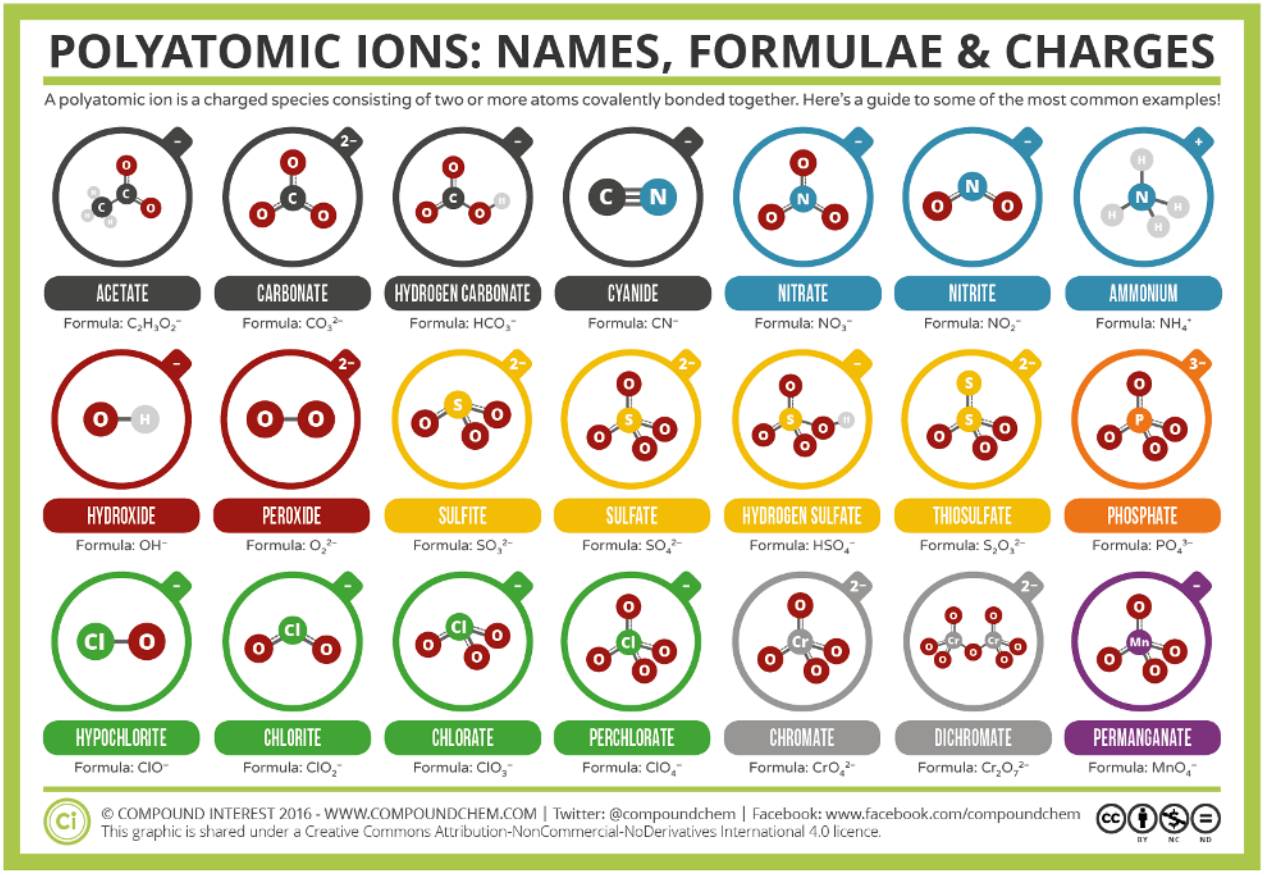
CuS

Answer c:

Cu_2S

Polyatomic Ions

Some ions consist of groups of atoms ***covalently*** bonded together and have an **overall electric charge**. Because these ions contain more than one atom, they are called polyatomic ions. The Lewis structures, names and formulas of some polyatomic ions are found in Table 3.3.1.



Some Polyatomic Ions

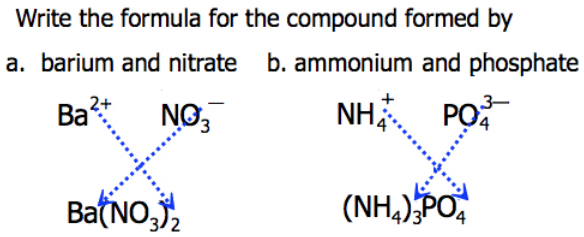
Polyatomic ions have defined formulas, names, and charges that cannot be modified in any way. Table **3.1.2** lists the ion names and ion formulas of the most common polyatomic ions. For example, $\mathbf{NO_3^-}$ is the nitrate ion; it has one nitrogen atom and three oxygen atoms and an overall 1− charge. Figure **3.1.2** lists the most common polyatomic ions.

Table **3.1.2**: Ion Names and Ion Formulas of Common Polyatomic Ions

Ion Name	Ion Formula
ammonium ion	NH_4^{+1}
hydroxide ion	OH^{-1}
cyanide ion	CN^{-1}
carbonate ion	CO_3^{-2}
bicarbonate or hydrogen carbonate	HCO_3^-
acetate ion	$C_2H_3O_2^{-1}$ **or** $CH_3CO_2^{-1}$
nitrate ion	NO_3^{-1}
nitrite ion	NO_2^{-1}
sulfate ion	SO_4^{-2}
sulfite ion	SO_3^{-2}
phosphate ion	PO_4^{-3}
phosphite ion	PO_3^{-3}

Note that only one polyatomic ion in this Table, the ammonium ion ($NH_4^{+1)}$, is a cation. This polyatomic ion contains one nitrogen and four hydrogens that collectively bear a +1 charge. The remaining polyatomic ions are all negatively-charged and, therefore, are classified as anions. However, only two of these, the hydroxide ion and the cyanide ion, are named using the "-ide" suffix that is typically indicative of negatively-charged particles. The remaining polyatomic anions, which all contain oxygen, in combination with another non-metal, exist as part of a series in which the number of oxygens within the polyatomic unit can vary. As has been repeatedly emphasized in several sections of this text, no two chemical formulas should share a common chemical name. A single suffix, "-ide," is insufficient for distinguishing the names of the anions in a related polyatomic series. Therefore, "-ate" and "-ite" suffixes are employed, in order to denote that the corresponding polyatomic ions are part of a series. Additionally, these suffixes also indicate the relative number of oxygens that are contained within the polyatomic ions. Note that all of the polyatomic ions whose names end in "-ate" contain one more oxygen than those polyatomic anions whose names end in "-ite." Unfortunately, much like the common system for naming transition metals, these suffixes only indicate the *relative* number of oxygens that are contained within the polyatomic ions. For example, the nitrate ion, which is symbolized as NO_3^{-1}, has one more oxygen than the nitrite ion, which is symbolized as NO_2^{-1}. However, the sulfate ion is symbolized as SO_4^{-2}. While both the nitrate ion and the sulfate ion share an "-ate" suffix, the former contains three oxygens, but the latter contains four. Additionally, both the nitrate ion and the sulfite ion contain three oxygens, but these polyatomic ions do not share a common suffix. Unfortunately, the relative nature of these suffixes mandates that the ion formula/ion name combinations of the polyatomic ions must simply be memorized.

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. Two examples are shown below:



The image asks a two-part question: Write the formula for the compound formed by (a) barium and nitrate, and (b) ammonium and phosphate. For (a), Ba has a charge of 2+ and NO_3 has a charge of -1. By crossing charges, the formula is $Ba(NO_3)_2$. For (b), NH_4 has a charge of +1 and PO_4 has a charge of 3-, so by crossing charges the formula is $(NH_4)_3PO_4$.

Example 3.1.2

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

a. the potassium ion and the sulfate ion
b. the calcium ion and the nitrate ion

Solution

a. 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 $\mathbf{K_2SO_4}$.
b. Calcium ions have a charge of 2+, while nitrate ions have a charge of 1−. We will need two nitrate ions to balance the charge on each calcium ion. The formula for nitrate must be enclosed in parentheses. Thus, we write $\mathbf{Ca(NO_3)_2}$ as the formula for this ionic compound.

Exercise 3.1.2

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:

Mg^{2+} and $CO_3^{2-} = MgCO_3$

Answer b:

Al^{3+} and $C_2H_3O_2^- = Al(C_2H_3O_2)_3$

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 2A metal) and a nonmetallic element (bromine, a group 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 5A, and oxygen, from group 6A). It is not an ionic compound; it belongs to the category of covalent compounds discuss 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 $\mathbf{Ba(NO_3)_2}$, you may recognize the "NO_3" part as the nitrate ion, $\mathbf{NO_3^-}$. (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 $\mathbf{Ba^{2+}}$ ion, with the 2+ charge balancing the overall 2− charge from the two nitrate ions. Thus, this compound is also ionic.

Example 3.1.3

Identify each compound as ionic or not ionic.

a. Na_2O
b. PCl_3
c. NH_4Cl
d. OF_2

Solution

a. Sodium is a metal, and oxygen is a nonmetal; therefore, Na_2O is expected to be ionic.
b. Both phosphorus and chlorine are nonmetals. Therefore, PCl_3 is not ionic.
c. The NH_4 in the formula represents the ammonium ion, NH_4^+, which indicates that this compound is ionic.
d. Both oxygen and fluorine are nonmetals. Therefore, OF_2 is not ionic.

Exercise 3.1.3

Identify each compound as ionic or not ionic.

a. N_2O
b. $FeCl_3$
c. $(NH_4)_3PO_4$
d. $SOCl_2$

Answer a:

not ionic

Answer b:

ionic

Answer c:

ionic

Answer d:

not ionic

Looking Closer: Blood and Seawater

Science has long recognized that blood and seawater have similar compositions. After all, both liquids have ionic compounds dissolved in them. The similarity may be more than mere coincidence; many scientists think that the first forms of life on Earth arose in the oceans. A closer look, however, shows that blood and seawater are quite different. A 0.9% solution of sodium chloride approximates the salt concentration found in blood. In contrast, seawater is principally a 3% sodium chloride solution, over three times the concentration in blood. Here is a comparison of the amounts of ions in blood and seawater:

Table showing a comparison of the amounts of ions in blood and seawater.

Ion	Percent in Seawater	Percent in Blood
Na^+	2.36	0.322
Cl^-	1.94	0.366
Mg^{2+}	0.13	0.002
SO_4^{2-}	0.09	—
K^+	0.04	0.016
Ca^{2+}	0.04	0.0096
HCO_3^-	0.002	0.165
HPO_4^{2-}, $H_2PO_4^-$	—	0.01

Most ions are more abundant in seawater than they are in blood, with some important exceptions. There are far more hydrogen carbonate ions ($\mathbf{HCO_3^-}$) in blood than in seawater. This difference is significant because the hydrogen carbonate ion and some related ions have a crucial role in controlling the acid-base properties of blood. The amount of hydrogen phosphate ions—$\mathbf{HPO_4^{2-}}$ and $\mathbf{H_2PO_4^-}$—in seawater is very low, but they are present in higher amounts in blood, where they also affect acid-base properties. Another notable difference is that blood does not have significant amounts of the sulfate ion ($\mathbf{SO_4^{2-}}$), but this ion is present in seawater.

Key Takeaways

- Proper chemical formulas for ionic compounds balance the total positive charge with the total negative charge.
- Groups of atoms with an overall charge, called polyatomic ions, also exist.

EXERCISES

1. What information is contained in the formula of an ionic compound?

- Why do the chemical formulas for some ionic compounds contain subscripts, while others do not?

3. Write the chemical formula for the ionic compound formed by each pair of ions.

   a. Mg^{2+} and I^-
   b. Na^+ and O^{2-}

4. Write the chemical formula for the ionic compound formed by each pair of ions.

   a. Na^+ and Br^-
   b. Mg^{2+} and Br^-
   c. Mg^{2+} and S^{2-}

5. Write the chemical formula for the ionic compound formed by each pair of ions.

   a. K^+ and Cl^-
   b. Mg^{2+} and Cl^-
   c. Mg^{2+} and Se^{2-}

6. Write the chemical formula for the ionic compound formed by each pair of ions.

   a. Na^+ and N^{3-}
   b. Mg^{2+} and N^{3-}
   c. Al^{3+} and S^{2-}

7. Write the chemical formula for the ionic compound formed by each pair of ions.

   a. Li^+ and N^{3-}
   b. Mg^{2+} and P^{3-}

c. Li^{+} and P^{3-}

8. Write the chemical formula for the ionic compound formed by each pair of ions.

a. Fe^{3+} and Br^{-}
b. Fe^{2+} and Br^{-}
c. Au^{3+} and S^{2-}
d. Au^{+} and S^{2-}

9. Write the chemical formula for the ionic compound formed by each pair of ions.

a. Cr^{3+} and O^{2-}
b. Cr^{2+} and O^{2-}
c. Pb^{2+} and Cl^{-}
d. Pb^{4+} and Cl^{-}

10. Write the chemical formula for the ionic compound formed by each pair of ions.

a. Cr^{3+} and NO_3^{-}
b. Fe^{2+} and PO_4^{3-}
c. Ca^{2+} and CrO_4^{2-}
d. Al^{3+} and OH^{-}

11. Write the chemical formula for the ionic compound formed by each pair of ions.

a. NH_4^{+} and NO_3^{-}
b. H^{+} and $Cr_2O_7^{2-}$
c. Cu^{+} and CO_3^{2-}
d. Na^{+} and HCO_3^{-}

12. For each pair of elements, determine the charge for their ions and write the proper formula for the resulting ionic compound between them.

a. Ba and S
b. Cs and I

13. For each pair of elements, determine the charge for their ions and write the proper formula for the resulting ionic compound between them.

a. K and S
b. Sc and Br

14. Which compounds would you predict to be ionic?

a. Li_2O
b. $(NH_4)_2O$
c. CO_2
d. $FeSO_3$
e. C_6H_6
f. C_2H_6O

15. Which compounds would you predict to be ionic?

a. $Ba(OH)_2$
b. CH_2O
c. NH_2CONH_2
d. $(NH_4)_2CrO_4$
e. C_8H_{18}
f. NH_3

Answers

1. the ratio of each kind of ion in the compound

2. Sometimes more than one ion is needed to balance the charge on the other ion in an ionic compound.

3.
    a. MgI_2
    b. Na_2O

4.
    a. NaBr
    b. $MgBr_2$
    c. MgS

5.
    a. KCl
    b. $MgCl_2$
    c. MgSe

6.
    a. Na_3N
    b. Mg_3N_2
    c. Al_2S_3

7.
    a. Li_3N
    b. Mg_3P_2
    c. Li_3P

8.
    a. $FeBr_3$
    b. $FeBr_2$
    c. Au_2S_3
    d. Au_2S

9.
    a. Cr_2O_3
    b. CrO
    c. $PbCl_2$
    d. $PbCl_4$

10.
    a. $Cr(NO_3)_3$
    b. $Fe_3(PO_4)_2$
    c. $CaCrO_4$
    d. $Al(OH)_3$

11.
    a. NH_4NO_3
    b. $H_2Cr_2O_7$
    c. Cu_2CO_3
    d. $NaHCO_3$

12.

a. Ba^{2+}, S^{2-}, BaS
b. Cs^{+}, I^{-}, CsI

13.

a. K^{+}, S^{2-}, K_2S
b. Sc^{3+}, Br^{-}, $ScBr_3$

14.

a. ionic
b. ionic
c. not ionic
d. ionic
e. not ionic
f. not ionic

15.

a. ionic
b. not ionic
c. not ionic
d. ionic
e. not ionic
f. not ionic

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3.2: Ionic Nomenclature

Learning Objectives

- To use the rules for naming 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. 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***, 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 **3.2.1**: The Common System of Cation Names

Element	Stem	Charge	Name
iron	ferr-	2+	ferrous ion
		3+	ferric ion
copper	cupr-	1+	cuprous ion
		2+	cupric ion
tin	stann-	2+	stannous ion
		4+	stannic ion
lead	plumb-	2+	plumbous ion
		4+	plumbic ion
chromium	chrom-	2+	chromous ion
		3+	chromic ion
gold	aur-	1+	aurous ion
		3+	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 **3.2.1** lists the elements that use the common system, along with their respective cation names.

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 **3.2.2** lists the names of some common monatomic ions.

Table **3.2.2**: 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 polyatomic ions have their own characteristic names, as discussed earlier.

✔ Example 3.2.1

Name each ion.

a. Ca^{2+}
b. S^{2-}
c. SO_3^{2-}
d. NH_4^+
e. Cu^+

Answer a

the calcium ion

Answer b

the sulfide ion (from Table **3.2.2**)

Answer c

the sulfite ion

Answer d

the ammonium ion

Answer e

the copper(I) ion or the cuprous ion (copper can form cations with either a 1+ or 2+ charge, so we have to specify which charge this ion has

? Exercise 3.2.1

Name each ion.

a. Fe^{2+}
b. Fe^{3+}
c. SO_4^{2-}

d. Ba^{2+}
e. HCO_3^-

Answer a

the iron (II) or ferrous ion

Answer b

the iron (III) or ferric ion

Answer c

the sulfate ion

Answer d

the barium ion

Answer e

the bicarbonate ion or hydrogen carbonate ion

Example 3.2.2

Write the formula for each ion.

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

Answer a

Br^-

Answer b

PO_4^{3-}

Answer c

Cu^{2+}

Answer d

Mg^{2+}

Exercise 3.2.2

Write the formula for each ion.

a. the fluoride ion
b. the carbonate ion
c. the ferrous ion
d. the potassium ion

Answer a

F^-

Answer b

CO_3^{2-}

Answer c

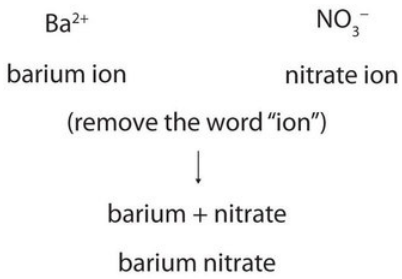
Fe^{2+}

Answer d

K^+

Naming Compounds

Now that we know how to name ions, we are ready to name ionic compounds. We do so by placing the name of the cation first, followed by the name of the anion, and dropping the word *ion* from both parts. For example, what is the name of the compound whose formula is $\mathbf{Ba(NO_3)_2}$?



The compound's name does not indicate that there are two nitrate ions for every barium ion. You must determine the relative numbers of ions by balancing the positive and negative charges.

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 $\mathbf{FeCl_2}$ and $\mathbf{FeCl_3}$. In the first compound, the iron ion has a 2+ charge because there are two $\mathbf{Cl^-}$ 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 $\mathbf{Cl^-}$ 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. If we were to use the stems and suffixes of the common system, the names would be ferrous chloride and ferric chloride, respectively.

✔ Example 3.2.3

Name each ionic compound, using both Stock and common systems if necessary.

a. $Ca_3(PO_4)_2$
b. $(NH_4)_2Cr_2O_7$
c. KCl
d. CuCl
e. SnF_2

Answer a

calcium phosphate

Answer b

ammonium dichromate (the prefix *di-* is part of the name of the anion)

Answer c

potassium chloride

Answer d

copper(I) chloride or cuprous chloride

Answer e

tin(II) fluoride or stannous fluoride

? Exercise 3.2.3

Name each ionic compound, using both Stock and common systems if necessary.

a. $ZnBr_2$
b. $Fe(NO_3)_3$
c. Al_2O_3
d. CuF_2
e. AgF

Answer a

zinc bromide

Answer b

iron (III) nitrate or ferric nitrate

Answer c

aluminum oxide

Answer d

copper (II) fluoride or cupric fluoride

Answer e

silver fluoride

Figure 3.2.1 is a synopsis of how to name simple ionic compounds.

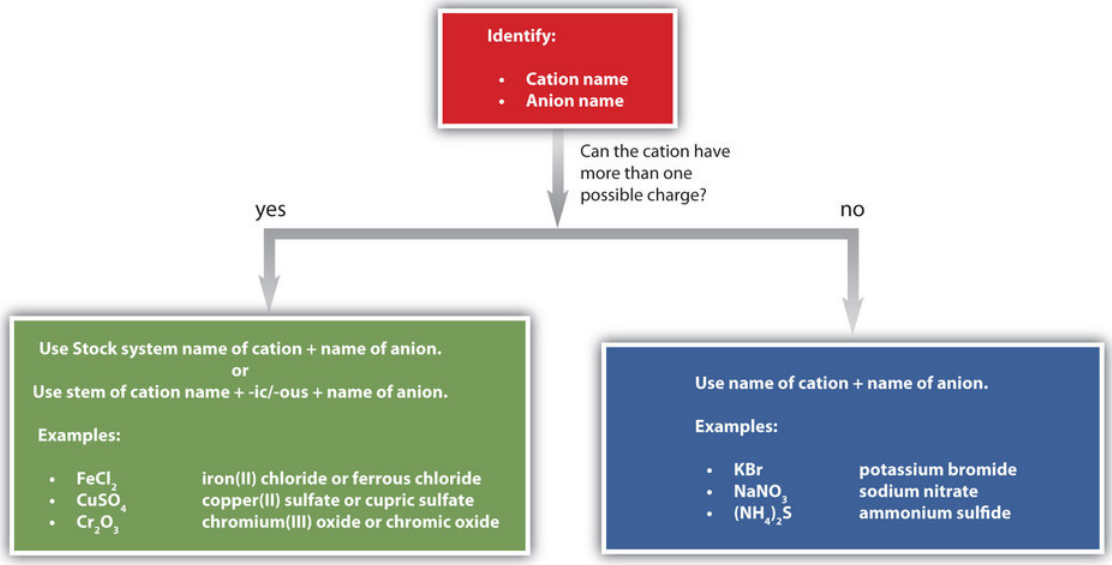


Figure 3.2.1: A Guide to Naming Simple Ionic Compounds. Follow these steps to name a simple ionic compound.

Identify the cation name and the anion name. If the cation can have more than one possible charge, either use the Stock system name of the cation and name of the anion, or use the stem of the cation name and -ic/-ous and the name of the anion. Examples of this would be $FeCl_2$, which is iron(II) chloride of ferrous chloride, $CuSO_4$, which is copper(II) sulfate or cupric sulfate, and Cr_2O_3, which is chromium(III) oxide or chromic oxide. If the cation can not have more than one possible charge, use the name of the cation and the name of the anion. Examples of this would be KBr, which is potassium bromide, $NaNO_3$, which is sodium nitrate, and $(NH_4)_2S$, which is ammonium sulfide.

KEY TAKEAWAY

- Each ionic compound has its own unique name that comes from the names of the ions.

EXERCISES

1. Briefly describe the process for naming an ionic compound.

- In what order do the names of ions appear in the names of ionic compounds?

3. Which ionic compounds can be named using two different systems? Give an example.

4. Name each ion.

   a. Ra^{2+}
   b. P^{3-}
   c. $H_2PO_4^-$
   d. Sn^{4+}

5. Name each ion.

   a. Cs^+
   b. As^{3-}
   c. HSO_4^-
   d. Sn^{2+}

6. Name the ionic compound formed by each pair of ions.

   a. Na^+ and Br^-
   b. Mg^{2+} and Br^-
   c. Mg^{2+} and S^{2-}

7. Name the ionic compound formed by each pair of ions.

   a. K^+ and Cl^-
   b. Mg^{2+} and Cl^-
   c. Mg^{2+} and Se^{2-}

8. Name the ionic compound formed by each pair of ions.

   a. Na^+ and N^{3-}
   b. Mg^{2+} and N^{3-}
   c. Al^{3+} and S^{2-}

9. Name the ionic compound formed by each pair of ions.

   a. Li^+ and N^{3-}
   b. Mg^{2+} and P^{3-}
   c. Li^+ and P^{3-}

10. Name the ionic compound formed by each pair of ions. Use both the Stock and common systems, where appropriate.

    a. Fe^{3+} and Br^-
    b. Fe^{2+} and Br^-
    c. Au^{3+} and S^{2-}
    d. Au^+ and S^{2-}

11. Name the ionic compound formed by each pair of ions. Use both the Stock and common systems, where appropriate.

    a. Cr^{3+} and O^{2-}
    b. Cr^{2+} and O^{2-}
    c. Pb^{2+} and Cl^-
    d. Pb^{4+} and Cl^-

12. Name the ionic compound formed by each pair of ions. Use both the Stock and common systems, where appropriate.

    a. Cr^{3+} and NO_3^-

b. Fe^{2+} and PO_4^{3-}
c. Ca^{2+} and CrO_4^{2-}
d. Al^{3+} and OH^-

13. Name the ionic compound formed by each pair of ions. Use both the Stock and common systems, where appropriate.

a. NH_4^+ and NO_3^-
b. K^+ and $Cr_2O_7^{2-}$
c. Cu^+ and CO_3^{2-}
d. Na^+ and HCO_3^-

14. Give two names for each compound.

a. $Al(HSO_4)_3$
b. $Mg(HSO_4)_2$

15. Give two names for each compound.

a. $Co(HCO_3)_2$
b. $LiHCO_3$

AnswerS

1. Name the cation and then the anion but don’t use numerical prefixes.
2. the cation name followed by the anion name
3. Ionic compounds in which the cation can have more than one possible charge have two naming systems. $FeCl_3$ is either iron(III) chloride or ferric chloride (answers will vary).

4.

a. the radium ion
b. the phosphide ion
c. the dihydrogen phosphate ion
d. the tin(IV) ion or the stannic ion

5.

a. the cesium ion
b. the arsenide ion
c. the hydrogen sulfate ion
d. the tin(II) ion or the stannous ion

6.

a. sodium bromide
b. magnesium bromide
c. magnesium sulfide

7.

a. potassium chloride
b. magnesium chloride
c. magnesium selenide

8.

a. sodium nitride
b. magnesium nitride
c. aluminum sulfide

9.

a. lithium nitride
b. magnesium phosphide
c. lithium phosphide

10.

a. iron(III) bromide or ferric bromide
b. iron(II) bromide or ferrous bromide
c. gold(III) sulfide or auric sulfide
d. gold(I) sulfide or aurous sulfide

11.

a. chromium(III) oxide or chromic oxide
b. chromium(II) oxide or chromous oxide
c. lead(II) chloride or plumbous chloride
d. lead(IV) chloride or plumbic chloride

12.

a. chromium(III) nitrate or chromic nitrate
b. iron(II) phosphate or ferrous phosphate
c. calcium chromate
d. aluminum hydroxide

13.

a. ammonium nitrate
b. potassium dichromate
c. copper(I) carbonate or cuprous carbonate
d. sodium hydrogen carbonate or sodium bicarbonate

14.

a. aluminum hydrogen sulfate or aluminum bisulfate
b. magnesium hydrogen sulfate or magnesium bisulfate

15.

a. cobalt hydrogen carbonate or cobalt bicarbonate
b. lithium hydrogen carbonate or lithium bicarbonate

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3.3: Covalent Compounds - Formulas and Names

Learning Objectives

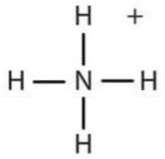
- Identify covalent and ionic compounds.
- Determine the chemical formula of a simple covalent compound from its name.
- Determine the name of a simple covalent compound from its chemical formula.

COVALENT AND IONIC COMPOUNDS

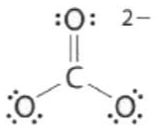
What elements make covalent bonds? Covalent bonds form when two or more nonmetals combine. For example, both hydrogen and oxygen are nonmetals, and when they combine to make water, they do so by forming covalent bonds. Compounds that are composed of only non-metals or semi-metals with non-metals will display covalent bonding and will be classified as molecular compounds.

As a general rule of thumb, compounds that involve a metal binding with either a non-metal or a semi-metal will display ionic bonding. Thus, the compound formed from sodium and chlorine will be ionic (a metal and a non-metal). Nitrogen monoxide (NO) will be a covalently bound molecule (two non-metals), silicon dioxide (SiO_2) will be a covalently bound molecule (a semi-metal and a non-metal) and $MgCl_2$ will be ionic (a metal and a non-metal).

A polyatomic ion is an ion composed of two or more atoms that have a charge as a group (poly = many). The ammonium ion (see figure below) consists of one nitrogen atom and four hydrogen atoms. Together, they comprise a single ion with a 1+ charge and a formula of NH_4^+. The carbonate ion (see figure below) consists of one carbon atom and three oxygen atoms and carries an overall charge of 2−. The formula of the carbonate ion is CO_3^{2-}.



ammonium ion



carbonate ion

The atoms of a polyatomic ion are tightly bonded together and so the entire ion behaves as a single unit. Several examples are found in Table 3.3.1. Nonmetal atoms in polyatomic ions are joined by covalent bonds, but the ion as a whole participates in ionic bonding. For example, ammonium chloride (NH_4Cl) has ionic bonding between a polyatomic ion, $\mathbf{NH_4^+}$, and $\mathbf{Cl^-}$ ions, but within the ammonium ion (NH_4^+), the nitrogen and hydrogen atoms are connected by covalent bonds (shown above).

Both ionic and covalent bonding are also found in calcium carbonate. Calcium carbonate ($CaCO_3$) has ionic bonding between calcium ion $\mathbf{Ca^{2+}}$ and a polyatomic ion, $\mathbf{CO_3^{2-}}$, but within the carbonate ion (CO_3^{2-}), the carbon and oxygen atoms are connected by covalent bonds (shown above).

Characteristics of Covalent (Molecular) Compounds

Compounds that contain covalent bonds (also called molecular compounds) exhibit different physical properties than ionic compounds. Because the attraction between molecules, which are electrically neutral, is weaker than that between electrically charged ions, covalent compounds generally have much lower melting and boiling points than ionic compounds (discussed in Section 3.6). For example, water (molecular compound) boils at 100 °C while sodium chloride (ionic compound) boils at 1413 °C. In fact, many covalent compounds are liquids or gases at room temperature, and, in their solid states, they are typically much softer than ionic solids. Furthermore, whereas ionic compounds are good conductors of electricity when dissolved in water, most covalent compounds, being electrically neutral, are poor conductors of electricity in any state. The attraction between molecules (called intermolecular forces) will be discussed in more detail in Section 8.1

Example 3.3.1

Is each compound formed from ionic bonds, covalent bonds, or both?

a. Na_2O
b. Na_3PO_4
c. N_2O_4

Answer a

The elements in Na_2O are a metal and a nonmetal, which form ionic bonds.

Answer b

Because sodium is a metal and we recognize the formula for the phosphate ion, we know that this compound is ionic. However, within the polyatomic phosphate ion, the atoms are held together by covalent bonds, so this compound contains both ionic and covalent bonds.

Answer c

The elements in N_2O_4| are both nonmetals, rather than a metal and a nonmetal. Therefore, the atoms form covalent bonds.

Exercise 3.3.1

Is each compound are formed from ionic bonds, covalent bonds, or both?

a. $Ba(OH)_2$
b. F_2
c. PCl_3

Answer a:

both

Answer b:

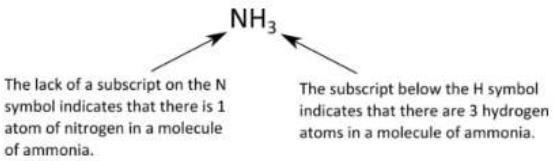
covalent

Answer c:

covalent

MOLECULAR FORMULAS

The chemical formulas for covalent compounds are referred to as **molecular formulas** because these compounds exist as separate, discrete molecules. Typically, a molecular formula begins with the nonmetal that is closest to the lower left corner of the periodic table, except that hydrogen is almost never written first (H_2O is the prominent exception). Then the other nonmetal symbols are listed. Numerical subscripts are used if there is more than one of a particular atom. For example, we have already seen CH_4, the molecular formula for methane. Below is the molecular formula of ammonia, NH_3.



NH_3. An arrow points to the N and says, "The lack of a subscript on the N symbol indicates that there is 1 atom of nitrogen in a molecule of ammonia". An arrow points to H and says, "The subscript below the H symbol indicates that there are 3 hydrogen atoms in a molecule of ammonia".

NAMING COVALENT COMPOUNDS

Naming *binary* (two-element) covalent compounds is similar to naming simple ionic compounds. The first element in the formula is simply listed using the name of the element. The second element is named by taking the stem of the element name and adding

the suffix *-ide*. A system of numerical prefixes is used to specify the number of atoms in a molecule. Table **3.3.1** lists these numerical prefixes. Normally, no prefix is added to the first element's name if there is only one atom of the first element in a molecule. If the second element is oxygen, the trailing vowel is usually omitted from the end of a polysyllabic prefix but not a monosyllabic one (that is, we would say "monoxide" rather than "monooxide" and "trioxide" rather than "troxide").

Table **3.3.1**: Numerical Prefixes for Naming Binary Covalent Compounds

Number of Atoms in Compound	Prefix on the Name of the Element
1	mono-*
2	di-
3	tri-
4	tetra-
5	penta-
6	hexa-
7	hepta-
8	octa-
9	nona-
10	deca-

*This prefix is not used for the first element's name.

Let us practice by naming the compound whose molecular formula is CCl_4. The name begins with the name of the first element—carbon. The second element, chlor*ine*, becomes chlor*ide*, and we attach the correct numerical prefix ("tetra-") to indicate that the molecule contains four chlorine atoms. Putting these pieces together gives the name *carbon tetrachloride* for this compound.

Example 3.3.2

Write the molecular formula for each compound.

a. chlorine trifluoride
b. phosphorus pentachloride
c. sulfur dioxide
d. dinitrogen pentoxide

Solution

If there is no numerical prefix on the first element's name, we can assume that there is only one atom of that element in a molecule.

a. ClF_3
b. PCl_5
c. SO_2
d. N_2O_5 (The *di-* prefix on nitrogen indicates that two nitrogen atoms are present.)

Exercise 3.3.2

Write the molecular formula for each compound.

a. nitrogen dioxide
b. dioxygen difluoride
c. sulfur hexafluoride

d. selenium monoxide

Answer a:

a. NO_2

Answer b:

O_2F_2

Answer c:

SF_6

Answer d:

SeO

Because it is so unreactive, sulfur hexafluoride is used as a spark suppressant in electrical devices such as transformers.

Example 3.3.3

Write the name for each compound.

a. BrF_5
b. S_2F_2
c. CO

Solution

a. bromine pentafluoride
b. disulfur difluoride
c. carbon monoxide

Exercise 3.3.3

Write the name for each compound.

a. CF_4
b. $SeCl_2$
c. SO_3

Answer a:

carbon tetrafluoride

Answer b:

selenium dichloride

Answer c:

sulfur trioxide

For some simple covalent compounds, we use common names rather than systematic names. We have already encountered these compounds, but we list them here explicitly:

- H_2O: water
- NH_3: ammonia
- CH_4: methane

Methane is the simplest organic compound. Organic compounds are compounds with carbon atoms and are named by a separate nomenclature system that we will introduce in in a separate section.

Key Takeaways

- The chemical formula of a simple covalent compound can be determined from its name.
- The name of a simple covalent compound can be determined from its chemical formula.

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3.4: Naming Acids



Figure 3.4.1 (CK-12 Curriculum Materials license; CK-12 Foundation via CK-12 Foundation)

How is gold tested?

A spot test for gold has been in use for decades. The sample is first treated with nitric acid. Other metals may react or dissolve in this acid, but gold will not. Then the sample is added to a mixture of nitric acid and hydrochloric acid. Gold will only dissolve in this mixture. The term "acid test" arose from the California gold rush in the late 1840s, when this combination was used to test for the presence of real gold. It has since come to mean "tested and approved" in a number of fields.

Acids

An **acid** can be defined in several ways. The most straightforward definition is that an acid is a molecular compound that contains one or more hydrogen atoms and produces hydrogen ions (H^+) when dissolved in water.



Figure 3.4.2: (A) Vinegar comes in a variety of types, but all contain acetic acid. (B) Citrus fruits like grapefruit contain citric and ascorbic acids. (CC BY 2.0; (A) Becky Cortino; (B) Flickr: isox4 via (A) http://www.flickr.com/photos/mediasavvy/8239231530; (B) http://www.flickr.com/photos/isox4/5167980026)

This is a different type of compound than the others we have seen so far. Acids are molecular, which means that in their pure state they are individual molecules and do not adopt the extended three-dimensional structures of ionic compounds like $NaCl$. However, when these molecules are dissolved in water, the chemical bond between the hydrogen atom and the rest of the molecule breaks, leaving a positively-charged hydrogen ion and an anion. This can be symbolized in a chemical equation:

$$HCl \rightarrow H^+ + Cl^-$$

Since acids produce H^+ cations upon dissolving in water, the H of an acid is written first in the formula of an inorganic acid. The remainder of the acid (other than the H) is the anion after the acid dissolves. Organic acids are also an important class of compounds, but will not be discussed here. A **binary acid** is an acid that consists of hydrogen and one other element. The most common binary acids contain a halogen. An **oxoacid** is an acid that consists of hydrogen, oxygen, and a third element. The third element is usually a nonmetal.

Naming Acids

Since all acids contain hydrogen, the name of an acid is based on the anion that goes with it. These anions can either be monatomic or polyatomic. The name of all monatomic ions ends in *-ide*. The majority of polyatomic ions end in either *-ate* or *-ite*, though there are a few exceptions such as the cyanide ion (CN^-). It is the suffix of the anion that determines how the acid is named, as displayed in the rules and table below.

Table 3.4.1: Naming System for Acids

Anion Suffix	Example	Name of Acid	Example
-ide	chloride (Cl^-)	hydro_____ic acid	hydrochloric acid (HCl)
-ate	sulfate (SO_4^{2-})	_____ic acid	sulfuric acid (H_2SO_4)
-ite	nitrite (NO_2^-)	____ous acid	nitrous acid (HNO_2)

The three different suffixes that are possible for the anions lead to three rules:

1. When the anion ends in *-ide*, the acid name begins with the prefix *hydro-*. The root of the anion name goes in the blank (*chlor* for chloride), followed by the suffix *-ic*. HCl is hydrochloric acid because Cl^- is the chloride ion. HCN is hydrocyanic acid because CN^- is the cyanide ion.
2. When the anion ends in *-ate*, the name of the acid is the root of the anion followed by the suffix *-ic*. There is no prefix. H_2SO_4 is sulfuric acid (not sulfic) because SO_4^{2-} is the sulfate ion.
3. When the anion ends in *-ite*, the name of the acid is the root of the anion followed by the suffix *-ous*. Again, there is no prefix. HNO_2 is nitrous acid because NO_2^- is the nitrite ion.

Note how the root for a sulfur-containing oxoacid is *sulfur-* instead of just *sulf-*. The same is true for a phosphorus-containing oxoacid. The root is *phosphor-* instead of simply *phosph-*.

Many foods and beverages contain citric acid. Vinegar is a dilute solution of acetic acid. Car batteries contain sulfuric acid that helps in the release of electrons to create electricity.

Writing Formulas for Acids

Like other compounds that we have studied, acids are electrically neutral. Therefore, the charge of the anion part of the formula must be exactly balanced out by the H^+ ions. Since H^+ ions carry a single positive charge, the number of H^+ ions in the formula is equal to the quantity of negative charge on the anion. Two examples from the table above illustrate this point. The chloride ion carries a $1-$ charge, so only one H is needed in the formula of the acid (HCl). The sulfate ion carries a $2-$ charge, so two Hs are needed in the formula of the acid (H_2SO_4). Another way to write the correct formula is to utilize the crisscross method, shown below for sulfuric acid.

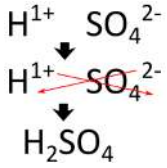
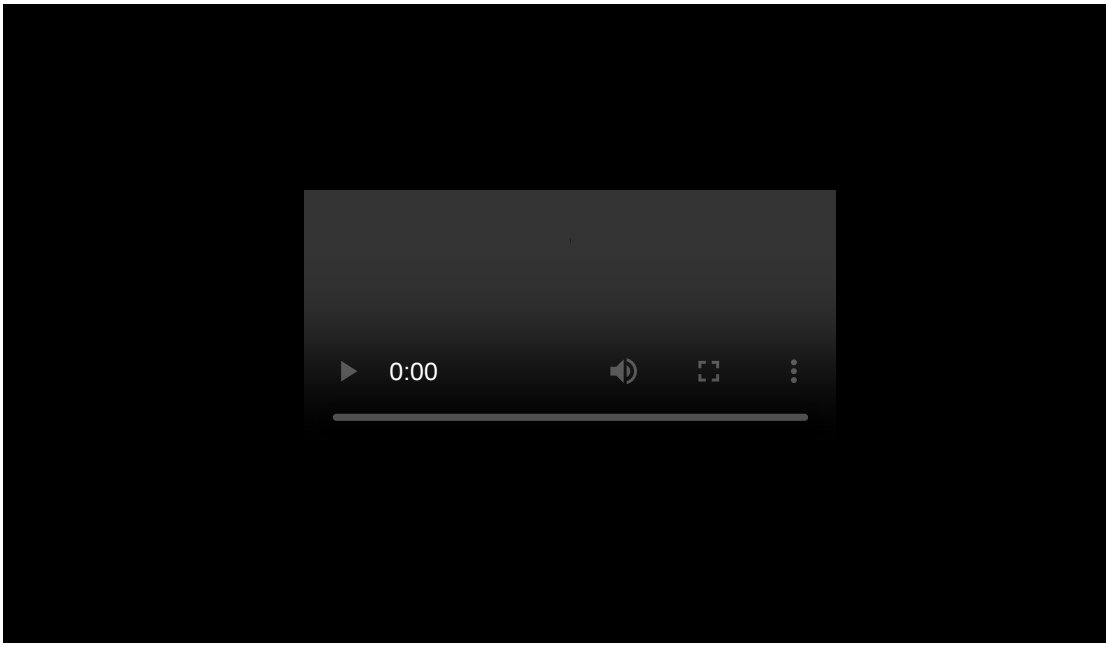


Figure **3.4.3**: Crisscross approach to writing the formula for sulfuric acid. (CC BY-NC 3.0; Joy Sheng via CK-12 Foundation)



Summary

- Acids are molecular compounds that release hydrogen ions.
- A binary acid consists of hydrogen and one other element.
- Oxoacids contain hydrogen, oxygen, and one other element.
- The name of the acid is based on the anion attached to the hydrogen.
- Writing formulas for acids follows the same rules as for binary ionic compounds.

Review

1. Define “acid.”
2. What is a binary acid?
3. What is an oxoacid?

4. Name the following acids:
    a. H_2SO_4
    b. HCN
    c. HCl
    d. H_3PO_4
5. Write formulas for the following acids:
    a. hydrobromic acid
    b. perchloric acid
    c. nitrous acid

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3.5: Names and Formulas of Bases



Figure 3.5.1 (Public Domain; Unknown Author via Wikipedia)

What different things are these workers doing to make soap?

Soap making has a long history. Until recently, soap was made using animal fats and lye from wood ashes. The lye served as a base to break down the fats and help form the soap. Needless to say, unless the soap was washed to remove the lye, it was very harsh on the skin. Many families would make their own soap by boiling the lye and fat in a large kettle over an open fire—a long and hot task.

Bases

A **base** can be simply defined as an ionic compound that produces **hydroxide ions** when dissolved in water. One of the most commonly used bases is sodium hydroxide, illustrated below.

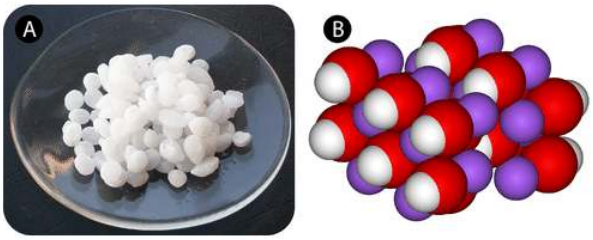


Figure 3.5.2: (A) Sodium hydroxide, a base, is a solid that is typically produced as small white pellets. (B) The structure of sodium hydroxide is an extended three-dimensional network. The purple spheres are the sodium ions (Na^+). The red and white spheres are oxygen and hydrogen atoms, respectively, which are bonded together to form hydroxide ions (OH^-). (Public Domain; (A) Martin Walker (Wikimedia: Walkerma); (B) Ben Mills (Wikimedia: Benjah-bmm27) via (A) http://commons.wikimedia.org/wiki/File:SodiumHydroxide.jpg; (B) http://commons.wikimedia.org/wiki/File:Sodium-hydroxide-crystal-3D-vdW.png)

Names and Formulas of Bases

There is no special system for naming bases. Since they all contain the OH^- anion, names of bases end in *hydroxide*. The cation is simply named first. Some examples of names and formulas for bases are shown in the table below.

Names and Formulas of Bases

Table 3.5.1

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

Notice that because bases are ionic compounds, the number of hydroxides in the formula does not affect the name. The compound must be neutral, so the charges of the ions are balanced just as for other ionic compounds. The sodium ion (Na^+) requires one OH^-

ion to balance the charge, so the formula is $NaOH$. Calcium (Ca^{2+}) requires two OH^- ions to balance the charge, so the formula is $Ca(OH)_2$. Hydroxide ion is a polyatomic ion, and must be in parentheses when there is more than one in a formula.

Summary

- Bases are ionic compounds that produce hydroxide ions when dissolved in water.
- The cation is named first followed by "*hydroxide*."

Review

1. What is a base?
2. What is the charge on the hydroxide anion?
3. Name the following bases:
    a. LiOH
    b. $Mg(OH)_2$
    c. $Fe(OH)_3$
4. Write the formulas for the following bases:
    a. nickel (II) hydroxide
    b. aluminum hydroxide
    c. silver hydroxide

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CHAPTER OVERVIEW

4: Chemical Calculations 1

4.1: Prelude to Introduction to Chemical Reactions
4.2: The Law of Conservation of Matter
4.3: Chemical Equations
4.4: Some Types of Chemical Reactions
4.5: Single Replacement Reactions
4.6: Activity Series
4.7: Double Replacement Reactions
4.8: Avogadro's Number
4.9: The Mole
4.10: Molar Mass
4.11: Atomic and Molar Masses
4.12: Mole-Mass Conversions
4.13: Percent Composition
4.14: Percent of Water in a Hydrate

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4.1: Prelude to Introduction to Chemical Reactions

Although yeast has been used for thousands of years, its true nature has been known only for the last two centuries. Yeasts are single-celled fungi. About 1,000 species are recognized, but the most common species is *Saccharomyces cerevisiae*, which is used in bread making. Other species are used for the fermentation of alcoholic beverages. Some species can cause infections in humans.

Yeasts live primarily on sugars, such as glucose ($\mathrm{C_6H_{12}O_6}$). They convert glucose into carbon dioxide ($\mathrm{CO_2}$) and ethanol ($\mathrm{C_2H_5OH}$) in a chemical transformation that is represented as follows:

$$\mathrm{C_6H_{12}O_6\,(s) \longrightarrow 2\,CO_2\,(g) + 2\,C_2H_5OH(\ell)}$$

Bread making depends on the production of carbon dioxide. The gas, which is produced in tiny pockets in bread dough, acts as a leavening agent: it expands during baking and makes the bread rise. Leavened bread is softer, lighter, and easier to eat and chew than unleavened bread. The other major use of yeast, fermentation, depends on the production of ethanol, which results from the same chemical transformation. Some alcoholic beverages, such as champagne, can also be carbonated using the carbon dioxide produced by the yeast.

Yeast is among the simplest life forms on Earth, yet it is absolutely necessary for at least two major food industries. Without yeast to turn dough into bread and juice into wine, these foods and food industries would not exist today.

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4.2: The Law of Conservation of Matter

Learning Objectives

- Correctly define a law as it pertains to science.
- State the law of conservation of matter.

In science, a law is a general statement that explains a large number of observations. Before being accepted, a law must be verified many times under many conditions. Laws are therefore considered the highest form of scientific knowledge and are generally thought to be inviolable. Scientific laws form the core of scientific knowledge. One scientific law that provides the foundation for understanding in chemistry is the law of conservation of matter. It states that in any given system that is closed to the transfer of matter (in and out), the amount of matter in the system stays constant. A concise way of expressing this law is to say that the amount of matter in a system is *conserved*.

With the development of more precise ideas on elements, compounds and mixtures, scientists began to investigate how and why substances react. French chemist A. Lavoisier laid the foundation to the scientific investigation of matter by describing that substances react by following certain laws. These laws are called the laws of chemical combination. These eventually formed the basis of Dalton's Atomic Theory of Matter.

Law of Conservation of Mass

According to this law, during any physical or chemical change, the total mass of the products remains equal to the total mass of the reactants.

$$\underbrace{\overbrace{\mathrm{HgO\,(s)}}^{\text{Mercuric oxide}}}_{100\ \mathrm{g}} \rightarrow \underbrace{\overbrace{\mathrm{Hg\,(l)}}^{\text{Mercury}}}_{92.6\ \mathrm{g}} + \underbrace{\overbrace{\mathrm{O_2\,(g)}}^{\text{Oxygen}}}_{7.4\ \mathrm{g}}$$

Another way of stating this is, "In a chemical reaction, matter is neither created nor destroyed." The law of conservation of mass is also known as the "law of indestructibility of matter."

Example 4.2.1

If heating 10 grams of $\mathrm{CaCO_3}$ produces 4.4 g of $\mathrm{CO_2}$ and 5.6 g of CaO, show that these observations are in agreement with the law of conservation of mass.



A sample of calcium carbonate (CaCO3). (Public Domain; Walkerma).

Solution

- Mass of the reactants, $\mathrm{CaCO_3}$: $10\,g$
- Mass of the products, $\mathrm{CO_2}$ and CaO: $4.4\,g + 5.6\,g = 10\,g$.

Because the mass of the reactants = the mass of the products, the observations are in agreement with the law of conservation of mass.

What does this mean for chemistry? In any chemical change, one or more initial substances change into a different substance or substances. Both the initial and final substances are composed of atoms because all matter is composed of atoms. According to the

law of conservation of matter, matter is neither created nor destroyed, so we must have the **same number and kind of atoms** after the chemical change as were present before the chemical change.

It may seem as though burning destroys matter, but the same amount, or mass, of matter still exists after a campfire as before. Figure 5.1.1 shows that when wood burns, it combines with oxygen and changes not only to ashes, but also to carbon dioxide and water vapor. The gases float off into the air, leaving behind just the ashes. Suppose we had measured the mass of the wood before it burned and the mass of the ashes after it burned. Also suppose we had been able to measure the oxygen used by the fire and the gases produced by the fire. What would we find? The total mass of matter after the fire would be the same as the total mass of matter before the fire.

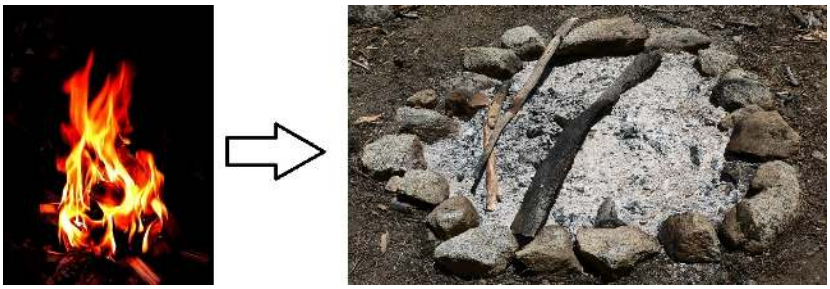


Figure 5.1.1: Burning is a chemical process. The flames are caused as a result of a fuel undergoing combustion (burning). Images used with permission (CC BY-SA 2.5; Einar Helland Berger for fire and for ash).

? Exercise 4.2.1

a. What is the law of conservation of matter?
b. How does the law of conservation of matter apply to chemistry?

Answer a:

The law of conservation of matter states that in any given system that is closed to the transfer of matter, the amount of matter in the system stays constant

Answer b:

The law of conservation of matter says that in chemical reactions, the total mass of the products must equal the total mass of the reactants.

Key Takeaway

The amount of matter in a closed system is conserved.

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4.3: Chemical Equations

Learning Objectives

- Define chemical reaction.
- Use a balanced chemical equation to represent a chemical reaction.

Water (H_2O) is composed of hydrogen and oxygen. Suppose we imagine a process in which we take some elemental hydrogen (H_2) and elemental oxygen (O_2) and let them react to make water. The statement

"hydrogen and oxygen react to make water"

is one way to represent that process, which is called a chemical reaction. Figure **4.3.1** shows a rather dramatic example of this very reaction.

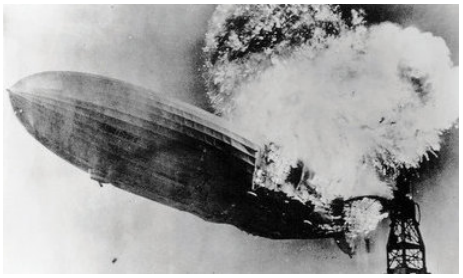


Figure **4.3.1**: The Formation of Water. Hydrogen and oxygen combine to form water. Here, the hydrogen gas in the zeppelin *SS Hindenburg* reacts with oxygen in the air to make water. Source: Photo courtesy of the US Navy. For a video of this see www.youtube.com/watch?v=CgWHbpMVQ1U.

To simplify the writing of reactions, we use formulas instead of names when we describe a reaction. We can also use symbols to represent other words in the reaction. A **plus sign** connects the initial substances (and final substances, if there is more than one), and an **arrow** (→) represents the chemical change:

$$\mathrm{H_2 + O_2 \rightarrow H_2O} \tag{4.3.1}$$

This statement is one example of a **chemical equation**, an abbreviated way of using symbols to represent a **chemical change**. The substances on the left side of the arrow are called **reactants**, and the substances on the right side of the arrow are called **products**. It is not uncommon to include a phase label with each formula—(s) for solid, (ℓ) for liquid, (g) for gas, and (aq) for a substance dissolved in water, also known as an *aqueous solution*. If we included phase labels for the reactants and products, under normal environmental conditions, the reaction would be as follows:

$$\mathrm{H_2(g) + O_2(g) \rightarrow H_2O\ (\ell)} \tag{4.3.2}$$

Chemical equations can also be used to describe physical changes. We will see examples of this soon.

This equation is still not complete because *it does not satisfy the* ***law of conservation of matter***. Count the **number of atoms of each element** on each side of the arrow. On the reactant side, there are two H atoms and two O atoms; on the product side, there are two H atoms and only one oxygen atom. The equation is **not balanced** because the number of oxygen atoms on each side is not the same (Figure **4.3.2**).

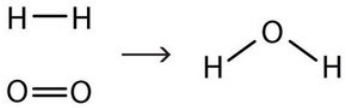


Figure **4.3.2**: Balanced—Yes or No?. By counting the atoms of each element, we can see that the reaction is not balanced as written.

To make this chemical equation conform to the law of conservation of matter, we must revise the amounts of the reactants and the products as necessary to get the same number of atoms of a given element on each side. Because every substance has a characteristic chemical formula, we cannot change the chemical formulas of the individual substances. For example, we cannot

change the formula for elemental oxygen to O. However, we can assume that different numbers of reactant molecules or product molecules may be involved. For instance, perhaps two water molecules are produced, not just one:

$$H_2(g) + O_2(g) \rightarrow 2H_2O(\ell) \tag{4.3.3}$$

The **2** preceding the formula for water is called a **coefficient**. It implies that two water molecules are formed. There are now two oxygen atoms on each side of the equation.

> This point is so important that we should repeat it. You **cannot** change the formula of a chemical substance to balance a chemical reaction! You **must** use the proper chemical formula of the substance.

Unfortunately, by inserting the coefficient 2 in front of the formula for water, we have also changed the number of hydrogen atoms on the product side as well. As a result, we no longer have the same number of hydrogen atoms on each side. This can be easily fixed, however, by putting a coefficient of 2 in front of the diatomic hydrogen reactant:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell) \tag{4.3.4}$$

Now we have four hydrogen atoms and two oxygen atoms on each side of the equation. The **law of conservation of matter is satisfied** because we now have the same number of atoms of each element in the reactants and in the products. We say that the reaction is **balanced** (Figure **4.3.3**). The diatomic oxygen has a coefficient of 1, which typically is not written but assumed in balanced chemical equations.

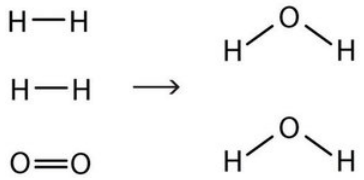


Figure **4.3.3**: Balanced—Yes or No?. By counting the atoms of each element, we can see that the reaction is now balanced.

Proper chemical equations should be balanced. Writing balanced reactions is a chemist's way of acknowledging the law of conservation of matter.

✔ Example 4.3.1

Is each chemical equation balanced?

a. $2Na(s) + O_2(g) \longrightarrow 2Na_2O(s)$
b. $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell)$
c. $AgNO_3(aq) + 2KCl(aq) \longrightarrow AgCl(s) + KNO_3(aq)$

Solution

a. By counting, we find two sodium atoms and two oxygen atoms in the reactants and four sodium atoms and two oxygen atoms in the products. This equation is not balanced.
b. The reactants have one carbon atom, four hydrogen atoms, and four oxygen atoms. The products have one carbon atom, four hydrogen atoms, and four oxygen atoms. This equation is balanced.
c. The reactants have one silver atom, one nitrogen atom, three oxygen atoms, two potassium atoms, and two chlorine atoms. The products have one silver atom, one chlorine atom, one potassium atom, one nitrogen atom, and three oxygen atoms. Because there are different numbers of chlorine and potassium atoms, this equation is not balanced.

? Exercise 4.3.1

Is each chemical equation balanced?

a. $2Hg(l) + O_2(g) \longrightarrow Hg_2O_2(s)$
b. $C_2H_4(g) + 2O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$
c. $Mg(NO_3)_2(s) + 2Li(s) \longrightarrow Mg(s) + 2LiNO_3(s)$.

Answer a:

balanced

Answer b:

O is not balanced; the 4 atoms of oxygen on the left does not balance with the 6 oxygen atoms on the right

Answer c:

balanced

How does one balance a chemical equation, starting with the correct formulas of the reactants and products? Basically, a **back-and-forth approach** is adopted, counting the number of atoms of one element on one side, checking the number of atoms of that element on the other side, and changing a coefficient if necessary. Then check another element, going back and forth from one side of the equation to another, until each element has the same number of atoms on both sides of the arrow. In many cases, it does not matter which element is balanced first and which is balanced last, as long as all elements have the same number of atoms on each side of the equation.

Below are guidelines for writing and balancing chemical equations.

Writing and Balancing Chemical Equations

1. Determine the correct chemical formulas for each reactant and product. Write the skeleton equation.
2. 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.
3. Balance each element one at a time by placing coefficients in front of the formulas. No coefficient is written for a 1. It is best to begin by balancing elements that only appear in one chemical formula on each side of the equation. NEVER change the subscripts in a chemical formula - you can only balance equations by using coefficients.
4. Check each atom or polyatomic ion to be sure that they are equal on both sides of the equation.
5. Make sure that all coefficients are in the lowest possible ratio. If necessary, reduce to the lowest ratio.

For example, to balance the equation

$$\mathrm{CH_4 + Cl_2 \rightarrow CCl_4 + HCl}$$

Step 1: Write the skeleton equation with the correct formulas.

$$\mathrm{CH_4 + Cl_2 \rightarrow CCl_4 + HCl} \tag{4.3.5}$$

Step 2: Count the number of each atom or polyatomic ion on both sides of the equation.

Reactants	Products
1 C atom	1 C atom
4 H ions	1 H ions
2 Cl atom	5 Cl atoms

Step 3: We find that both sides are already balanced with one carbon atom. So we proceed to balance the hydrogen atoms. We find that the reactant side has four hydrogen atoms, so the product side must also have four hydrogen atoms. This is balanced by putting a 4 in front of the HCl:

$$\mathrm{CH_4 + Cl_2 \rightarrow CCl_4 + 4\,HCl} \tag{4.3.6}$$

Reactants	Products
1 C atom	1 C atom
4 H ions	4 H ions
2 Cl atom	8 Cl atoms

Now each side has four hydrogen atoms. The product side has a total of eight chlorine atoms (four from the $\mathrm{CCl_4}$ and four from the four molecules of HCl), so we need eight chlorine atoms as reactants. Because elemental chlorine is a diatomic molecule, we need four chlorine molecules to get a total of eight chlorine atoms. We add another 4 in front of the $\mathrm{Cl_2}$ reactant:

$$CH_4 + 4\,Cl_2 \rightarrow CCl_4 + 4\,HCl \tag{4.3.7}$$

Reactants	Products
1 C atom	1 C atom
4 H ions	4 H ions
8 Cl atom	8 Cl atoms

Step 3: Now we check: each side has one carbon atom, four hydrogen atoms, and eight chlorine atoms. The chemical equation is balanced. And, the coefficients are in the lowest possible ratio.

Example 4.3.2

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: Write the skeleton equation with the correct formulas.

$$Pb(NO_3)_2\,(aq) + NaCl\,(aq) \rightarrow NaNO_3\,(aq) + PbCl_2\,(s)$$

Step 2: 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

Step 3: Solve. The nitrate ions and the chlorine atoms are unbalanced. Start by placing a 2 in front of the $NaCl$. This increases the reactant counts to 2 Na atoms and 2 Cl atoms. Then place a 2 in front of the $NaNO_3$. The result is:

$$Pb(NO_3)_2\,(aq) + 2NaCl\,(aq) \rightarrow 2NaNO_3\,(aq) + PbCl_2\,(s)$$

Step 4: 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 5: Think about the result.

The equation is now balanced since there are equal numbers of atoms of each element on both sides of the equation. And, the coefficients are in the lowest possible ratio.

Exercise 4.3.2

Fermentation is a biochemical process that enables yeast cells to live in the absence of oxygen. Humans have exploited it for centuries to produce wine and beer and make bread rise. In fermentation, sugars such as glucose ($C_6H_{12}O_6$) are converted to ethanol (C_2H_5OH) and carbon dioxide CO_2. Write a balanced chemical reaction for the fermentation of glucose.



Commercial use of fermentation. (a) Microbrewery vats are used to prepare beer. (b) The fermentation of glucose by yeast cells is the reaction that makes beer production possible.

Answer

$$C_6H_{12}O_6\,(s) \longrightarrow 2\,C_2H_5OH\,(l) + 2\,CO_2\,(g)$$

Key Takeaway

Chemical reactions are represented by chemical equations that list reactants and products. Proper chemical equations are balanced; the same number of each element's atoms appears on each side of the equation.

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4.4: Some Types of Chemical Reactions

Learning Objectives

- To classify a given chemical reaction into a variety of types.

Although there are untold millions of possible chemical reactions, most can be classified into a small number of general reaction types. Classifying reactions has two purposes: it helps us to recognize similarities among them, and it enables us to predict the products of certain reactions. A particular reaction may fall into more than one of the categories that we will define in this book.

Combination (composition) Reactions

A combination (composition) reaction is a chemical reaction that makes a single substance from two or more reactants. There may be more than one molecule of product in the balanced chemical equation, but there is only one substance produced. For example, the equation

$$4\,Fe + 3\,O_2 \rightarrow 2\,Fe_2O_3$$

is a combination reaction that produces Fe_2O_3 from its constituent elements — Fe and O_2. Combination reactions do not have to combine elements, however. The chemical equation

$$Fe_2O_3 + 3\,SO_3 \rightarrow Fe_2(SO_4)_3$$

shows a combination reaction in which Fe_2O_3 combines with three molecules of SO_3 to make $Fe_2(SO_4)_3$.

Example 4.4.1

Which equations are combination reactions?

a. $Co\,(s) + Cl_2\,(g) \longrightarrow CoCl_2\,(s)$
b. $CO\,(g) + Cl_2\,(g) \longrightarrow COCl_2\,(g)$
c. $N_2H_4(\ell) + O_2\,(g) \longrightarrow N_2\,(g) + 2\,H_2O(\ell)$

Solution

a. This is a combination reaction.
b. This is a combination reaction. (The compound $COCl_2$ is called phosgene and, in the past, was used as a gassing agent in chemical warfare.)
c. This is not a combination reaction.

Exercise 4.4.1

Which equations are combination reactions?

a. $P_4\,(s) + 6\,Cl_2\,(g) \longrightarrow 4\,PCl_3\,(g)$
b. $SO_3(\ell) + H_2O(\ell) \longrightarrow H_2SO_4(\ell)$
c. $NaOH\,(s) + HCl\,(g) \longrightarrow NaCl\,(s) + H_2O(\ell)$

Answer

a and b are combination reactions

Decomposition Reactions

A decomposition reaction is the reverse of a combination reaction. In a decomposition reaction, a single substance is converted into two or more products. There may be more than one molecule of the reactant, but there is only one substance initially. For example, the equation

$$2\,NaHCO_3\,(s) \rightarrow Na_2CO_3\,(s) + CO_2\,(g) + H_2O\,(\ell)$$

is a decomposition reaction that occurs when $NaHCO_3$ is exposed to heat. Another example is the decomposition of $KClO_3$:

$$2\,KClO_3\,(s) \rightarrow 2\,KCl\,(s) + 3\,O_2\,(g)$$

This reaction was once commonly used to generate small amounts of oxygen in the chemistry lab.

> The decomposition reaction of $NaHCO_3$ is the reaction that occurs when baking soda is poured on a small kitchen fire. The intent is that the H_2O and CO_2 produced by the decomposition will smother the flames.

Combustion Reactions

A combustion reaction occurs when a substance combines with molecular oxygen to make oxygen-containing compounds of other elements in the reaction. Many combustion reactions occur with a hydrocarbon, a compound made up solely of carbon and hydrogen. The products of the combustion of hydrocarbons are carbon dioxide and water. Many hydrocarbons are used as fuel because their combustion releases very large amounts of heat energy. An example is propane (C_3H_8), a gaseous hydrocarbon that is commonly used as the fuel source in gas grills.

$$C_3H_8\,(g) + 5\,O_2\,(g) \longrightarrow 3\,CO_2\,(g) + 4\,H_2O\,(g)$$

Another example is the burning of acetylene (C_2H_2) in welding torches:

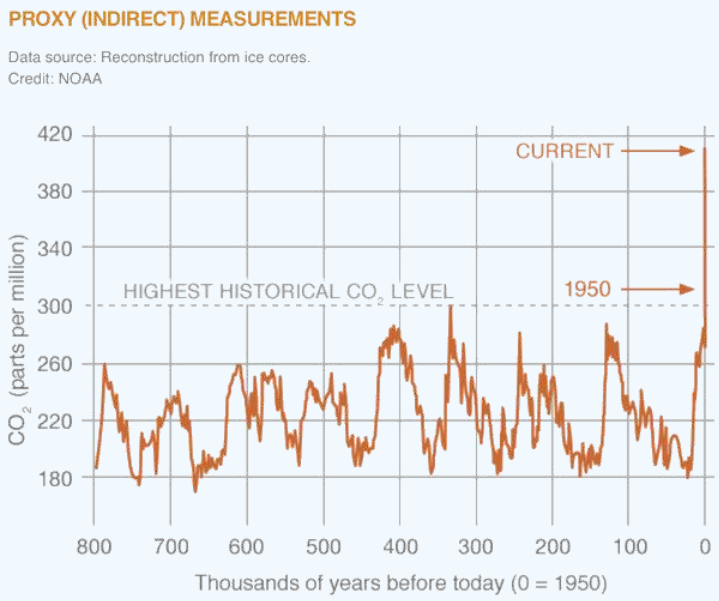
$$2\,C_2H_2 + 5\,O_2 \rightarrow 4\,CO_2 + 2\,H_2O$$

Oxygen (in its elemental form) is a crucial reactant in combustion reactions.

> *Energy in the form of heat is usually given off as a product in a combustion reaction as well.*

Example 4.4.2

Carbon dioxide (CO_2) is an important heat-trapping (greenhouse) gas, which is released through human activities such as deforestation and burning fossil fuels, as well as natural processes such as respiration and volcanic eruptions. The graph above shows CO_2 levels during the last three glacial cycles, as reconstructed from ice cores.



Carbon dioxide is the primary greenhouse gas emitted through human activities. In 2015, CO_2 accounted for about 82.2% of all U.S. greenhouse gas emissions from human activities. Carbon dioxide is naturally present in the atmosphere as part of the Earth's carbon cycle (the natural circulation of carbon among the atmosphere, oceans, soil, plants, and animals). Human activities are altering the carbon cycle–both by adding more CO_2 to the atmosphere and by influencing the ability of natural sinks, like forests, to remove CO_2 from the atmosphere. While CO_2 emissions come from a variety of natural sources, human-related emissions are responsible for the increase that has occurred in the atmosphere since the industrial revolution.

The main human activity that emits CO_2 is the combustion of fossil fuels (coal, natural gas, and oil) for energy and transportation, although certain industrial processes and land-use changes also emit CO_2. An example of how CO_2 can be generated is the **combustion of octane** (C_8H_{10}), a component of gasoline.

Write the balanced equation to represent the combustion of octane.

Solution

$$2\,C_8H_{18}\,(l) + 25\,O_2\,(g) \longrightarrow 16\,CO_2\,(g) + 18\,H_2O\,(g)$$

The balanced reaction argues that for every two molecules of octane that are burned, 16 molecules of CO_2 are generated.

Example 4.4.2

Identify each type of reaction.

a. $2\,K\,(s) + S\,(s) + 2\,O_2\,(g) \longrightarrow K_2SO_4\,(s)$
b. $(NH_4)_2Cr_2O_7\,(s) \longrightarrow N_2\,(g) + Cr_2O_3\,(s) + 4\,H_2O(\ell)$
c. $CH_4\,(g) + 2\,O_2\,(g) \longrightarrow CO_2\,(g) + 2\,H_2O(\ell)$

Solution

a. Multiple reactants are combining to make a single product, so this reaction is a combination reaction.
b. A single substance reacts to make several products, so we have a decomposition reaction.
c. Oxygen reacts with a compound to make carbon dioxide (an oxide of carbon) and water (an oxide of hydrogen). This is a combustion reaction.

Exercise 4.4.2

Identify each type of reaction.

a. $C_2H_5OH + 3\,O_2 \longrightarrow 2\,CO_2 + 3\,H_2O$
b. $2\,Mg\,(s) + O_2\,(g) \longrightarrow 2\,MgO\,(s)$
c. $CaCO_3\,(s) \longrightarrow CaO\,(s) + CO_2\,(g)$

Answer a

combustion

Answer b

combination (also combustion)

Answer c

decomposition

Key Takeaway

There are several recognizable types of chemical reactions: combination, decomposition, and combustion reactions are examples.

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https://chem.libretexts.org/@go/page/270396

4.5: Single Replacement Reactions



Figure 4.5.1 (Pixabay License; wisteriax via Pixabay)

Why is the silver dark?

The platter and pitcher shown above provides an example of tarnish, a chemical reaction caued when silver metal reacts with hydrogen sulfide gas produced by some industrial processes or as a result of decaying animal or plant materials:

$$2Ag + H_2S \rightarrow Ag_2S + H_2$$

The tarnish can be removed using a number of polishes, but the process also removes a small amount of silver along with the tarnish.

Single-Replacement Reactions

A **single-replacement reaction** is a reaction in which one element replaces a similar element in a compound. The general form of a single-replacement (also called single-displacement) reaction is:

$$A + BC \rightarrow AC + B$$

In this general reaction, element A is a metal and replaces element B (also a metal) in the compound. When the element that is doing the replacing is a nonmetal, it must replace another nonmetal in a compound, and the general equation becomes:

$$Y + XZ \rightarrow XY + Z$$

(Where Y is a nonmetal and replaces the nonmetal Z in the compound with X.)

Metal Replacement

Magnesium is a more reactive metal than copper. When a strip of magnesium metal is placed in an aqueous solution of copper (II) nitrate, it replaces the copper. The products of the reaction are aqueous magnesium nitrate and solid copper metal.

$$Mg\,(s) + Cu(NO_3)_2\,(aq) \rightarrow Mg(NO_3)_2\,(aq) + Cu\,(s)$$

This subcategory of single-replacement reactions is called a metal replacement reaction because it is a metal that is being replaced (copper).

Hydrogen Replacement

Many metals react easily with acids and when they do so, one of the products of the reaction is hydrogen gas. Zinc reacts with hydrochloric acid to produce aqueous zinc chloride and hydrogen (figure below).

$$Zn\,(s) + 2HCl\,(aq) \rightarrow ZnCl_2\,(aq) + H_2\,(g)$$

In a hydrogen replacement reaction, the hydrogen in the acid is replaced by an active metal.



Figure 4.5.2: Zinc metal reacts with hydrochloric acid to give off hydrogen gas in a single-displacement reaction. (Public Domain; User: Chemicalinterest/Wikimedia Commons via Wikipedia)

Some metals are so reactive that they are capable of replacing the hydrogen in water. The products of such a reaction are the metal hydroxide and hydrogen gas. All group 1 metals undergo this type of reaction. Sodium reacts vigorously with water to produce aqueous sodium hydroxide and hydrogen (see figure below).

$$\mathrm{2Na}\,(s) + \mathrm{2H_2O}\,(l) \rightarrow \mathrm{2NaOH}\,(aq) + \mathrm{H_2}\,(g)$$



Figure 4.5.3: Sodium metal reacts vigorously with water, giving off hydrogen gas. A large piece of sodium will often generate so much heat that the hydrogen will ignite. (Public Domain; User:Ajhalls/Wikimedia Commons via Wikipedia)

Halogen Replacement

The element chlorine reacts with an aqueous solution of sodium bromide to produce aqueous sodium chloride and elemental bromine:

$$\mathrm{Cl_2}\,(g) + \mathrm{2NaBr}\,(aq) \rightarrow \mathrm{2NaCl}\,(aq) + \mathrm{Br_2}\,(l)$$

The reactivity of the halogen group (group 17) decreases from top to bottom within the group. Fluorine is the most reactive halogen, while iodine is the least. Since chlorine is above bromine, it is more reactive than bromine and can replace it in a halogen replacement reaction.



Summary

- The activity series describes the relative reactivities of metals and halogens.

Review

1. What is a metal replacement reaction?
2. Will a non-metal replace a metal?
3. What is the most reactive halogen?
4. What products will I get if I add potassium metal to water?

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4.6: Activity Series



Figure **4.6.1**: Copy and Paste Caption here. (Public Domain; Sodium: User: Ajhalls/Wikimedia Commons; Silver: User:Daderot/Wikimedia Commons via Sodium: http://commons.wikimedia.org/wiki/File:Large_Sodium_Explosion.jpg; Silver: http://commons.wikimedia.org/wiki/File:Camp_cup_and_tumbler,_1795-1800,_Paul_Revere_silver_collection,_Worcester_Art_Museum_-_IMG_7624.JPG)

What's the difference between the two pictures above?

We see above two metals that can be exposed to water. The picture on the left is of sodium, which gives a violent reaction when it comes in contact with water. The picture on the right is of silver, a metal so unreactive with water that it can be made into drinking vessels. Both metals have a single s electron in their outer shell, so you would predict similar reactivities. However, we have a better tool that allows us to make better prediction about what will react with what.

The Activity Series

Single-replacement reactions only occur when the element that is doing the replacing is more reactive than the element that is being replaced. Therefore, it is useful to have a list of elements in order of their relative reactivities. The **activity series** is a list of elements in decreasing order of reactivity. Since metals replace other metals, while nonmetals replace other nonmetals, they each have a separate activity series. The table below is an activity series of most common metals, and of the halogens.

Table **4.6.1**: Activity Series

Activity of Metals		Activity of Halogens
Elements	**Reaction Occurring**	**Elements**
Li K Ba Sr Ca Na	React with cold water, replacing hydrogen.	F_2 Cl_2 Br_2 I_2
Mg Al Zn Cr Fe Cd	React with steam, but not cold water, replacing hydrogen.	
Co Ni Sn Pb	Do not react with water. React with acids, replacing hydrogen.	
H_2		
Cu Hg Ag Pt Au	Unreactive with water or acids.	

For a single-replacement reaction, a given element is capable of replacing an element that is below it in the activity series. This can be used to predict if a reaction will occur. Suppose that small pieces of the metal nickel were placed into two separate aqueous solutions: one of iron (III) nitrate and one of lead (II) nitrate. Looking at the activity series, we see that nickel is below iron, but above lead. Therefore, the nickel metal will be capable of replacing the lead in a reaction, but will not be capable of replacing iron.

$$\mathrm{Ni}\,(s) + \mathrm{Pb(NO_3)_2}\,(aq) \rightarrow \mathrm{Ni(NO_3)_2}\,(aq) + \mathrm{Pb}\,(s)$$

$$\mathrm{Ni}\,(s) + \mathrm{Fe(NO_3)_3}\,(aq) \rightarrow \mathrm{NR\ (no\ reaction)}$$

In the descriptions that accompany the activity series of metals, a given metal is also capable of undergoing the reactions described below that section. For example, lithium will react with cold water, replacing hydrogen. It will also react with steam and with acids, since that requires a lower degree of reactivity.



Example 4.6.1: Single-Replacement Reactions

Use the activity series to predict if the following reactions will occur. If not, write **NR**. If the reaction does occur, write the products of the reaction and balance the equation.

a. $\mathrm{Al}\,(s) + \mathrm{Zn(NO_3)_2}\,(aq) \rightarrow$

b. $\mathrm{Ag}\,(s) + \mathrm{HCl}\,(aq) \rightarrow$

Solution

Step 1: Plan the problem.

For A, compare the placements of aluminum and zinc on the activity series. For B, compare the placements of silver and hydrogen.

Step 2: Solve.

Since aluminum is above zinc, it is capable of replacing it and a reaction will occur. The products of the reaction will be aqueous aluminum nitrate and solid zinc. Take care to write the correct formulas for the products before balancing the equation. Aluminum adopts a $+3$ charge in an ionic compound, so the formula for aluminum nitrate is $\mathrm{Al(NO_3)_3}$. The balanced equation is:

$$2\mathrm{Al}\,(s) + 3\mathrm{Zn(NO_3)_2}\,(aq) \rightarrow 2\mathrm{Al(NO_3)_3}\,(aq) + 3\mathrm{Zn}\,(s)$$

Since silver is below hydrogen, it is not capable of replacing hydrogen in a reaction with an acid.

$$\mathrm{Ag}\,(s) + \mathrm{HCl}\,(aq) \rightarrow \mathrm{NR}$$



Summary

- Metals and halogens are ranked according to their ability to displace other metals or halogens below them in the series.

Review

1. What does the activity series tell us?
2. Can a metal undergo any of the reactions listed below it in the series?
3. List two metals that cobalt will displace and two that will displace it.

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4.7: Double Replacement Reactions



Figure 4.7.1 (Public Domain; F. S. Church, published in Harper's Weekly, January 17, 1874, p. 61 via Wikipedia)

Want to trade?

The practice of barter (trading one thing for another) has been in existence for a very long time. In the illustration above, items like chickens were bartered for newspapers. You have something I want, and I have something you want. So we trade and we each have something new. Some chemical reactions are like that. Compounds swap parts and you have new materials.

Double-Replacement Reactions

A **double-replacement reaction** is a reaction in which the positive and negative ions of two ionic compounds exchange places to form two new compounds. The general form of a double-replacement (also called double-displacement) reaction is:

$$\mathrm{AB + CD \rightarrow AD + CB}$$

In this reaction, A and C are positively-charged cations, while B and D are negatively-charged anions. Double-replacement reactions generally occur between substances in aqueous solution. In order for a reaction to occur, one of the products is usually a solid precipitate, a gas, or a molecular compound such as water.

Formation of a Precipitate

A precipitate forms in a double-replacement reaction when the cations from one of the reactants combine with the anions from the other reactant to form an insoluble ionic compound. When aqueous solutions of potassium iodide and lead (II) nitrate are mixed, the following reaction occurs:

$$\mathrm{2KI\,(\mathit{aq}) + Pb(NO_3)_2\,(\mathit{aq}) \rightarrow 2KNO_3\,(\mathit{aq}) + PbI_2\,(\mathit{s})}$$

There are very strong attractive forces that occur between $\mathrm{Pb^{2+}}$ and $\mathrm{I^-}$ ions and the result is a brilliant yellow precipitate (see figure below). The other product of the reaction, potassium nitrate, remains soluble.



Figure 4.7.2: Formation of lead iodide precipitate. (CC-BY 2.0; Paige Powers - "Lead Iodide" via Flickr)

Formation of a Gas

Some double-replacement reactions produce a gaseous product which then bubbles out of the solution and escapes into the air. When solutions of sodium sulfide and hydrochloric acid are mixed, the products of the reaction are aqueous sodium chloride and hydrogen sulfide gas.

$$\mathrm{Na_2S\,(\mathit{aq}) + 2HCl\,(\mathit{aq}) \rightarrow 2NaCl\,(\mathit{aq}) + H_2S\,(\mathit{g})}$$

Formation of a Molecular Compound

Another kind of double-replacement reaction is one that produces a molecular compound as one of its products. Many examples in this category are reactions that produce water. When aqueous hydrochloric acid is reacted with aqueous sodium hydroxide, the

products are aqueous sodium chloride and water:

$$\mathrm{HCl}\,(aq) + \mathrm{NaOH}\,(aq) \rightarrow \mathrm{NaCl}\,(aq) + \mathrm{H_2O}\,(l)$$

Example 4.7.1: Double-Replacement Reactions

Write a complete and balanced chemical equation for the following double-replacement reactions. One product is indicated as a guide.

a. $\mathrm{NaCN}\,(aq) + \mathrm{HBr}\,(aq) \rightarrow$ (hydrogen cyanide gas is formed)
b. $(\mathrm{NH_4})_2\mathrm{SO_4}\,(aq) + \mathrm{Ba(NO_3)_2}\,(aq) \rightarrow$ (a precipitate of barium sulfate forms)

Solution

Step 1: Plan the problem.

In A, the production of a gas drives the reaction. In B, the production of a precipitate drives the reaction. In both cases, use the ionic charges of both reactants to construct the correct formulas of the products.

Step 2: Solve.

A. The cations of both reactants are $+1$ charged ions, while the anions are -1 charged ions. After exchanging partners, the balanced equation is:

$$\mathrm{NaCN}\,(aq) + \mathrm{HBr}\,(aq) \rightarrow \mathrm{NaBr}\,(aq) + \mathrm{HCN}\,(g)$$

B. Ammonium ion and nitrate ion are $1+$ and $1-$ respectively, while barium and sulfate are $2+$ and $2-$. This must be taken into account when exchanging partners and writing the new formulas. Then, the equation is balanced.

$$(\mathrm{NH_4})_2\mathrm{SO_4}\,(aq) + \mathrm{Ba(NO_3)_2}\,(aq) \rightarrow 2\mathrm{NH_4NO_3}\,(aq) + \mathrm{BaSO_4}\,(s)$$

Step 3: Think about your result.

Both are double replacement reactions. All formulas are correct and the equations are balanced.

Occasionally, a reaction will produce both a gas and a molecular compound. The reaction of a sodium carbonate solution with hydrochloric acid produces aqueous sodium chloride, carbon dioxide gas, and water.

$$\mathrm{Na_2CO_3}\,(aq) + 2\mathrm{HCl}\,(aq) \rightarrow 2\ \mathrm{NaCl}\,(aq) + \mathrm{CO_2}\,(g) + \mathrm{H_2O}\,(l)$$



Summary

- The double-replacement reaction generally takes the form of AB + CD → AD + CB where A and C are positively-charged cations, while B and D are negatively-charged anions.
- In a double replacement reactions, typically one of the products is a precipitate, a gas, or a molecular compound.

Review

1. In a double-replacement reaction, what type of compounds are usually the reactants? A double-replacement reaction occurs between sodium sulfide and hydrogen chloride. Write the rest of the chemical equation and balance it.
2. $Na_2S + HCl \rightarrow$
3. In double-replacement reaction, one of three possible types of products usually form. What are the three types?

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4.8: Avogadro's Number



Figure 4.8.1 (Public Domain; User:OSX/Wikimedia Commons via Wikipedia)

Is there an easier way to load this truck?

When the weather is nice, many people begin to work on their yards and homes. For many projects, sand is needed as a foundation for a walk or to add to other materials. You could order up twenty million grains of sand and have people really stare at you. You could order by the pound, but that takes a lot of time weighing out. The best bet is to order by the yard, meaning a cubic yard. The loader can easily scoop up what you need and put it directly in your truck.

Avogadro's Number

It certainly is easy to count objects such as bananas, or something as large as elephants (as long as you stay out of their way). However, counting grains of sugar from a sugar canister would take a long, long time. Atoms and molecules are extremely small—far, far smaller than grains of sugar. Counting atoms or molecules is not only unwise, it is absolutely impossible. One drop of water contains about 10^{22} molecules of water. If you counted 10 molecules every second for 50 years, without stopping, you would have counted only 1.6×10^{10} molecules. Put another way, at that counting rate, it would take you over 30 trillion years to count the water molecules in one tiny drop.

Chemists of the past needed a name that could stand for a very large number of items. Amadeo Avogadro (1776-1856), an Italian scientist, provided such a number. He is responsible for the counting unit of measure called the mole. A **mole** (mol) is the amount of a substance that contains 6.02×10^{23} representative particles of that substance. The mole is the SI unit for amount of a substance. Just like the dozen and the gross, it is a name that stands for a number. There are therefore 6.02×10^{23} water molecules in a mole of water molecules. There also would be 6.02×10^{23} bananas in a mole of bananas, if such a huge number of bananas ever existed.



Figure 4.8.2: Italian scientist Amadeo Avogadro, whose work led to the concept of the mole as a counting unit in chemistry. (Public Domain; C. Sentier via Wikipedia)

The number 6.02×10^{23} is called **Avogadro's number**, the number of representative particles in a mole. It is an experimentally determined number. A **representative particle** is the smallest unit in which a substance naturally exists. For the majority of elements, the representative particle is the atom. Iron, carbon, and helium consist of iron atoms, carbon atoms, and helium atoms, respectively. Seven elements exist in nature as diatomic molecules and they are H_2, N_2, O_2, F_2, Cl_2, Br_2, and I_2. The representative particle for these elements is the molecule. Likewise, all molecular compounds such as H_2O and CO_2 exist as molecules and so the molecule is their representative particle. For ionic compounds such as $NaCl$ and $Ca(NO_3)_2$, the representative particle is the formula unit. A mole of any substance contains Avogadro's number $\left(6.02 \times 10^{23}\right)$ of representative particles.



Figure 4.8.3: The animal mole is very different than the counting unit of the mole. Chemists nonetheless have adopted the mole as their unofficial mascot. National Mole Day is a celebration of chemistry that occurs on October 23rd (10/23) of each year. ((left; Left: Michael David Hill, 2005 (Mikiwikipikidikipedia); Right: chrisbb@prodigy.net;(left) Michael David Hill, 2005 (Mikiwikipikidikipedia); (right) chrisbb@prodigy.net via Left: http://commons.wikimedia.org/wiki/File:Close-up_of_mole.jpg; Right: http://www.flickr.com/photos/chrisbrenschmidt/436990097;(left) http://commons.wikimedia.org/wiki/File:Close-up_of_mole.jpg; (right) http://www.flickr.com/photos/chrisbrenschmidt/436990097) CC-BY 2.5; (right) CC-BY 2.0)



Summary

- A mole of any substance contains Avogadro's number (6.02×10^{23}) of representative particles.

Review

1. What is the SI unit for amount of a substance?
2. What is the representative particle for an element?
3. The formula unit is the representative particle for what?

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4.9: The Mole

Learning Objectives

- To define the mole unit.

Figure **4.9.1** shows that we need 2 hydrogen atoms and 1 oxygen atom to make 1 water molecule. If we want to make 2 water molecules, we will need 4 hydrogen atoms and 2 oxygen atoms. If we want to make 5 molecules of water, we need 10 hydrogen atoms and 5 oxygen atoms. The ratio of atoms we will need to make any number of water molecules is the same: 2 hydrogen atoms to 1 oxygen atom.

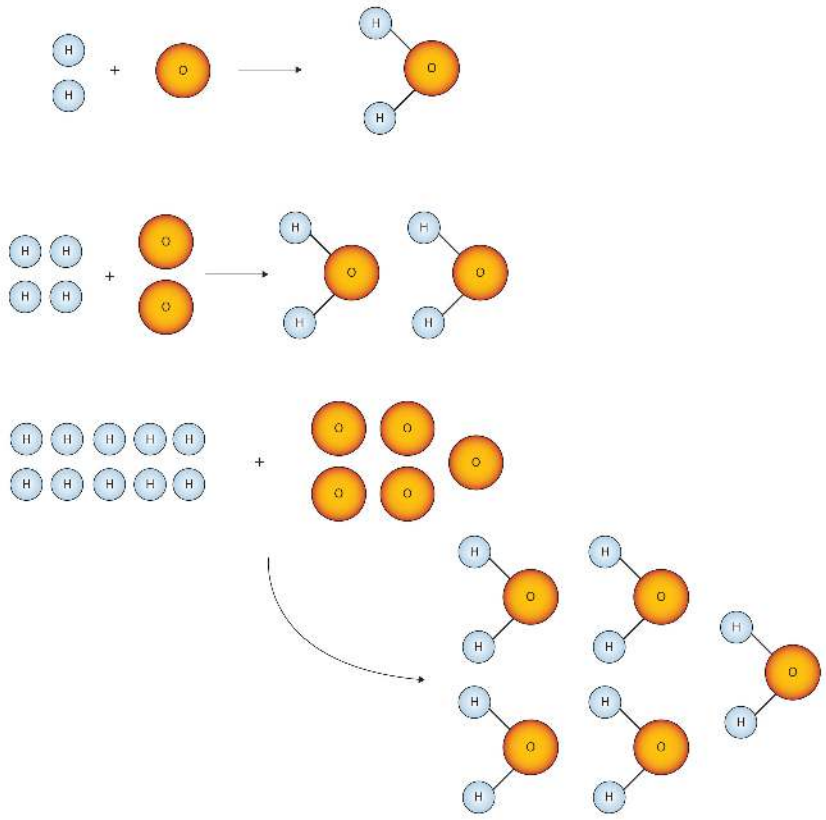


Figure **4.9.1** Water Molecules. The ratio of hydrogen atoms to oxygen atoms used to make water molecules is always 2:1, no matter how many water molecules are being made.

One problem we have, however, is that it is extremely difficult, if not impossible, to organize atoms one at a time. As stated in the introduction, we deal with billions of atoms at a time. How can we keep track of so many atoms (and molecules) at a time? We do it by using mass rather than by counting individual atoms.

A hydrogen atom has a mass of approximately 1 u. An oxygen atom has a mass of approximately 16 u. The ratio of the mass of an oxygen atom to the mass of a hydrogen atom is therefore approximately 16:1.

If we have 2 atoms of each element, the ratio of their masses is approximately 32:2, which reduces to 16:1—the same ratio. If we have 12 atoms of each element, the ratio of their total masses is approximately (12 × 16):(12 × 1), or 192:12, which also reduces to 16:1. If we have 100 atoms of each element, the ratio of the masses is approximately 1,600:100, which again reduces to 16:1. As long as we have equal numbers of hydrogen and oxygen atoms, the ratio of the masses will always be 16:1.

The same consistency is seen when ratios of the masses of other elements are compared. For example, the ratio of the masses of silicon atoms to equal numbers of hydrogen atoms is always approximately 28:1, while the ratio of the masses of calcium atoms to equal numbers of lithium atoms is approximately 40:7.

So we have established that the masses of atoms are constant with respect to each other, as long as we have the same number of each type of atom. Consider a more macroscopic example. If a sample contains 40 g of Ca, this sample has the same number of atoms as there are in a sample of 7 g of Li. What we need, then, is a number that represents a convenient quantity of atoms so we can relate macroscopic quantities of substances. Clearly even 12 atoms are too few because atoms themselves are so small. We need a number that represents billions and billions of atoms.

Chemists use the term **mole** to represent a large number of atoms or molecules. Just as a dozen implies 12 things, a **mole** (abbreviated as ***mol***) represents **6.022×10^{23} things**. The number 6.022×10^{23}, called Avogadro's number after the 19th-century chemist Amedeo Avogadro, is the number we use in chemistry to represent macroscopic amounts of atoms and molecules. Thus, if we have 6.022×10^{23} Na atoms, we say we have 1 mol of Na atoms. If we have 2 mol of Na atoms, we have $2 \times (6.022 \times 10^{23})$ Na atoms, or 1.2044×10^{24} Na atoms. Similarly, if we have 0.5 mol of benzene (C_6H_6) molecules, we have $0.5 \times (6.022 \times 10^{23})$ C_6H_6 molecules, or 3.011×10^{23} C_6H_6 molecules.

> A mole represents a very large number! If 1 mol of quarters were stacked in a column, it could stretch back and forth between Earth and the sun *6.8 billion* times.

Notice that we are applying the mole unit to different types of **chemical entities**. The word *mole* represents a number of things—6.022×10^{23} of them—but does not by itself specify what "they" are. The chemical entities can be ***atoms, molecules***, ***formula units*** and ***ions***. This specific information needs to be specified accurately. Most students find this confusing hence, we need to review the composition of elements, covalent and ionic compounds.

Most elements are made up of individual ***atoms,*** such as helium. However, some elements consist of ***molecules***, such as the diatomic elements, nitrogen, hydrogen, oxygen, etc. One mole of He consists of 6.022×10^{23} He ***atoms*** but one mole of nitrogen contains 6.022×10^{23} N_2 ***molecules***. The basic units of covalent (molecular) compounds are ***molecules*** as well. The molecules of "compounds" consist of different kinds of atoms while the molecules of "elements" consist of only one type of atom. For example, the molecules of ammonia (NH_3) consist of nitrogen and hydrogen atoms while N_2 molecules have N atoms only. Compounds that are ionic, like NaCl, are represented by ionic formulas. One mole of NaCl, for example, refers to 6.022×10^{23} ***formula units*** of NaCl. And, one formula unit of NaCl consists of one sodium ***ion*** and one chloride ***ion***. Figure 6.1.2 summarizes the basic units of elements, covalent and ionic compounds

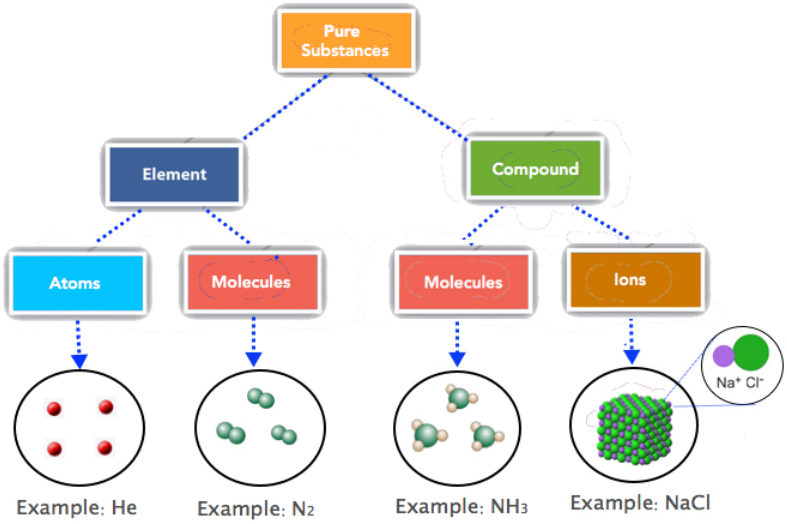


Figure **4.9.2**: The basic units of elements (atoms or molecules), covalent compounds (molecules) and ionic compounds (formula units of ions).

Conversion Between Moles and Atoms, Molecules and Ions

Using our unit conversion techniques learned in Chapter 1, we can use the mole relationship and the chemical formula to convert back and forth between the moles and the number of chemical entities (atoms, molecules or ions).

Because 1 N_2 molecule contains 2 N atoms, 1 mol of N_2 molecules (6.022×10^{23} molecules) has 2 mol of N atoms. Using formulas to indicate how many atoms of each element we have in a substance, we can relate the number of moles of molecules to the number of moles of atoms. For example, in 1 mol of ethanol (C_2H_6O), we can construct the following relationships (Table **4.9.1**):

Table **4.9.1**: Molecular Relationships

1 Molecule of C_2H_6O Has	1 Mol of C_2H_6O Has	Molecular Relationships
2 C atoms	2 mol of C atoms	$\frac{2\ \text{mol C atoms}}{1\ \text{mol } C_2H_6O\ \text{molecules}}$ or $\frac{1\ \text{mol } C_2H_6O\ \text{molecules}}{2\ \text{mol C atoms}}$
6 H atoms	6 mol of H atoms	$\frac{6\ \text{mol H atoms}}{1\ \text{mol } C_2H_6O\ \text{molecules}}$ or $\frac{1\ \text{mol } C_2H_6O\ \text{molecules}}{6\ \text{mol H atoms}}$
1 O atom	1 mol of O atoms	$\frac{1\ \text{mol O atoms}}{1\ \text{mol } C_2H_6O\ \text{molecules}}$ or $\frac{1\ \text{mol } C_2H_6O\ \text{molecules}}{1\ \text{mol O atoms}}$

The following example illustrates how we can use these relationships as conversion factors.

Example 4.9.1

If a sample consists of 2.5 mol of ethanol (C_2H_6O), how many moles of carbon atoms, hydrogen atoms, and oxygen atoms does it have?

Solution

Using the relationships in Table **4.9.1**, we apply the appropriate conversion factor for each element:

$$2.5\ \text{mol } C_2H_6O\ \text{molecules} \times \underbrace{\frac{2\ \text{mol C atoms}}{1\ \text{mol } C_2H_6O\ \text{molecules}}}_{\text{conversion factor}} = 5.0\ \text{mol C atoms}$$

Note how the unit *mol C_2H_6O molecules* cancels algebraically. Similar equations can be constructed for determining the number of H and O atoms:

$$2.5\ \text{mol } C_2H_6O\ \text{molecules} \times \frac{6\ \text{mol H atoms}}{1\ \text{mol } C_2H_6O\ \text{molecules}} = 15\ \text{mol H atoms}$$

$$2.5\ \text{mol } C_2H_6O\ \text{molecules} \times \frac{1\ \text{mol O atoms}}{1\ \text{mol } C_2H_6O\ \text{molecules}} = 2.5\ \text{mol O atoms}$$

Exercise 4.9.1

If a sample contains 6.75 mol of Na_2SO_4, how many moles of sodium atoms, sulfur atoms, and oxygen atoms does it have?

Answer

13.5 mol Na, 6.75 mol S and 27 mol O.

We can use Avogadro's number as a conversion factor, or ratio, in dimensional analysis problems. For example, if we are dealing with element X, the mole relationship is expressed as follows:

$$1\ \text{mol X} = 6.022 \times 10^{23}\ \text{X atoms}$$

We can convert this relationship into two possible conversion factors shown below:

$$\frac{1\ \text{mol X}}{6.022 \times 10^{23}\ \text{X atoms}} \text{ or } \frac{6.022 \times 10^{23}\ \text{X atoms}}{1\ \text{mol X}}$$

If the number of "atoms of element X" is given, we can convert it into "moles of X" by multiplying the given value with the conversion factor at the left. However, if the number of "mol of X" is given, the appropriate conversion factor to use is the one at

the right.

If we are dealing with a molecular compound (such as C_4H_{10}), the mole relationship is expressed as follows:

$$1 \text{ mol } C4H10 = 6.022 \times 10^{23} \text{ } C4H10 \text{ molecules}$$

If working with ionic compounds (such as NaCl), the mole relationship is expressed as follows:

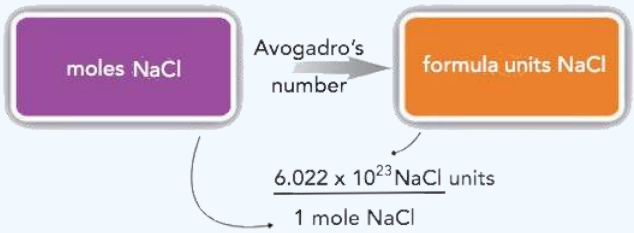
$$1 \text{ mol NaCl} = 6.022 \times 10^{23} \text{ NaCl formula units}$$

Example 4.9.2

How many formula units are present in 2.34 mol of NaCl? How many ions are in 2.34 mol?

Solution

Typically in a problem like this, we start with what we are given and apply the appropriate conversion factor. Here, we are given a quantity of 2.34 mol of NaCl, to which we can apply the definition of a **mole as a conversion factor**:



$$2.34 \text{ mol NaCl} \times \frac{6.022 \times 10^{23} \text{ NaCl units}}{1 \text{ mol NaCl}} = 1.41 \times 10^{24} \text{ NaCl units}$$

Because there are two ions per formula unit, there are

$$1.41 \times 10^{24} \text{ NaCl units} \times \frac{2 \text{ ions}}{\text{NaCl units}} = 2.82 \times 10^{24} \text{ ions}$$

in the sample.

Exercise 4.9.2

How many molecules are present in 16.02 mol of C_4H_{10}? How many atoms are in 16.02 mol?

Answer

9.647 x 10^{24}molecules, 1.351 x 10^{26} atoms.

Key Takeaway

- A mole is 6.022×10^{23} things.

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4.10: Molar Mass



Figure 4.10.1 (Public Domain; Ben Mills (Wikimedia: Benjah-bmm27) via Wikipedia)

When creating a solution, how do I know how much of each substance to put in?

I want to make a solution that contains 1.8 moles of potassium dichromate. You do not have a balance calibrated in moles, but you do have one calibrated in grams. If you know the relationship between moles and the number of grams in a mole, you can use your balance to measure out the needed amount of material.

Molar Mass

Molar mass is defined as the mass of one mole of representative particles of a substance. By looking at a periodic table, we can conclude that the molar mass of lithium is $6.94\ \text{g}$, the molar mass of zinc is $65.38\ \text{g}$, and the molar mass of gold is $196.97\ \text{g}$. Each of these quantities contains 6.02×10^{23} atoms of that particular element. The units for molar mass are grams per mole, or g/mol.

Molar Masses of Compounds

The molecular formula of the compound carbon dioxide is CO_2. One molecule of carbon dioxide consists of 1 atom of carbon and 2 atoms of oxygen. We can calculate the mass of one molecule of carbon dioxide by adding together the masses of 1 atom of carbon and 2 atoms of oxygen:

$$12.01\ \text{amu} + 2\,(16.00\ \text{amu}) = 44.01\ \text{amu}$$

The **molecular mass** of a compound is the mass of one molecule of that compound. The molecular mass of carbon dioxide is $44.01\ \text{amu}$.

The molar mass of any compound is the mass in grams of one mole of that compound. One mole of carbon dioxide molecules has a mass of $44.01\ \text{g}$, while one mole of sodium sulfide formula units has a mass of $78.04\ \text{g}$. The molar masses are $44.01\ \text{g/mol}$ and $78.04\ \text{g/mol}$ respectively. In both cases, that is the mass of 6.02×10^{23} representative particles. The representative particle of CO_2 is the molecule, while for Na_2S it is the formula unit.

Example 4.10.1: Molar Mass of a Compound

Calcium nitrate, $\text{Ca(NO}_3)_2$, is used as a component in fertilizer. Determine the molar mass of calcium nitrate.

Solution

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

Known

- Formula $= \text{Ca(NO}_3)_2$
- Molar mass $\text{Ca} = 40.08\ \text{g/mol}$
- Molar mass $\text{N} = 14.01\ \text{g/mol}$
- Molar mass $\text{O} = 16.00\ \text{g/mol}$

Unknown

- molar mass $\text{Ca(NO}_3)_2$

First we need to analyze the formula. Since the **Ca** lacks a subscript, there is one **Ca** atom per formula unit. The 2 outside the parentheses means that there are two nitrate ions per formula unit and each nitrate ion consists of one nitrogen atom and three oxygen atoms per formula unit. Thus, **1 mol** of calcium nitrate contains **1 mol** of **Ca** atoms, **2 mol** of **N** atoms, and **6 mol** of **O** atoms.

Step 2: Calculate

Use the molar masses of each atom together with the number of atoms in the formula and add together.

$$1\ \text{mol Ca} \times \frac{40.08\ \text{g Ca}}{1\ \text{mol Ca}} = 40.08\ \text{g Ca}$$

$$2\ \text{mol N} \times \frac{14.01\ \text{g N}}{1\ \text{mol N}} = 28.02\ \text{g N}$$

$$6\ \text{mol O} \times \frac{16.00\ \text{g O}}{1\ \text{mol O}} = 96.00\ \text{g O}$$

Molar mass of $\text{Ca(NO}_3)_2 = 40.08\ \text{g} + 28.02\ \text{g} + 96.00\ \text{g} = 164.10\ \text{g/mol}$



Summary

- Calculations are described for the determination of molar mass of an atom or a compound.

Review

1. What is the molar mass of Pb?
2. Where do you find the molar mass of an element?
3. How many moles of Cl are in one mole of the $CaCl_2$?
4. How many moles of H are in one mole of the compound $(NH_4)_3PO_4$?
5. Calculate the molar mass of $CaCl_2$.

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4.11: Atomic and Molar Masses

Learning Objectives

- To learn how the masses of moles of atoms and molecules are expressed.

Now that we have introduced the mole and practiced using it as a conversion factor, we ask the obvious question: why is the mole *that particular* number of things? Why is it 6.022×10^{23} and not 1×10^{23} or even 1×10^{20}?

The number in a mole, Avogadro's number, is related to the relative sizes of the **atomic mass unit** and **gram mass units**. Whereas one hydrogen atom has a mass of approximately 1 u, **1 mol of H atoms** has a mass of approximately **1 *gram***. And whereas one sodium atom has an approximate mass of 23 u, 1 mol of Na atoms has an approximate mass of 23 *grams*.

One mole of a substance has the same mass in grams that one atom or molecule has in atomic mass units. The numbers in the periodic table that we identified as the atomic masses of the atoms not only tell us the mass of one atom in u but also tell us the mass of 1 mol of atoms in grams.

> One mole of a substance has the same mass in grams that one atom or molecule has in atomic mass units.

Example 4.11.1: Moles to Mass Conversion with Elements

What is the mass of each quantity?

a. 1 mol of Al atoms
b. 2 mol of U atoms

Solution

a. One mole of Al atoms has a mass in grams that is numerically equivalent to the atomic mass of aluminum. The periodic table shows that the atomic mass (rounded to two decimal points) of Al is 26.98, so 1 mol of Al atoms has a mass of 26.98 g.
b. According to the periodic table, 1 mol of U has a mass of 238.0 g, so the mass of 2 mol is twice that, or 476.0 g.

Exercise 4.11.1: Moles to Mass Conversion with Elements

What is the mass of each quantity?

a. 1 mol of Au atoms
b. 5 mol of Br atoms

Answer a

197.0 g

Answer b

5 mol Br atoms x 79.90 g/mol = 399.5 g

The mole concept can be extended to masses of formula units and molecules as well. The mass of 1 mol of molecules (or formula units) in grams is numerically equivalent to the mass of one molecule (or formula unit) in atomic mass units. For example, a single molecule of O_2 has a mass of 32.00 u, and 1 mol of O_2 molecules has a mass of 32.00 g. As with atomic mass unit–based masses, to obtain the mass of 1 mol of a substance, we simply sum the masses of the individual atoms in the formula of that substance. The mass of 1 mol of a substance is referred to as its **molar mass**, whether the substance is an element, an ionic compound, or a covalent compound.

Example 4.11.2: Moles to Mass Conversion with Compounds

What is the mass of 1 mol of each substance?

a. NaCl
b. bilirubin ($C_{33}H_{36}N_4O_6$), the principal pigment present in bile (a liver secretion)

Solution a

1. Summing the molar masses of the atoms in the NaCl formula unit gives

Solutions to Example 6.2.2, Summing the molar masses of the atoms in the NaCl formula unit gives

1 Na molar mass:	22.99 g
1 Cl molar mass:	35.45 g
Total:	58.44 g

The mass of 1 mol of NaCl is 58.44 g.

Solution b

Multiplying the molar mass of each atom by the number of atoms of that type in bilirubin's formula and adding the results, we get

Solutions to Example 6.2.2, Multiplying the molar mass of each atom by the number of atoms of that type in bilirubin's formula and adding the results, we get

33 C molar mass:	33 × 12.01 g	396.33 g
36 H molar mass:	36 × 1.01 =	36.36 g
4 N molar mass:	4 × 14.01 =	56.04 g
6 O molar mass:	6 × 16.00 =	96.00 g
Total:		584.73 g

The mass of 1 mol of bilirubin is 584.73 g.

Exercise 4.11.2: Moles to Mass Conversion with Compounds

What is the mass of 1 mol of each substance?

a. barium sulfate ($BaSO_4$), used to take X rays of the gastrointestional tract
b. adenosine ($C_{10}H_{13}N_5O_4$), a component of cell nuclei crucial for cell division

Answer a

233.36 g

Answer b

267.28 g

Be careful when counting atoms. In formulas with polyatomic ions in parentheses, the subscript outside the parentheses is applied to every atom inside the parentheses. For example, the molar mass of $Ba(OH)_2$ requires the sum of 1 mass of Ba, 2 masses of O, and 2 masses of H:

The molar mass of Ba(OH)2 requires the sum of 1 mass of Ba, 2 masses of O, and 2 masses of H:

1 Ba molar mass:	1 × 137.3 g =	137.3 g
2 O molar mass:	2 × 16.00 g =	32.00 g
2 H molar mass:	2 × 1.01 g =	2.02 g
Total:		171.32 g

Because molar mass is defined as the mass for 1 mol of a substance, we can refer to molar mass as grams per mole (g/mol). The division sign (/) implies "per," and "1" is implied in the denominator. Thus, the molar mass of bilirubin can be expressed as 584.73 g/mol, which is read as "five hundred eighty four point seventy three grams per mole."

Key Takeaway

- The mass of moles of atoms and molecules is expressed in units of grams.

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4.12: Mole-Mass Conversions

Learning Objectives

- To convert quantities between mass units and mole units.

A previous Example stated that the mass of 2 mol of U is twice the molar mass of uranium. Such a straightforward exercise does not require any formal mathematical treatment. Many questions concerning mass are not so straightforward, however, and require some mathematical manipulations.

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 **4.12.1**). 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:

$$\frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \quad \text{and} \quad \frac{26.98 \text{ g Al}}{1 \text{ mol Al}}$$

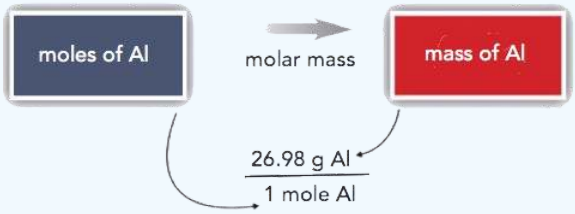
The first conversion factor can be used to convert from mass to moles, and the second converts from moles to mass. Both can be used to solve problems that would be hard to do “by eye.”

Example 4.12.1

What is the mass of 3.987 mol of Al?

Solution

The first step in a conversion problem is to decide what conversion factor to use. Because we are starting with mole units, we want a conversion factor that will cancel the mole unit and introduce the unit for mass in the numerator. Therefore, we should use the $\frac{26.98 \text{ g Al}}{1 \text{ mol Al}}$ conversion factor. We start with the given quantity and multiply by the conversion factor:



$$3.987 \text{ mol Al} \times \frac{26.98 \text{ g Al}}{1 \text{ mol Al}}$$

Note that the mol units cancel algebraically. (The quantity 3.987 mol is understood to be in the numerator of a fraction that has 1 in the unwritten denominator.) Canceling and solving gives

$$3.987 \text{ mol Al} \times \frac{26.98 \text{ g Al}}{1 \text{ mol Al}} = 107.6 \text{ g Al}$$

Our final answer is expressed to four significant figures.

Exercise 4.12.1

How many moles are present in 100.0 g of Al? (Hint: you will have to use the other conversion factor we obtained for aluminum.)

Answer

$$100.0\ \text{g Al} \times \frac{1\ \text{mol Al}}{26.98\ \text{g Al}} = 3.706\ \text{mol Al}$$

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 **4.12.1** is a chart for determining what conversion factor is needed, and Figure **4.12.2** is a flow diagram for the steps needed to perform a conversion.

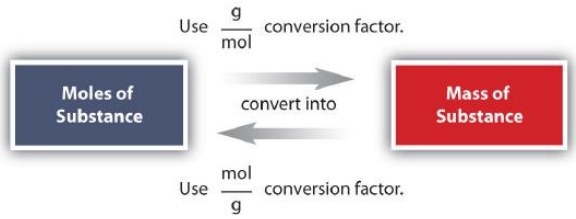


Figure **4.12.1** A Simple Flowchart for Converting between Mass and Moles of a Substance. It takes one mathematical step to convert from moles to mass or from mass to moles.

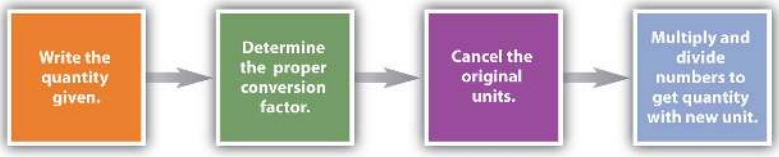


Figure **4.12.2** A Flowchart Illustrating the Steps in Performing a Unit Conversion. When performing many unit conversions, the same logical steps can be taken.

Example 4.12.2

A biochemist needs 0.00655 mol of bilirubin ($C_{33}H_{36}N_4O_6$) for an experiment. How many grams of bilirubin will that be?

Solution

To convert from moles to mass, we need the molar mass of bilirubin, which we can determine from its chemical formula:

Solutions to Example 6.3.2

33 C molar mass:	33 × 12.01 g =	396.33 g
36 H molar mass:	36 × 1.01 g =	36.36 g
4 N molar mass:	4 × 14.01 g =	56.04 g
6 O molar mass:	6 × 16.00 g =	96.00 g
Total:		584.73 g

The molar mass of bilirubin is 584.73 g. Using the relationship

1 mol bilirubin = 584.73 g bilirubin

we can construct the appropriate conversion factor for determining how many grams there are in 0.00655 mol. Following the steps from Figure **4.12.2**:

$$0.00655\ \text{mol bilirubin} \times \frac{584.73\ \text{g bilirubin}}{\text{mol bilirubin}} = 3.83\ \text{g bilirubin}$$

The mol bilirubin unit cancels. The biochemist needs 3.83 g of bilirubin.

Exercise 4.12.2

A chemist needs 457.8 g of $KMnO_4$ to make a solution. How many moles of $KMnO_4$ is that?

Answer

$$457.8\ \text{g KMnO}_4 \times \frac{1\ \text{mol KMnO}_4}{158.04\ \text{g KMnO}_4} = 2.897\ \text{mol KMnO}_4$$

To Your Health: Minerals

For our bodies to function properly, we need to ingest certain substances from our diets. Among our dietary needs are minerals, the noncarbon elements our body uses for a variety of functions, such developing bone or ensuring proper nerve transmission. The US Department of Agriculture has established some recommendations for the RDIs of various minerals. The accompanying table lists the RDIs for minerals, both in mass and moles, assuming a 2,000-calorie daily diet.

Table **4.12.1**: Essential Minerals and their Composition in Humans

Mineral	Male (age 19–30 y)		Female (age 19–30 y)	
Ca	1,000 mg	0.025 mol	1,000 mg	0.025 mol
Cr	35 µg	6.7×10^{-7} mol	25 µg	4.8×10^{-7} mol
Cu	900 µg	1.4×10^{-5} mol	900 µg	1.4×10^{-5} mol
F	4 mg	2.1×10^{-4} mol	3 mg	1.5×10^{-4} mol
I	150 µg	1.2×10^{-6} mol	150 µg	1.2×10^{-6} mol
Fe	8 mg	1.4×10^{-4} mol	18 mg	3.2×10^{-4} mol
K	3,500 mg	9.0×10^{-2} mol	3,500 mg	9.0×10^{-2} mol
Mg	400 mg	1.6×10^{-2} mol	310 mg	1.3×10^{-2} mol
Mn	2.3 mg	4.2×10^{-5} mol	1.8 mg	3.3×10^{-5} mol
Mo	45 mg	4.7×10^{-7} mol	45 mg	4.7×10^{-7} mol
Na	2,400 mg	1.0×10^{-1} mol	2,400 mg	1.0×10^{-1} mol
P	700 mg	2.3×10^{-2} mol	700 mg	2.3×10^{-2} mol
Se	55 µg	7.0×10^{-7} mol	55 µg	7.0×10^{-7} mol
Zn	11 mg	1.7×10^{-4} mol	8 mg	1.2×10^{-4} mol

Table **4.12.1** illustrates several things. First, the needs of men and women for some minerals are different. The extreme case is for iron; women need over twice as much as men do. In all other cases where there is a different RDI, men need more than women.

Second, the amounts of the various minerals needed on a daily basis vary widely—both on a mass scale and a molar scale. The average person needs 0.1 mol of Na a day, which is about 2.5 g. On the other hand, a person needs only about 25–35 µg of Cr per day, which is under one millionth of a mole. As small as this amount is, a deficiency of chromium in the diet can lead to diabetes-like symptoms or neurological problems, especially in the extremities (hands and feet). For some minerals, the body does not require much to keep itself operating properly.

Although a properly balanced diet will provide all the necessary minerals, some people take dietary supplements. However, too much of a good thing, even minerals, is not good. Exposure to too much chromium, for example, causes a skin irritation, and certain forms of chromium are known to cause cancer (as presented in the movie *Erin Brockovich*).

Key Takeaway

- It is possible to convert between moles of material and mass of material.

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4.13: Percent Composition



Figure **4.13.1** (CC BY-NC 3.0; Joy Sheng via CK-12 Foundation)

Is there anything healthy in this jar?

Packaged foods that you eat typically have nutritional information provided on the label. The label on a jar of peanut butter (shown above) reveals that one serving size is considered to be $32\ \text{g}$. The label also gives the masses of various types of compounds that are present in each serving. One serving contains $7\ \text{g}$ of protein, $15\ \text{g}$ of fat, and $3\ \text{g}$ of sugar. By calculating the fraction of protein, fat, or sugar in one serving size of peanut butter and converting to percent values, we can determine the composition of peanut butter on a percent by mass basis.

Percent Composition

Chemists often need to know what elements are present in a compound and in what percentage. The **percent composition** is the percent by mass of each element in a compound. It is calculated in a similar way to what was just indicated for the peanut butter.

$$\%\ \text{by mass} = \frac{\text{mass of element}}{\text{mass of compound}} \times 100\%$$

Percent Composition from Mass Data

The sample problem below shows the calculation of the percent composition of a compound based on mass data.

Example 4.13.1: Percent Composition from Mass

A certain newly synthesized compound is known to contain the elements zinc and oxygen. When a $20.00\ \text{g}$ sample of the compound is decomposed, $16.07\ \text{g}$ of zinc remains. Determine the percent composition of the compound.

Solution

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

Known

- Mass of compound $= 20.00\ \text{g}$
- Mass of $\text{Zn} = 16.07\ \text{g}$

Unknown

- Percent $\text{Zn} = ?\%$
- Percent $\text{O} = ?\%$

Subtract to find the mass of oxygen in the compound. Divide each element's mass by the mass of the compound to find the percent by mass.

Step 2: Calculate.

$$\text{Mass of oxygen} = 20.00\ \text{g} - 16.07\ \text{g} = 3.93\ \text{g O}$$

$$\%\ \text{Zn} = \frac{16.07\ \text{g Zn}}{20.00\ \text{g}} \times 100\% = 80.35\%\ \text{Zn}$$

$$\%\ \text{O} = \frac{3.93\ \text{g O}}{20.00\ \text{g}} \times 100\% = 19.65\%\ \text{O}$$

Step 3: Think about your result.

The calculations make sense because the sum of the two percentages adds up to 100%. By mass, the compound is mostly zinc.

Percent Composition from a Chemical Formula

The percent composition of a compound can also be determined from the formula of the compound. The subscripts in the formula are first used to calculate the mass of each element in one mole of the compound. That is divided by the molar mass of the compound and multiplied by 100%.

$$\%\text{ by mass} = \frac{\text{mass of element in 1 mol}}{\text{molar mass of compound}} \times 100\%$$

The percent composition of a given compound is always the same as long as the compound is pure.

Example 4.13.2: Percent Composition from Chemical Formula

Dichlorineheptoxide (Cl_2O_7) is a highly reactive compound used in some organic synthesis reactions. Calculate the percent composition of dichlorineheptoxide.

Solution

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

Known

- Mass of Cl in $1\text{ mol } Cl_2O_7 = 70.90\text{ g}$
- Mass of O in $1\text{ mol } Cl_2O_7 = 112.00\text{ g}$
- Molar mass of $Cl_2O_7 = 182.90\text{ g/mol}$

Unknown

- Percent Cl $=?\%$
- Percent O $=?\%$

Calculate the percent by mass of each element by dividing the mass of that element in 1 mole of the compound by the molar mass of the compound and multiplying by 100%.

Step 2: Calculate.

$$\%\text{Cl} = \frac{70.90\text{ g Cl}}{182.90\text{ g}} \times 100\% = 38.76\%\text{ Cl}$$

$$\%\text{ O} = \frac{112.00\text{ g O}}{182.90\text{ g}} \times 100\% = 61.24\%\text{ O}$$

Step 3: Think about your result.

The percentages add up to 100%.

Percent composition can also be used to determine the mass of a certain element that is contained in any mass of a compound. In the previous sample problem, it was found that the percent composition of dichlorine heptoxide is 38.76% Cl and 61.24% O. Suppose that you need 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.



Science Friday: Stained Glass Conservation

Stained glass from the Middle Ages is often hundreds of years old. Unfortunately, many of these relics are in need of cleaning and maintenance. In this video by Science Friday, conservator Mary Higgins discusses the methods used to protect the stained glass.



Summary

- Processes are described for calculating the percent composition of a material based on mass or on chemical composition.

Review

1. What is the formula for calculating percent composition?
2. What information do you need to calculate percent composition by mass?
3. What do subscripts in a chemical formula tell you?

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4.14: Percent of Water in a Hydrate



Figure 4.14.1 (Public Domain; Doug Smith (Wikimedia: Xsmith) via Wikipedia)

Why does the color change?

If you look at a typical bottle of copper sulfate, it will be a bluish-green. If someone were to tell you that copper sulfate is white, you likely would not believe them. However, it turns out that you are both right; it just depends on the copper sulfate. Your blue-green copper sulfate has several water molecules attached to it, while your friend's copper sulfate is anhydrous (no water attached). Why the difference? The water molecules interact with some of the d electrons in the copper ion and produce the color. When the water is removed, the electron configuration changes and the color disappears.

Percent of Water in a Hydrate

Many ionic compounds naturally contain water as part of the crystal lattice structure. A **hydrate** is a compound that has one or more water molecules bound to each formula unit. Ionic compounds that contain a transition metal are often highly colored. Interestingly, it is common for the hydrated form of a compound to be of a different color than the **anhydrous** form, which has no water in its structure. A hydrate can usually be converted to the anhydrous compound by heating. For example, the anhydrous compound cobalt (II) chloride is blue, while the hydrate is a distinctive magenta color.

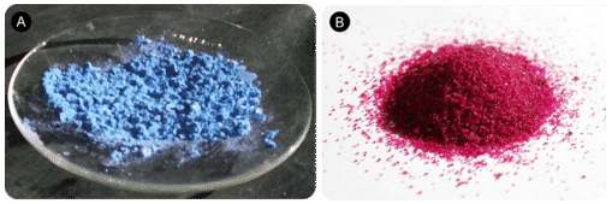


Figure 4.14.2: On the left is anhydrous cobalt (II) chloride, $CoCl_2$. On the right is the hydrated form of the compound called cobalt (II) chloride hexahydrate, $CoCl_2 \cdot 6H_2O$. (Public Domain; (A) Martin Walker (Wikimedia: Walkerma); (B) Ben Mills (Wikimedia: Benjah-bmm27) via (A) http://commons.wikimedia.org/wiki/File:Cobalt%2528II%2529_chloride.jpg; (B) http://commons.wikimedia.org/wiki/File:Cobalt%2528II%2529-chloride-hexahydrate-sample.jpg)

The hydrated form of cobalt (II) chloride contains six water molecules in each formula unit. The name of the compound is cobalt (II) chloride hexahydrate and its formula is $CoCl_2 \cdot 6H_2O$. The formula for water is set apart at the end of the formula with a dot, followed by a coefficient that represents the number of water molecules per formula unit.

It is useful to know the percent of water contained within a hydrate. The sample problem below demonstrates the procedure.

Example 4.14.1: Percent of Water in a Hydrate

Find the percent water in cobalt (II) chloride hexahydrate, $CoCl_2 \cdot 6H_2O$.

Solution

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

The mass of water in the hydrate is the coefficient (6) multiplied by the molar mass of H_2O. The molar mass of the hydrate is the molar mass of the $CoCl_2$ plus the mass of water.

Known

- Mass of H_2O in 1 mol hydrate = 108.12 g

- Mass of $\mathbf{H_2O}$ in 1 mol hydrate $= \mathbf{108.12\ g}$
- Molar mass of hydrate $= \mathbf{237.95\ g/mol}$

Unknown

- percent H_2O = ?%

Calculate the percent by mass of water by dividing the mass of $\mathbf{H_2O}$ in 1 mole of the hydrate by the molar mass of the hydrate and multiplying by $\mathbf{100\%}$.

Step 2: Calculate.

$$\mathbf{\%\ H_2O = \frac{108.12\ g\ H_2O}{237.95\ g} \times 100\% = 45.44\%\ H_2O}$$

Step 3: Think about your result.

Nearly half of the mass of the hydrate is composed of water molecules within the crystal.



Summary

- The process of calculating the percent water in a hydrate is described.

Review

1. What is a hydrate?
2. How can you convert a hydrate to an anhydrous compound?
3. What does hexahydrate mean?

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CHAPTER OVERVIEW

5: Chemical Calculations 2

5.1: Everyday Stoichiometry
5.2: Mole Ratios
5.3: Quantitative Relationships Based on Chemical Equations
5.4: Mole-Mole Relationships in Chemical Reactions
5.5: Mole-Mass and Mass-Mass Problems
5.6: Mass-Volume and Volume-Mass Stoichiometry
5.7: Concentration
5.8: Limiting Reactant
5.9: Determining the Limiting Reactant
5.10: Theoretical Yield and Percent Yield
5.11: Percent Error

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5.1: Everyday Stoichiometry



Figure 5.1.1 (Public Domain; User:Skatebiker/Wikipedia via Wikipedia)

How much equipment do you need for an experiment?

You are in charge of setting out the lab equipment for a chemistry experiment. If you have twenty students in the lab (and they will be working in teams of two) and the experiment calls for three beakers and two test tubes, how much glassware do you need to set out? Figuring this out involves a type of balanced equation and the sort of calculations that you would do for a chemical reaction.

Everyday Stoichiometry

You have learned about chemical equations and the techniques used in order to balance them. Chemists use balanced equations to allow them to manipulate chemical reactions in a quantitative manner. Before we look at a chemical reaction, let's consider an equation for the ideal ham sandwich.



Figure 5.1.2: The ideal ham sandwich. (CK-12 Curriculum Materials license; CK-12 Foundation via CK-12 Foundation)

Our ham sandwich is composed of 2 slices of ham (**H**), a slice of cheese (**C**), a slice of tomato (**T**), 5 pickles (**P**), and 2 slices of bread (**B**). The equation for our sandwich is:

$$\mathbf{2H + C + T + 5P + 2B \rightarrow H_2CTP_5B_2}$$

Now let us suppose that you are having some friends over and need to make five ham sandwiches. How much of each sandwich ingredient do you need? You take the number of each ingredient required for one sandwich (its coefficient in the above equation) and multiply by five. Using ham and cheese as examples, and using a conversion factor, you can calculate:

$$\mathbf{5H_2CTP_5B_2} \times \frac{\mathbf{2\,H}}{\mathbf{1H_2CTP_5B_2}} = \mathbf{10\,H}$$

$$\mathbf{5H_2CTP_5B_2} \times \frac{\mathbf{1C}}{\mathbf{1H_2CTP_5B_2}} = \mathbf{5\,C}$$

The conversion factors contain the coefficient of each specific ingredient as the numerator and the formula of one sandwich as the denominator. The result is what you would expect. In order to make five ham sandwiches, you need 10 slices of ham and 5 slices of cheese.

This type of calculation demonstrates the use of stoichiometry. **Stoichiometry** is the calculation of the amount of substances in a chemical reaction from the balanced equation. The sample problem below is another stoichiometry problem involving ingredients of the ideal ham sandwich.

Example 5.1.1: Ham Sandwich Stoichiometry

Kim looks in the refrigerator and finds that she has 8 slices of ham. In order to make as many sandwiches as possible, how many pickles does she need? Use the equation above.

Solution

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

- Have 8 ham slices (H)
- $2\,\mathrm{H} = 5\,\mathrm{P}$ (conversion factor)

Unknown

- How many pickles (P) needed?

The coefficients for the two reactants (ingredients) are used to make a conversion factor between ham slices and pickles.

Step 2: Solve.

$$8\,\mathrm{H} \times \frac{5\,\mathrm{P}}{2\,\mathrm{H}} = 20\,\mathrm{P}$$

Since 5 pickles combine with 2 ham slices in each sandwich, 20 pickles are needed to fully combine with 8 ham slices.

Step 3: Think about your result.

The 8 ham slices will make 4 ham sandwiches. With 5 pickles per sandwich, the 20 pickles are used in the 4 sandwiches.

Summary

- An example of everyday stoichiometry is given.

Review

1. A smoothie contains 1 banana (B), 4 strawberries (St), 1 container of yogurt (Y), and 3 ice cubes (Ic). Write a balanced equation to describe the relationship.
2. Write a conversion factor to show the relationship between the number of ice cubes and the number of smoothies produced.
3. How many strawberries would you need to make 12 smoothies?

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5.2: Mole Ratios



Figure 5.2.1 (Public Domain; User:Ilemme/Wikipedia via Commons Wikimedia, File:Col 03 scup porch chairs.JPG [commons.wikimedia.org])

What does this porch need?

You want to add some sections to the porch seen above. Before you go to the hardware store to buy lumber, you need to determine the unit composition (the material between two large uprights). You count how many posts, how many boards, how many rails – then you decide how many sections you want to add before you calculate the amount of building material needed for your porch expansion.

Mole Ratios

Stoichiometry problems can be characterized by two things: (1) the information *given* in the problem, and (2) the information that is to be solved for, referred to as the *unknown*. The given and the unknown may both be reactants, both be products, or one may be a reactant while the other is a product. The amounts of the substances can be expressed in moles. However, in a laboratory situation, it is common to determine the amount of a substance by finding its mass in grams. The amount of a gaseous substance may be expressed by its volume. In this concept, we will focus on the type of problem where both the given and the unknown quantities are expressed in moles.

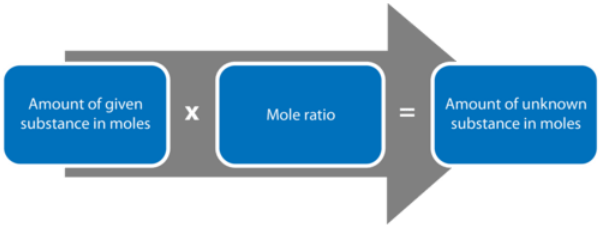


Figure 5.2.2: Mole ratio relationship. (CC BY-NC 3.0; Christopher Auyeung via CK-12 Foundation)

Chemical equations express the amounts of reactants and products in a reaction. The coefficients of a balanced equation can represent either the number of molecules or the number of moles of each substance. The production of ammonia (NH_3) from nitrogen and hydrogen gases is an important industrial reaction called the Haber process, after German chemist Fritz Haber.

$$N_2\,(g) + 3H_2\,(g) \rightarrow 2NH_3\,(g)$$

The balanced equation can be analyzed in several ways, as shown in the figure below.

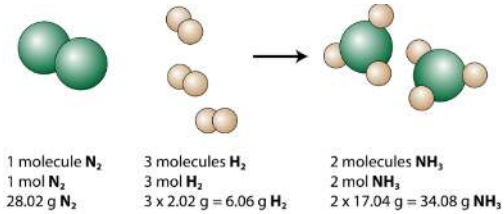


Figure 5.2.3: This representation of the production of ammonia from nitrogen and hydrogen shows several ways to interpret the quantitative information of a chemical reaction. (CC BY-NC 3.0; Christopher Auyeung via CK-12 Foundation)

We see that 1 molecule of nitrogen reacts with 3 molecules of hydrogen to form 2 molecules of ammonia. This is the smallest possible relative amount of the reactants and products. To consider larger relative amounts, each coefficient can be multiplied by the same number. For example, 10 molecules of nitrogen would react with 30 molecules of hydrogen to produce 20 molecules of ammonia.

The most useful quantity for counting particles is the mole. So if each coefficient is multiplied by a mole, the balanced chemical equation tells us that 1 mole of nitrogen reacts with 3 moles of hydrogen to produce 2 moles of ammonia. This is the conventional way to interpret any balanced chemical equation.

Finally, if each mole quantity is converted to grams by using the molar mass, we can see that the law of conservation of mass is followed. $\mathbf{1\ mol}$ of nitrogen has a mass of $\mathbf{28.02\ g}$, while $\mathbf{3\ mol}$ of hydrogen has a mass of $\mathbf{6.06\ g}$, and $\mathbf{2\ mol}$ of ammonia has a mass of $\mathbf{34.08\ g}$.

$$\mathbf{28.02\ g\ N_2 + 6.06\ g\ H_2 \rightarrow 34.08\ g\ NH_3}$$

Mass and the number of atoms must be conserved in any chemical reaction. The number of molecules is not necessarily conserved.



Figure 5.2.4: An apparatus for running the Haber process. (Public Domain; User: JGvBerkel/Wikimedia Commons via Commons Wikimedia, Haber Ammonia [commons.wikimedia.org])

A **mole ratio** is a conversion factor that relates the amounts in moles of any two substances in a chemical reaction. The numbers in a conversion factor come from the coefficients of the balanced chemical equation. The following six mole ratios can be written for the ammonia forming reaction above.

$$\frac{\mathbf{1\ mol\ N_2}}{\mathbf{3\ mol\ H_2}} \quad or \quad \frac{\mathbf{3\ mol\ H_2}}{\mathbf{1\ mol\ N_2}}$$
$$\frac{\mathbf{1\ mol\ N_2}}{\mathbf{2\ mol\ NH_3}} \quad or \quad \frac{\mathbf{2\ mol\ NH_3}}{\mathbf{1\ mol\ N_2}}$$
$$\frac{\mathbf{3\ mol\ H_2}}{\mathbf{2\ mol\ NH_3}} \quad or \quad \frac{\mathbf{2\ mol\ NH_3}}{\mathbf{3\ mol\ H_2}}$$

In a mole ratio problem, the given substance, expressed in moles, is written first. The appropriate conversion factor is chosen in order to convert from moles of the given substance to moles of the unknown.

Example 5.2.1: Mole Ratio

How many moles of ammonia are produced if 4.20 moles of hydrogen are reacted with an excess of nitrogen?

Solution

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

Known

- given: H_2 = 4.20 mol

Unknown

- mol of NH_3

The conversion is from $\mathbf{mol\ H_2}$ to $\mathbf{mol\ NH_3}$. The problem states that there is an excess of nitrogen, so we do not need to be concerned with any mole ratio involving $\mathbf{N_2}$. Choose the conversion factor that has the $\mathbf{NH_3}$ in the numerator and the $\mathbf{H_2}$ in the denominator.

Step 2: Solve.

$$4.20\ \text{mol H}_2 \times \frac{2\ \text{mol NH}_3}{3\ \text{mol H}_2} = 2.80\ \text{mol NH}_3$$

The reaction of $\mathbf{4.20\ mol}$ of hydrogen with excess nitrogen produces $\mathbf{2.80\ mol}$ of ammonia.

Step 3: Think about your result.

The result corresponds to the 3:2 ratio of hydrogen to ammonia from the balanced equation.



Summary

- Mole ratios allow comparison of the amounts of any two materials in a balanced equation.
- Calculations can be made to predict how much product can be obtained from a given number of moles of reactant.

Review

- If a reactant is in excess, why do we not worry about the mole ratios involving that reactant?
- What is the mole ratio of H to N in the ammonia molecule?
- The formula for ethanol is CH_3CH_2OH. What is the mole ratio of H to C in this molecule?

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5.3: Quantitative Relationships Based on Chemical Equations

Learning Objectives

- To calculate the amount of one substance that will react with or be produced from a given amount of another substance.

A balanced chemical equation not only describes some of the chemical properties of substances—by showing us what substances react with what other substances to make what products—but also shows numerical relationships between the reactants and the products. The study of these numerical relationships is called stoichiometry. The stoichiometry of chemical equations revolves around the coefficients in the balanced chemical equation because these coefficients determine the molecular ratio in which reactants react and products are made.

> *The word stoichiometry is pronounced "stow-eh-key-OM-et-tree." It is of mixed Greek and English origins, meaning roughly "measure of an element."*

Looking Closer: Stoichiometry in Cooking

Let us consider a stoichiometry analogy from the kitchen. A recipe that makes 1 dozen biscuits needs 2 cups of flour, 1 egg, 4 tablespoons of shortening, 1 teaspoon of salt, 1 teaspoon of baking soda, and 1 cup of milk. If we were to write this as a chemical equation, we would write

$$\text{2 c flour + 1 egg + 4 tbsp shortening + 1 tsp salt + 1 tsp baking soda + 1 c milk} \rightarrow \text{12 biscuits}$$

(Unlike true chemical reactions, this one has all 1 coefficients written explicitly—partly because of the many different units here.) This equation gives us ratios of how much of what reactants are needed to make how much of what product. Two cups of flour, when combined with the proper amounts of the other ingredients, will yield 12 biscuits. One teaspoon of baking soda (when also combined with the right amounts of the other ingredients) will make 12 biscuits. One egg must be combined with 1 cup of milk to yield the product food. Other relationships can also be expressed.

We can use the ratios we derive from the equation for predictive purposes. For instance, if we have 4 cups of flour, how many biscuits can we make if we have enough of the other ingredients? It should be apparent that we can make a double recipe of 24 biscuits.

But how would we find this answer formally, that is, mathematically? We would set up a conversion factor, much like we did in Chapter 1. Because 2 cups of flour make 12 biscuits, we can set up an equivalency ratio:

$$\frac{\text{12 biscuits}}{\text{2 c flour}}$$

We then can use this ratio in a formal conversion of flour to biscuits:

$$\text{4 c flour} \times \frac{\text{12 biscuits}}{\text{2 c flour}} = \text{24 biscuits}$$

Similarly, by constructing similar ratios, we can determine how many biscuits we can make from any amount of ingredient. When you are doubling or halving a recipe, you are doing a type of stoichiometry. Applying these ideas to chemical reactions should not be difficult if you use recipes when you cook.



A recipe shows how much of each ingredient is needed for the proper reaction to take place. (CC BY-SA 3.0 Unported; Peng via Wikipedia)

Consider the following balanced chemical equation:

$$2\,C_2H_2 + 5\,O_2 \rightarrow 4\,CO_2 + 2\,H_2O \tag{5.3.1}$$

The coefficients on the chemical formulas give the ratios in which the reactants combine and the products form. Thus, we can make the following statements and construct the following ratios:

Table uses a statement from the balanced chemical reaction to show ratios and inverse ratios.

Statement from the Balanced Chemical Reaction	Ratio	Inverse Ratio
two C_2H_2 molecules react with five O_2 molecules	$\frac{2C_2H_2}{5O_2}$	$\frac{5O_2}{2C_2H_2}$
two C_2H_2 molecules react to make four CO_2 molecules	$\frac{2C_2H_2}{4CO_2}$	$\frac{4CO_2}{2C_2H_2}$
five O_2 molecules react to make two H_2O molecules	$\frac{5O_2}{2H_2O}$	$\frac{2H_2O}{5O_2}$
four CO_2 molecules are made at the same time as two H_2O molecules	$\frac{2H_2O}{4CO_2}$	$\frac{4CO_2}{2H_2O}$

Other relationships are possible; in fact, 12 different conversion factors can be constructed from this balanced chemical equation. In each ratio, the unit is assumed to be molecules because that is how we are interpreting the chemical equation.

Any of these fractions can be used as a conversion factor to relate an amount of one substance to an amount of another substance. For example, suppose we want to know how many CO_2 molecules are formed when 26 molecules of C_2H_2 are reacted. As usual with a conversion problem, we start with the amount we are given—$26C_2H_2$—and multiply it by a conversion factor that cancels out our original unit and introduces the unit we are converting to—in this case, CO_2. That conversion factor is $\frac{4CO_2}{2C_2H_2}$, which is composed of terms that come directly from the balanced chemical equation. Thus, we have

$$26C_2H_2 \times \frac{4CO_2}{2C_2H_2}$$

The molecules of C_2H_2 cancel, and we are left with molecules of CO_2. Multiplying through, we get

$$26C_2H_2 \times \frac{4CO_2}{2C_2H_2} = 52CO_2$$

Thus, 52 molecules of CO_2 are formed.

This application of stoichiometry is extremely powerful in its predictive ability, as long as we begin with a balanced chemical equation. Without a balanced chemical equation, the predictions made by simple stoichiometric calculations will be incorrect.

Example 5.3.1

Start with this balanced chemical equation.

$$\mathbf{KMnO_4 + 8\,HCl + 5\,FeCl_2 \longrightarrow 5\,FeCl_3 + MnCl_2 + 4\,H_2O + KCl}$$

a. Verify that the equation is indeed balanced.
b. Give 2 ratios that give the relationship between $\mathbf{HCl}$ and $\mathbf{FeCl_3}$.

Solution a

Each side has 1 K atom and 1 Mn atom. The 8 molecules of HCl yield 8 H atoms, and the 4 molecules of H_2O also yield 8 H atoms, so the H atoms are balanced. The Fe atoms are balanced, as we count 5 Fe atoms from 5 $FeCl_2$ reactants and 5 $FeCl_3$ products. As for Cl, on the reactant side, there are 8 Cl atoms from HCl and 10 Cl atoms from the 5 $FeCl_2$ formula units, for a total of 18 Cl atoms. On the product side, there are 15 Cl atoms from the 5 $FeCl_3$ formula units, 2 from the $MnCl_2$ formula unit, and 1 from the KCl formula unit. This is a total of 18 Cl atoms in the products, so the Cl atoms are balanced. All the elements are balanced, so the entire chemical equation is balanced.

Solution b

Because the balanced chemical equation tells us that 8 HCl molecules react to make 5 $FeCl_3$ formula units, we have the following 2 ratios: $\mathbf{\frac{8HCl}{5FeCl_3}}$ and $\mathbf{\frac{5FeCl_3}{8HCl}}$. There are a total of 42 possible ratios. Can you find the other 40 relationships?

Exercise 5.3.1

Start with this balanced chemical equation.

$$\mathbf{2KMnO_4 + 3CH_2{=}CH_2 + 4H_2O \rightarrow 2MnO_2 + 3HOCH_2CH_2OH + 2KOH}$$

a. Verify that the equation is balanced.
b. Give 2 ratios that give the relationship between $KMnO_4$ and $CH_2{=}CH_2$. (A total of 30 relationships can be constructed from this chemical equation. Can you find the other 28?)

Answer a:

Each side has 2 K atoms and 2 Mn atoms. On the reactant side, 3 $CH_2{=}CH_2$ yield 6 C atoms and on the product side, 3 $HOCH_2CH_2OH$ also yield 6 C atoms, so the C atoms are balanced. There are 20 H atoms on the reactants side: 12 H atoms from 3 $CH_2{=}CH_2$ and 8 H atoms from 4 H_2O. On the product side, there are also 20 H atoms: 18 H atoms from 3 $HOCH_2CH_2OH$ and 2 H atoms from 2 KOH. So, the H atoms are balanced. As for O, on the reactant side, there are 8 O atoms from 2 $KMnO_4$ and 4 O atoms from 4 H_2O, for a total of 12 O atoms. On the product side, there are 4 O atoms from the 2 MnO_2 formula units, 6 O atoms from 3 $HOCH_2CH_2OH$, and 2 O atoms from the 2 KOH formula units. This is a total of 12 O atoms in the products, so the O atoms are balanced. All the elements are balanced, so the entire chemical equation is balanced.

Answer b:

Because the balanced chemical equation tells us that 2 $KMnO_4$ formula units react with 3 $CH_2{=}CH_2$ molecules, we have the following 2 ratios: $\mathbf{\frac{2KMnO_4}{3CH_2{=}CH_2}}$ and $\mathbf{\frac{3CH_2{=}CH_2}{2KMnO_4}}$. There are a total of 30 possible ratios. Can you find the other 28 relationships?

Key Takeaway

The coefficients in a balanced chemical equation give the ratios in which molecules of substances react and are produced in a chemical reaction.

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5.4: Mole-Mole Relationships in Chemical Reactions

Learning Objectives

- To use a balanced chemical reaction to determine molar relationships between the substances.

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

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

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

$$4\,H_2 + 2\,O_2 \longrightarrow 4\,H_2O$$

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

$$22\,H_2 + 11\,O_2 \longrightarrow 22\,H_2O$$

because 22:11:22 also reduces to 2:1:2.

Suppose we want to use larger numbers. Consider the following coefficients:

$$12.044 \times 10^{23}\ H_2 + 6.022 \times 10^{23}\ O_2 \rightarrow 12.044 \times 10^{23}\ H_2O$$

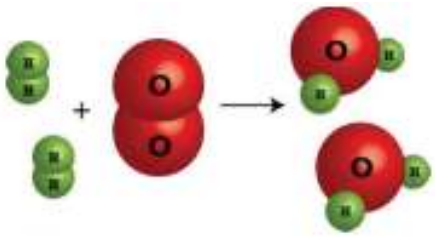
These coefficients also have the ratio 2:1:2 (check it and see), so this equation is balanced. But 6.022×10^{23} is 1 mol, while 12.044×10^{23} is 2 mol (and the number is written that way to make this more obvious), so we can simplify this version of the equation by writing it as

$$2\ \text{mol}\ \ H_2 + 1\ \ \text{mol}\ \ O_2 \longrightarrow 2\ \text{mol}\ \ H_2O$$

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

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

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.”



2 molecules H_2 1 molecule O_2 2 molecules H_2O

2 moles H_2 1 mole O_2 2 moles H_2O

2 x 2.02 g=4.04 g H_2 32.0 g O_2 2 x 18.02 g=36.04 g H_2O

Figure **5.4.1**: This representation of the production of water from oxygen and hydrogen show several ways to interpret the quantitative information of a chemical reaction.

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*.** The ratio of coefficients in a balanced chemical equation, used in computations relating amounts of reactants and products is called the **stoichiometric factor.**

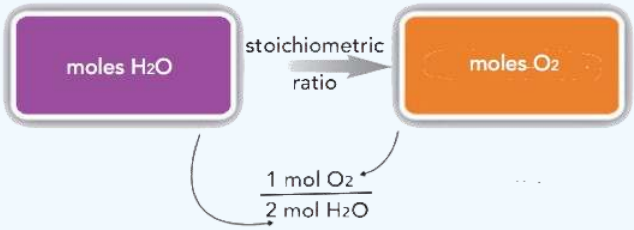
Example 5.4.1

How many moles of oxygen react with hydrogen to produce 27.6 mol of H_2O? The balanced equation is as follows:

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

Solution

Because we are dealing with quantities of H_2O and O_2, we will use the **stoichiometric ratio** that relates those two substances. Because we are given an amount of H_2O and want to determine an amount of O_2, we will use the ratio that has H_2O in the denominator (so it cancels) and O_2 in the numerator (so it is introduced in the answer). Thus,



$$27.6\ \text{mol}\ H_2O \times \frac{1\ \text{mol}\ O_2}{2\ \text{mol}\ H_2O} = 13.8\ \text{mol}\ O_2$$

To produce 27.6 mol of H_2O, 13.8 mol of O_2 react.

Exercise 5.4.1

Using $2H_2 + O_2 \rightarrow 2H_2O$, how many moles of hydrogen react with 3.07 mol of oxygen to produce H_2O?

Answer

$$3.07\ \text{mol}\ O_2 \times \frac{2\ \text{mol}\ H_2}{1\ \text{mol}\ O_2} = 6.14\ \text{mol}\ H_2$$

Key Takeaway

- The balanced chemical reaction can be used to determine molar relationships between substances.

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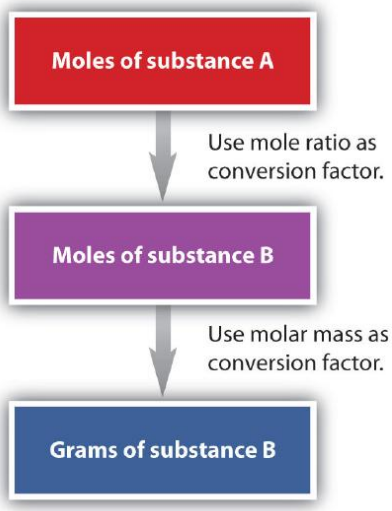
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5.5: Mole-Mass and Mass-Mass Problems

Learning Objectives

- To convert from mass or moles of one substance to mass or moles of another substance in a chemical reaction.

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

$$\mathrm{Fe_2O_3 + 3\,SO_3 \rightarrow Fe_2(SO_4)_3}$$

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.

The first step resembles the exercises we did in Section 6.4. As usual, we start with the quantity we were given:

$$\mathrm{3.59\ mol\ Fe_2O_3 \times \frac{3\ mol\ SO_3}{1\ mol\ Fe_2O_3} = 10.77\ mol\ SO_3}$$

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:

$$\mathrm{10.77\ mol\ SO_3 \times \frac{80.07\ g\ SO_3}{1\ mol\ SO_3} = 862.4\ g\ SO_3}$$

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:



$$3.59 \text{ mol } Fe_2O_3 \times \underbrace{\frac{3 \text{ mol } SO_3}{1 \text{ mol } Fe_2O_3}}_{\text{converts to moles of } SO_3} \times \underbrace{\frac{80.07 \text{ g } SO_3}{1 \text{ mol } SO_3}}_{\text{converts to grams of } SO_3} = 862.4 \text{ g } SO_3$$

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 5.5.1

How many grams of CO_2 are produced if 2.09 mol of HCl are reacted according to this balanced chemical equation?

$$CaCO_3 + 2\,HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

Solution

Our strategy will be to convert from moles of HCl to moles of CO_2 and then from moles of CO_2 to grams of CO_2. We will need the molar mass of CO_2, which is 44.01 g/mol. Performing these two conversions in a single-line gives 46.0 g of CO_2:

$$2.09 \text{ mol } HCl \times \underbrace{\frac{1 \text{ mol } CO_2}{2 \text{ mol } HCl}}_{\text{from the coefficients of the balanced equation}} \times \frac{44.01 \text{ g } CO_2}{1 \text{ mol } CO_2} = 46.0 \text{ g } CO_2$$

The molar ratio between CO_2 and HCl comes from the balanced chemical equation.

Exercise

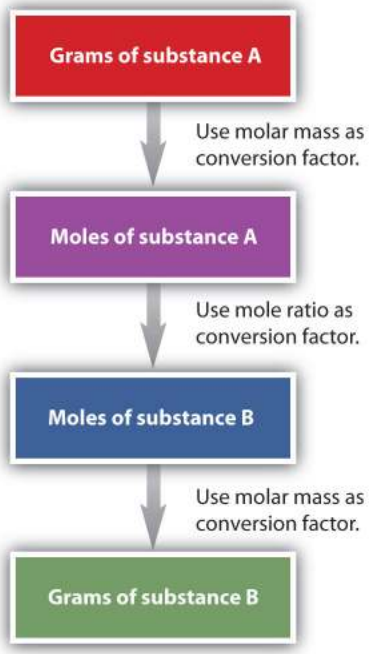
How many grams of glucose ($C_6H_{12}O_6$) are produced if 17.3 mol of H_2O are reacted according to this balanced chemical equation?

$$6\,CO_2 + 6\,H_2O \rightarrow C_6H_{12}O_6 + 6\,O_2$$

Answer

$$17.3 \text{ mol } H_2O \times \frac{1 \text{ mol } C_6H_{12}O_6}{6 \text{ mol } H_2O} \times \frac{180.18 \text{ g } C_6H_{12}O_6}{1 \text{ mol } C_6H_{12}O_6} = 520 \text{ g } C_6H_{12}O_6$$

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 5.5.2: Chlorination of Carbon

Methane can react with elemental chlorine to make carbon tetrachloride (CCl_4). The balanced chemical equation is as follows:

$$CH_4 + 4\,Cl_2 \rightarrow CCl_4 + 4\,HCl$$

How many grams of HCl are produced by the reaction of 100.0 g of CH_4?

Solution

First, let us work the problem in stepwise fashion. We begin by converting the mass of CH_4 to moles of CH_4, using the molar mass of CH_4 (16.05 g/mol) as the conversion factor:

$$100.0\ g\ CH_4 \times \frac{1\ mol\ CH_4}{16.05\ g\ CH_4} = 6.231\ mol\ CH_4$$

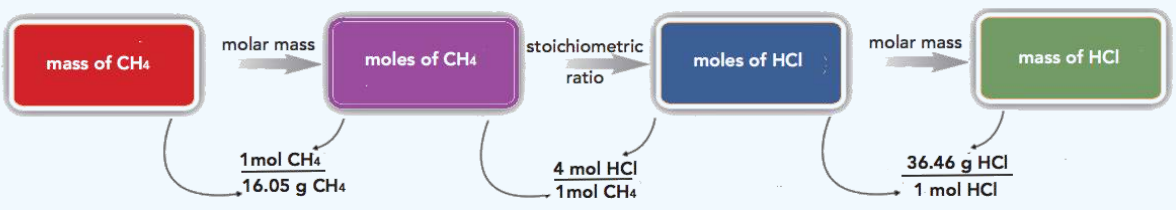
Note that we inverted the molar mass so that the gram units cancel, giving us an answer in moles. Next, we use the balanced chemical equation to determine the ratio of moles CCl_4 and moles HCl and convert our first result into moles of HCl:

$$6.231\ mol\ CH_4 \times \frac{4\ mol\ HCl}{1\ mol\ CH_4} = 24.92\ mol\ HCl$$

Finally, we use the molar mass of HCl (36.46 g/mol) as a conversion factor to calculate the mass of 24.92 mol of HCl:

$$24.92\ mol\ HCl \times \frac{36.46\ g\ HCl}{1\ mol\ HCl} = 908.5\ g\ HCl$$

In each step, we have limited the answer to the proper number of significant figures. If desired, we can do all three conversions on a single line:



$$100.0\ \text{g CH}_4 \times \frac{1\ \text{mol CH}_4}{16.05\ \text{g CH}_4} \times \frac{4\ \text{mol HCl}}{1\ \text{mol CH}_4} \times \frac{36.46\ \text{g HCl}}{1\ \text{mol HCl}} = 908.7\ \text{g HCl}$$

This final answer is slightly different from our first answer because only the final answer is restricted to the proper number of significant figures. In the first answer, we limited each intermediate quantity to the proper number of significant figures. As you can see, both answers are essentially the same.

? Exercise 5.5.2: Oxidation of Propanal

The oxidation of propanal (CH_3CH_2CHO) to propionic acid (CH_3CH_2COOH) has the following chemical equation:

$$CH_3CH_2CHO + 2K_2Cr_2O_7 \rightarrow CH_3CH_2COOH + \text{other products}$$

How many grams of propionic acid are produced by the reaction of 135.8 g of $K_2Cr_2O_7$?

Answer

$$135.8\ \text{g K}_2\text{Cr}_2\text{O}_7 \times \frac{1\ \text{mol K}_2\text{Cr}_2\text{O}_7}{294.20\ \text{g K}_2\text{Cr}_2\text{O}_7} \times \frac{1\ \text{mol CH}_3\text{CH}_2\text{COOH}}{2\ \text{mol K}_2\text{Cr}_2\text{O}_7} \times \frac{74.09\ \text{g CH}_3\text{CH}_2\text{COOH}}{1\ \text{mol CH}_3\text{CH}_2\text{COOH}} = 17.10\ \text{g CH}_3\text{CH}_2\text{COOH}$$

To Your Health: The Synthesis of Taxol

Taxol is a powerful anticancer drug that was originally extracted from the Pacific yew tree (*Taxus brevifolia*). As you can see from the accompanying figure, taxol is a very complicated molecule, with a molecular formula of $C_{47}H_{51}NO_{14}$. Isolating taxol from its natural source presents certain challenges, mainly that the Pacific yew is a slow-growing tree, and the equivalent of six trees must be harvested to provide enough taxol to treat a single patient. Although related species of yew trees also produce taxol in small amounts, there is significant interest in synthesizing this complex molecule in the laboratory.

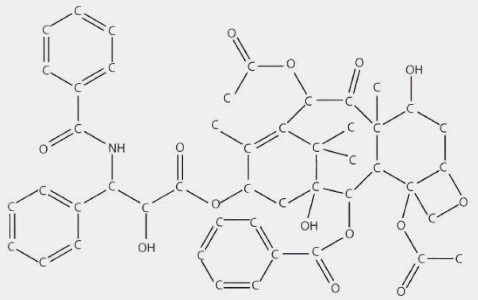


Figure 5.5.1 The Structure of the Cancer Drug Taxol. Because of the complexity of the molecule, hydrogen atoms are not shown, but they are present on every atom to give the atom the correct number of covalent bonds (four bonds for each carbon atom).

After a 20-year effort, two research groups announced the complete laboratory synthesis of taxol in 1994. However, each synthesis required over 30 separate chemical reactions, with an overall efficiency of less than 0.05%. To put this in perspective, to obtain a single 300 mg dose of taxol, you would have to begin with 600 g of starting material. To treat the 26,000 women who are diagnosed with ovarian cancer each year with one dose, almost 16,000 kg (over 17 tons) of starting material must be converted to taxol. Taxol is also used to treat breast cancer, with which 200,000 women in the United States are diagnosed every year. This only increases the amount of starting material needed.

Clearly, there is intense interest in increasing the overall efficiency of the taxol synthesis. An improved synthesis not only will be easier but also will produce less waste materials, which will allow more people to take advantage of this potentially life-saving drug.

Key Takeaway

- A balanced chemical equation can be used to relate masses or moles of different substances in a reaction.

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5.6: Mass-Volume and Volume-Mass Stoichiometry



Figure 5.6.1 (CK-12 Curriculum Materials license; CK-12 Foundation via CK-12 Foundation)

How much azide is needed to fill an air bag?

Cars and many other vehicles have air bags in them. In case of a collision, a reaction is triggered so that the rapid decomposition of sodium azide produces nitrogen gas, filling the air bag. If too little sodium azide is used, the air bag will not fill completely and will not protect the person in the vehicle. Too much sodium azide could cause the formation of more gas that the bag can safely handle. If the bag breaks from the excess gas pressure, all protection is lost.

Mass to Volume and Volume to Mass Problems

Chemical reactions frequently involve both solid substances whose masses can be measured, as well as gases, for which volume measurements are more appropriate. Stoichiometry problems of this type are called either mass-volume or volume-mass problems.

$$\textbf{mass of given} \rightarrow \textbf{moles of given} \rightarrow \textbf{moles of unknown} \rightarrow \textbf{volume of unknown}$$

$$\textbf{volume of given} \rightarrow \textbf{moles of given} \rightarrow \textbf{moles of unknown} \rightarrow \textbf{mass of unknown}$$

Because both types of problems involve a conversion from either moles of gas to volume or vice-versa, we can use the molar volume of $22.4\ \text{L/mol}$, provided that the conditions for the reaction are at STP.

Example 5.6.1: Mass-Volume Stoichiometry

Aluminum metal reacts rapidly with aqueous sulfuric acid to produce aqueous aluminum sulfate and hydrogen gas:

$$2\ \text{Al}\,(s) + 3\text{H}_2\text{SO}_4\,(aq) \rightarrow \text{Al}_2(\text{SO}_4)_3\,(aq) + 3\text{H}_2\,(g)$$

Determine the volume of hydrogen gas produced at STP when a $2.00\ \text{g}$ piece of aluminum completely reacts.

Solution:

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

Known

- Given: $2.00\ \text{g Al}$
- Molar mass $\text{Al} = 26.98\ \text{g/mol}$
- $2\ \text{mol Al} = 3\ \text{mol H}_2$

Unknown

- volume H_2 = ?

The grams of aluminum will first be converted to moles. Then the mole ratio will be applied to convert to moles of hydrogen gas. Finally, the molar volume of a gas will be used to convert to liters of hydrogen.

$$\text{g Al} \rightarrow \text{mol Al} \rightarrow \text{mol H}_2 \rightarrow \text{L H}_2$$

Step 2: Solve.

$$2.00\ \text{g Al} \times \frac{1\ \text{mol Al}}{26.98\ \text{g Al}} \times \frac{3\ \text{mol H}_2}{2\ \text{mol Al}} \times \frac{22.4\ \text{L H}_2}{1\ \text{mol H}_2} = 2.49\ \text{L H}_2$$

Step 3: Think about your result.

The volume result is in liters. For much smaller amounts, it may be convenient to convert to milliliters. The answer here has three significant figures. Because the molar volume is a measured quantity of $22.4\ \text{L/mol}$, three is the maximum number of significant figures for this type of problem.

Example 5.6.2: Volume-Mass Stoichiometry

Calcium oxide is used to remove sulfur dioxide generated in coal-burning power plants, according to the following reaction.

$$2\text{CaO}\,(s) + 2\text{SO}_2\,(g) + \text{O}_2\,(g) \rightarrow 2\text{CaSO}_4\,(s)$$

What mass of calcium oxide is required to react completely with $1.4 \times 10^3\ \text{L}$ of sulfur dioxide?

Solution:

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

Known

- Given: $1.4 \times 10^3\ \text{L} = \text{SO}_2$
- $2\ \text{mol}\ \text{SO}_2 = 2\ \text{mol}\text{CaO}$
- Molar mass $\text{CaO} = 56.08\ \text{g/mol}$

Unknown

- mass CaO = ? g

The volume of SO_2 will be converted to moles, followed by the mole ratio, and finally a conversion of moles of CaO to grams.

$$\text{L}\ \text{SO}_2 \rightarrow \text{mol}\ \text{SO}_2 \rightarrow \text{mol}\ \text{CaO} \rightarrow \text{g}\ \text{CaO}$$

Step 2: Solve.

$$1.4 \times 10^3\ \text{L}\ \text{SO}_2 \times \frac{1\ \text{mol}\ \text{SO}_2}{22.4\ \text{L}\ \text{SO}_2} \times \frac{2\ \text{mol}\ \text{CaO}}{2\ \text{mol}\ \text{SO}_2} \times \frac{56.08\ \text{g}\ \text{CaO}}{1\ \text{mol}\ \text{CaO}} = 3.5 \times 10^3\ \text{g}\ \text{CaO}$$

Step 3: Think about your result.

The resultant mass could be reported as $3.5\ \text{kg}$, with two significant figures. Even though the 2:2 mole ratio does not mathematically affect the problem, it is still necessary for unit conversion.



Summary

- Calculations are described for determining the amount of gas formed in a reaction.
- Calculations are described for determining amounts of a material needed to react with a gas.

Review

1. What are the conditions for all gases in these calculations?
2. How can you tell if all the ratios were set up correctly?
3. Why was 2 mol CaO/2mol SO_2 included in the second example if it did not affect the final number?

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5.7: Concentration

Learning Objectives

- Calculate percentage concentration (m/m, v/v, m/v), ppm and ppb.
- Calculate the molarity of a solution.
- Use concentration units to calculate the amount of solute in a solution.
- Use molarity to determine quantities in chemical reactions.
- Determine the resulting concentration of a diluted solution.

To define a solution precisely, we need to state its concentration: how much solute is dissolved in a certain amount of solvent. Words such as *dilute* or *concentrated* are used to describe solutions that have a little or a lot of dissolved solute, respectively, but these are relative terms whose meanings depend on various factors.

Solubility

There is usually a limit to how much solute will dissolve in a given amount of solvent. This limit is called the **solubility** of the solute. Some solutes have a very small solubility, while other solutes are soluble in all proportions. Table **5.7.1** lists the solubilities of various solutes in water. Solubilities vary with temperature, so Table **5.7.1** includes the temperature at which the solubility was determined.

Table **5.7.1**: Solubilities of Various Solutes in Water at 25°C (Except as Noted)

Substance	Solubility (g in 100 mL of H2O)
AgCl(s)	0.019
$C_6H_6(\ell)$ (benzene)	0.178
$CH_4(g)$	0.0023
$CO_2(g)$	0.150
$CaCO_3(s)$	0.058
$CaF_2(s)$	0.0016
$Ca(NO_3)_2(s)$	143.9
$C_6H_{12}O_6$ (glucose)	120.3 (at 30°C)
KBr(s)	67.8
$MgCO_3(s)$	2.20
NaCl(s)	36.0
$NaHCO_3(s)$	8.41
$C_{12}H_{22}O_{11}$ (sucrose)	204.0 (at 20°C)

If a solution contains so much solute that its solubility limit is reached, the solution is said to be **saturated**, and its concentration is known from information contained in Table **5.7.1**. If a solution contains less solute than the solubility limit, it is **unsaturated**. Under special circumstances, more solute can be dissolved even after the normal solubility limit is reached; such solutions are called ***supersaturated*** and are not stable. If the solute is solid, excess solute can easily recrystallize. If the solute is a gas, it can bubble out of solution uncontrollably, like what happens when you shake a soda can and then immediately open it.

Precipitation from Supersaturated Solutions

Recrystallization of excess solute from a supersaturated solution usually gives off energy as heat. Commercial heat packs containing supersaturated sodium acetate ($NaC_2H_3O_2$) take advantage of this phenomenon. You can probably find them at your local drugstore.



Video* 5.7.1*: Watered-down sodium acetate trihydrate. Needle crystal is truly wonderful structures

Most solutions we encounter are unsaturated, so knowing the solubility of the solute does not accurately express the amount of solute in these solutions. There are several common ways of specifying the concentration of a solution.

Percent Composition

There are several ways of expressing the concentration of a solution by using a percentage. The **mass/mass percent** (% m/m) is defined as the mass of a solute divided by the mass of a solution times 100:

$$\%\,\mathrm{m/m} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

If you can measure the masses of the solute and the solution, determining the mass/mass percent is easy. Each mass must be expressed in the same units to determine the proper concentration.

Example 5.7.1

A saline solution with a mass of 355 g has 36.5 g of NaCl dissolved in it. What is the mass/mass percent concentration of the solution?

Solution

We can substitute the quantities given in the equation for mass/mass percent:

$$\%\,\mathrm{m/m} = \frac{36.5\ \mathrm{g}}{355\ \mathrm{g}} \times 100\% = 10.3\%$$

Exercise 5.7.1

A dextrose (also called D-glucose, $C_6H_{12}O_6$) solution with a mass of 2.00×10^2 g has 15.8 g of dextrose dissolved in it. What is the mass/mass percent concentration of the solution?

Answer

7.90%

For gases and liquids, volumes are relatively easy to measure, so the concentration of a liquid or a gas solution can be expressed as a **volume/volume percent** (% v/v): the volume of a solute divided by the volume of a solution times 100:

$$\%\ \text{v/v} = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100\%$$

Again, the units of the solute and the solution must be the same. A hybrid concentration unit, **mass/volume percent** (% m/v), is commonly used for intravenous (IV) fluids (Figure 5.7.1). It is defined as the mass in grams of a solute, divided by volume in milliliters of solution times 100:

$$\%\ \text{m/v} = \frac{\text{mass of solute (g)}}{\text{volume of solution (mL)}} \times 100\%$$



Figure 5.7.1: Mass/Volume Percent.The 0.9% NaCl concentration on this IV bag is mass/volume percent (left). Such solution is used for other purposes and available in bottles (right). Figures used with permission from Wikipedia

Using Percent Composition in Calculations

The **percent concentration** can be used to produce a **conversion factor** between the **amount of solute** and the **amount of solution**. As such, concentrations can be useful in a variety of stoichiometry problems as discussed in Chapter 6. In many cases, it is best to use the original definition of the concentration unit; it is that definition that provides the conversion factor.

As an example, if the given concentration is **5% v/v solution of alcohol**, this means that there are 5 mL of alcohol dissolved in every 100 mL solution.

5 mL alcohol = 100 mL solution

The two possible conversion factors are written as follows:

$$\frac{\text{5 mL alcohol}}{\text{100 mL solution}} \text{ or } \frac{\text{100 mL solution}}{\text{5 mL alcohol}}$$

Use the first conversion factor to convert from a given amount of solution to amount of solute. The second conversion factor is used to convert from a given amount of solute to amount of solution. Given any two quantities in any percent composition, the third quantity can be calculated, as the following example illustrates.

Example 5.7.2

A sample of 45.0% v/v solution of ethanol (C_2H_5OH) in water has a volume of 115 mL. What volume of ethanol solute does the sample contain?

Solution

A percentage concentration is simply the number of parts of solute per 100 parts of solution. Thus, the percent concentration of 45.0% v/v implies the following:

$$45.0\%\ \text{v/v} \rightarrow \frac{\text{45 mL } C_2H_5OH}{\text{100 mL solution}}$$

That is, there are 45 mL of C_2H_5OH for every 100 mL of solution. We can use this fraction as a **conversion factor** to determine the amount of C_2H_5OH in 115 mL of solution:

$$115\ \text{mL solution} \times \frac{45\ \text{mL } C_2H_5OH}{100\ \text{mL solution}} = 51.8\ \text{mL } C_2H_5OH$$

? Exercise 5.7.2

What volume of a 12.75% m/v solution of glucose ($C_6H_{12}O_6$) in water is needed to obtain 50.0 g of $C_6H_{12}O_6$?

Answer

$$50.0\ \text{g } C_6H_12O_6 \times \frac{100\ \text{mL solution}}{12.75\ \text{g } C_6H_12O_6} = 392\ \text{mL solution}$$

✓ Example 5.7.3

A normal saline IV solution contains 9.0 g of NaCl in every liter of solution. What is the mass/volume percent of normal saline?

Solution

We can use the definition of mass/volume percent, but first we have to express the volume in milliliter units:

1 L = 1,000 mL

Because this is an exact relationship, it does not affect the significant figures of our result.

$$\%\ \text{m/v} = \frac{9.0\ \text{g NaCl}}{1,000\ \text{mL solution}} \times 100\% = 0.90\%\ \text{m/v}$$

? Exercise 5.7.3

The chlorine bleach that you might find in your laundry room is typically composed of 27.0 g of sodium hypochlorite (NaOCl), dissolved to make 500.0 mL of solution. What is the mass/volume percent of the bleach?

Answer

$$\%\ \text{m/v} = \frac{27.0\ \text{g NaOCl}}{500.0\ \text{mL solution}} \times 100\% = 5.40\%\ \text{m/v}$$

In addition to percentage units, the units for expressing the concentration of extremely dilute solutions are parts per million (ppm) and parts per billion (ppb). Both of these units are mass based and are defined as follows:

$$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 1,000,000$$

$$\text{ppb} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 1,000,000,000$$

> *Similar to parts per million and parts per billion, related units include parts per thousand (ppth) and parts per trillion (ppt).*

Concentrations of *trace elements* in the body—elements that are present in extremely low concentrations but are nonetheless necessary for life—are commonly expressed in parts per million or parts per billion. Concentrations of poisons and pollutants are also described in these units. For example, cobalt is present in the body at a concentration of 21 ppb, while the State of Oregon's Department of Agriculture limits the concentration of arsenic in fertilizers to 9 ppm.

> *In aqueous solutions, 1 ppm is essentially equal to 1 mg/L, and 1 ppb is equivalent to 1 µg/L.*

Example 5.7.4

If the concentration of cobalt in a human body is 21 ppb, what mass in grams of Co is present in a body having a mass of 70.0 kg?

Solution

A concentration of 21 ppb means "21 g of solute per 1,000,000,000 g of solution." Written as a **conversion factor,** this concentration of Co is as follows:

$$21 \text{ ppb Co} \rightarrow \frac{21 \text{ g Co}}{1,000,000,000 \text{ g solution}}$$

We can use this as a conversion factor, but first we must convert 70.0 kg to gram units:

$$70.0 \text{ kg} \times \frac{1,000 \text{ g}}{1 \text{ kg}} = 7.00 \times 10^4 \text{ g}$$

Now we determine the amount of Co:

$$7.00 \times 10^4 \text{ g solution} \times \frac{21 \text{ g Co}}{1,000,000,000 \text{ g solution}} = 0.0015 \text{ g Co}$$

This is only 1.5 mg.

Exercise 5.7.4

An 85 kg body contains 0.012 g of Ni. What is the concentration of Ni in parts per million?

Answer

0.14 ppm

Molarity

Another way of expressing concentration is to give the number of moles of solute per unit volume of solution. Such concentration units are useful for discussing chemical reactions in which a solute is a product or a reactant. Molar mass can then be used as a conversion factor to convert amounts in moles to amounts in grams.

Molarity is defined as the number of moles of a solute dissolved per liter of solution:

$$\text{molarity} = \frac{\text{number of moles of solute}}{\text{number of liters of solution}}$$

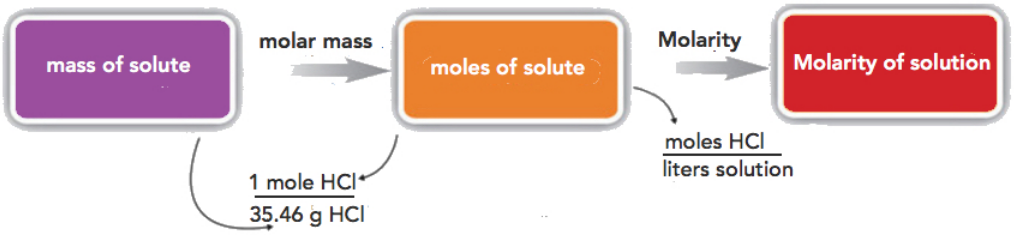
Molarity is abbreviated M (often referred to as "molar"), and the units are often abbreviated as mol/L. It is important to remember that "mol" in this expression refers to moles of solute and that "L" refers to liters of solution. For example, if you have 1.5 mol of NaCl dissolved in 0.500 L of solution, its molarity is therefore

$$\frac{1.5 \text{ mol NaCl}}{0.500 \text{ L solution}} = 3.0 \text{ M NaCl}$$

which is read as "three point oh **molar** sodium chloride." Sometimes (aq) is added when the solvent is water, as in "3.0 M NaCl(aq)."

Before a molarity concentration can be calculated, the amount of the **solute must be expressed in moles**, and the **volume of the solution** must be expressed in **liters**.

If the quantity of the solute is given in mass units, you must convert mass units to mole units before using the definition of molarity to calculate concentration. For example, what is the molar concentration of a solution of 22.4 g of HCl dissolved in 1.56 L?



Step 1: convert the **mass of solute** to **moles** using the **molar mass of HCl (36.46 g/mol):**

$$22.4\ \cancel{g HCl} \times \frac{1\ mol\ HCl}{36.46\ \cancel{g HCl}} = 0.614\ mol\ HCl$$

Step 2: use the **definition of molarity** to determine the concentration:

$$M = \frac{0.614\ mol\ HCl}{1.56 L\ solution} = 0.394\ M HCl$$

Example 5.7.5

What is the molarity of an aqueous solution of 25.0 g of NaOH in 750 mL?

Solution

Before we substitute these quantities into the definition of molarity, we must convert them to the proper units. The mass of NaOH must be converted to moles of NaOH. The molar mass of NaOH is 40.00 g/mol:

$$25.0\ \text{g NaOH} \times \frac{1\ \text{mol NaOH}}{40.00\ \text{g NaOH}} = 0.625\ \text{mol NaOH}$$

Next, we convert the volume units from milliliters to liters:

$$750\ \text{mL} \times \frac{1\ \text{L}}{1,000\ \text{mL}} = 0.750\ \text{L}$$

Now that the quantities are expressed in the proper units, we can substitute them into the definition of molarity:

$$\text{M} = \frac{0.625\ \text{mol NaOH}}{0.750\ \text{L}} = 0.833\ \text{M NaOH}$$

Exercise 5.7.5

If a 350 mL cup of coffee contains 0.150 g of caffeine ($C_8H_{10}N_4O_2$), what is the molarity of this caffeine solution?

Answer

0.00221 M

Using Molarity in Calculations

The definition of molarity can also be used to calculate a needed volume of solution, given its concentration and the number of moles desired, or the number of moles of solute (and subsequently, the mass of the solute), given its concentration and volume. As in the percent concentration, molarity can also be expressed as a **conversion factor**.

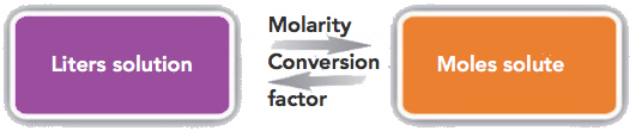
Molarity is defined as moles solute per liter solution. There is an understood 1 in the denominator of the conversion factor. For example, a **3.0 M solution of sucrose** means that there are three moles of sucrose dissolved in every **liter of solution**. Mathematically, this is stated as follows:

3.0 moles sucrose = 1 L solution

Dividing both sides of this expression by either side, we generate two possible conversion factors:

$$\frac{3.0\ \text{mol sucrose}}{1\ \text{L solution}} \text{ or } \frac{1\ \text{L solution}}{3.0\ \text{mol sucrose}}$$

The first conversion factor can be used to convert from *volume (L) of solution to moles solute*, and the *second converts from moles of solute to volume (L) of solution*.



For example, suppose we are asked how many moles of sucrose are present in 0.108 L of a 3.0 M sucrose solution. The given volume (0.108 L) is multiplied by the first conversion factor to cancel the L units, and find that 0.32 moles of sucrose are present.

$$0.108\ \cancel{L\ solution} \times \frac{3.0\ mol\ sucrose}{1\cancel{L\ solution}} = 0.32\ mol\ sucrose$$

How many liters of 3.0 M sucrose solution are needed to obtain 4.88 mol of sucrose? In such a conversion, we multiply the given (4.88 moles sucrose) with the second conversion factor. This cancels the moles units and converts it to liters of solution.

$$4.88\ \cancel{mol\ sucrose} \times \frac{1\ L\ solution}{3.0\cancel{mol\ sucrose}} = 1.63\ L\ solution$$

Example 5.7.6

1. What volume of a 0.0753 M solution of dimethylamine [$(CH_3)_2NH$] is needed to obtain 0.450 mol of the compound?
2. Ethylene glycol ($C_2H_6O_2$) is mixed with water to make auto engine coolants. How many grams of $C_2H_6O_2$ are in 5.00 L of a 6.00 M aqueous solution?

Solution

1. To solve for the volume, multiply the "given" (0.450 mol of dimethylamine) with the molarity conversion factor (0.0753 M). Use the proper conversion factor to cancel the unit "mol" and get the unit volume (L) of solution:

$$0.450\ \text{mol dimethylamine} \times \frac{1\ \text{L solution}}{0.0753\ \text{mol dimethylamine}} = 5.98\ \text{L solution}$$

2. The strategy in solving this problem is to convert the given volume (5.00 L) using the 6.00 M (conversion factor) to solve for moles of ethylene glycol, which can then be converted to grams.

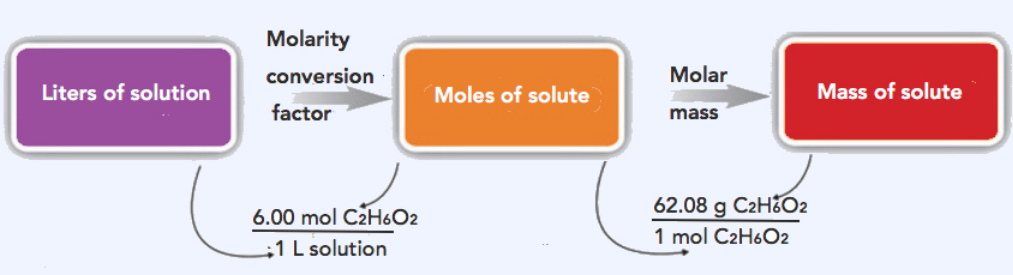
Step 1: Convert the given volume (5.00 L) to moles ethylene glycol.

$$5.00\ \text{L solution} \times \frac{6.00\ \text{mol}\ C_2H_6O_2}{1\ \text{L solution}} = 30.0\ \text{mol}\ C_2H_6O_2$$

Step 2: Convert 30.0 mols $C_2H_6O_2$ to grams $C_2H_6O_2$. Molar mass of $C_2H_6O_2$= 62.08 g/mol

$$30.0\ \text{mol}\ C_2H_6O_2 \times \frac{62.08\ \text{g}\ C_2H_6O_2}{1\ \text{mol}\ C_2H_6O_2} = 1,860\ \text{g}\ C_2H_6O_2$$

The same two-step problem can also be worked out in a single line, rather than as two separate steps, as follows:



$$5.00\ \text{L solution} \times \frac{6.00\ \text{mol}\ C_2H_6O_2}{1\ \text{L solution}} \times \frac{62.08\ \text{g}\ C_2H_6O_2}{1\ \text{mol}\ C_2H_6O_2} = 1,860\ \text{g}\ C_2H_6O_2$$

https://chem.libretexts.org/@go/page/270463

The final answer is rounded off to 3 significant figures. Thus, there are 1,860 g of $C_2H_6O_2$ in the specified amount of engine coolant.

Note: Dimethylamine has a “fishy” odor. In fact, organic compounds called amines cause the odor of decaying fish.

Example 5.7.6A

1. What volume of a 0.0753 M solution of dimethylamine [$(CH_3)_2NH$] is needed to obtain 0.450 mol of the compound?
2. Ethylene glycol ($C_2H_6O_2$) is mixed with water to make auto engine coolants. How many grams of $C_2H_6O_2$ are in 5.00 L of a 6.00 M aqueous solution?

Solution

This is an alternative method in case you don't want to use the conversion factor for molarity. In both parts, we will use the definition of molarity to solve for the desired quantity.

1. $$0.0753\ \text{M} = \frac{0.450\ \text{mol}\ (CH_3)_2NH}{\text{volume of solution}}$$

   To solve for the volume of solution, we multiply both sides by volume of solution and divide both sides by the molarity value to isolate the volume of solution on one side of the equation:

   $$\text{volume of solution} = \frac{0.450\ \text{mol}\ (CH_3)_2NH}{0.0753\ \text{M}} = 5.98\ \text{L}$$

   Note that because the definition of molarity is mol/L, the division of mol by M yields L, a unit of volume.

2. The molar mass of $C_2H_6O_2$ is 62.08 g/mol., so

   $$6.00\ \text{M} = \frac{\text{moles of solute}}{5.00\ \text{L}}$$

   To solve for the number of moles of solute, we multiply both sides by the volume:

   $$\text{moles of solute} = (6.00\ \text{M})(5.00\ \text{L}) = 30.0\ \text{mol}$$

   Note that because the definition of molarity is mol/L, the product M × L gives mol, a unit of amount. Now, using the molar mass of $C_3H_8O_3$, we convert mol to g:

   $$30.0\ \text{mol} \times \frac{62.08\ \text{g}}{\text{mol}} = 1,860\ \text{g}$$

   Thus, there are 1,860 g of $C_2H_6O_2$ in the specified amount of engine coolant.

Exercise 5.7.6

a. What volume of a 0.0902 M solution of formic acid (HCOOH) is needed to obtain 0.888 mol of HCOOH?
b. Acetic acid ($HC_2H_3O_2$) is the acid in vinegar. How many grams of $HC_2H_3O_2$ are in 0.565 L of a 0.955 M solution?

Answer

a. 9.84 L

b. 32.4 g

Using Molarity in Stoichiometry Problems

Of all the ways of expressing concentration, molarity is the one most commonly used in stoichiometry problems because it is directly related to the mole unit. Consider the following chemical equation:

$$HCl(aq) + NaOH(s) \rightarrow H_2O(\ell) + NaCl(aq)$$

Suppose we want to know how many liters of aqueous HCl solution will react with a given mass of NaOH. A typical approach to answering this question is as follows:

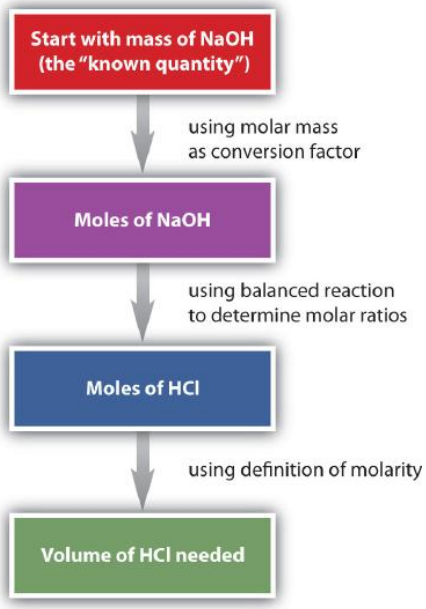


***Figure* 5.7.2**: *Typical approach to solving Molarity problems*

In itself, each step is a straightforward conversion. It is the combination of the steps that is a powerful quantitative tool for problem solving.

Example 5.7.7

How many milliliters of a 2.75 M HCl solution are needed to react with 185 g of NaOH? The balanced chemical equation for this reaction is as follows:

$$\mathrm{HCl(aq) + NaOH(s) \rightarrow H_2O(\ell) + NaCl(aq)}$$

Solution

We will follow the flowchart to answer this question. First, we convert the mass of NaOH to moles of NaOH using its molar mass, 40.00 g/mol:

$$\mathrm{185\ g\ NaOH \times \frac{1\ mol\ NaOH}{40.00\ g\ NaOH} = 4.63\ mol\ NaOH}$$

Using the balanced chemical equation, we see that there is a one-to-one ratio of moles of HCl to moles of NaOH. We use this to determine the number of moles of HCl needed to react with the given amount of NaOH:

$$\mathrm{4.63\ mol\ NaOH \times \frac{1\ mol\ HCl}{1\ mol\ NaOH} = 4.63\ mol\ HCl}$$

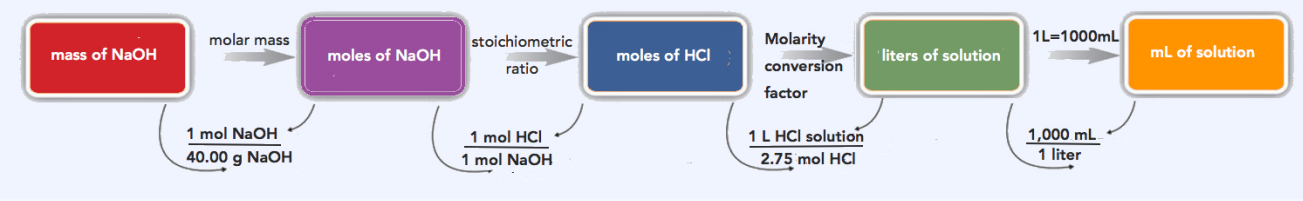
Finally, we use the definition of molarity to determine the volume of 2.75 M HCl needed:

$$\mathrm{2.75\ M\ HCl = \frac{4.63\ mol\ HCl}{volume\ of\ HCl\ solution}}$$

$$\mathrm{volume\ of\ HCl = \frac{4.63\ mol\ HCl}{2.75\ M\ HCl} = 1.68\ L \times \frac{1,000\ mL}{1\ L} = 1,680\ mL}$$

We need 1,680 mL of 2.75 M HCl to react with the NaOH.

The same multi-step problem can also be worked out in a single line, rather than as separate steps, as follows:



$$185\ \text{g NaOH} \times \frac{1\ \text{mol NaOH}}{40.00\ \text{g NaOH}} \times \frac{1\ \text{mol HCl}}{1\ \text{mol NaOH}} \times \frac{1\ \text{L HCl solution}}{2.75\ \text{mol HCl}} \times \frac{1000\ \text{mL HCl solution}}{1\ \text{L HCl solution}} = 1,680\ \text{mL HCl solution}$$

Our final answer (rounded off to three significant figures) is 1,680 mL HCl solution.

Exercise 5.7.7

How many milliliters of a 1.04 M H_2SO_4 solution are needed to react with 98.5 g of $Ca(OH)_2$? The balanced chemical equation for the reaction is as follows:

$$H_2SO_{4(aq)} + Ca(OH)_{2(s)} \rightarrow 2H_2O_{(\ell)} + CaSO_{4(aq)}$$

Answer

1,280 mL

The general steps for performing stoichiometry problems such as this are shown in Figure 5.7.3. You may want to consult this figure when working with solutions in chemical reactions. The double arrows in Figure 5.7.3 indicate that you can start at either end of the chart and, after a series of simple conversions, determine the quantity at the other end.

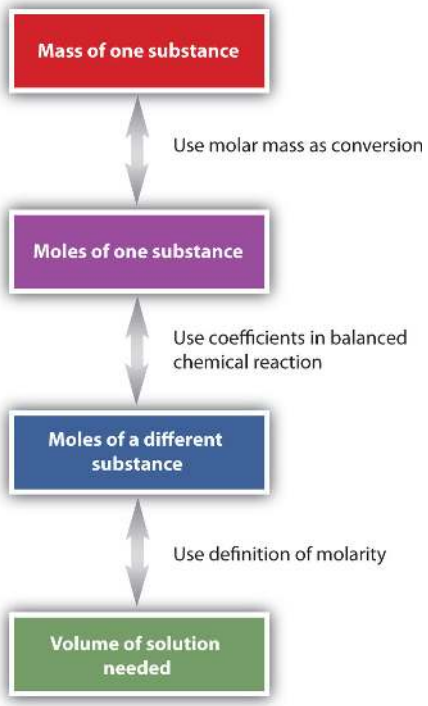


Figure 5.7.3: Diagram of Steps for Using Molarity in Stoichiometry Calculations. When using molarity in stoichiometry calculations, a specific sequence of steps usually leads you to the correct answer.

Many of the fluids found in our bodies are solutions. The solutes range from simple ionic compounds to complex proteins. Table 5.7.2 lists the typical concentrations of some of these solutes.

Table 5.7.2: Approximate Concentrations of Various Solutes in Some Solutions in the Body*

Solution	Solute	Concentration (M)
blood plasma	Na^+	0.138
	K^+	0.005
	Ca^{2+}	0.004
	Mg^{2+}	0.003
	Cl^-	0.110
	HCO_3^-	0.030
stomach acid	HCl	0.10
urine	NaCl	0.15
	PO_4^{3-}	0.05
	NH_2CONH_2 (urea)	0.30

*Note: Concentrations are approximate and can vary widely.

Looking Closer: The Dose Makes the Poison

Why is it that we can drink 1 qt of water when we are thirsty and not be harmed, but if we ingest 0.5 g of arsenic, we might die? There is an old saying: *the dose makes the poison*. This means that what may be dangerous in some amounts may not be dangerous in other amounts.

Take arsenic, for example. Some studies show that arsenic deprivation limits the growth of animals such as chickens, goats, and pigs, suggesting that arsenic is actually an essential trace element in the diet. Humans are constantly exposed to tiny amounts of arsenic from the environment, so studies of completely arsenic-free humans are not available; if arsenic is an essential trace mineral in human diets, it is probably required on the order of 50 ppb or less. A toxic dose of arsenic corresponds to about 7,000 ppb and higher, which is over 140 times the trace amount that may be required by the body. Thus, arsenic is not poisonous in and of itself. Rather, it is the amount that is dangerous: the dose makes the poison.

Similarly, as much as water is needed to keep us alive, too much of it is also risky to our health. Drinking too much water too fast can lead to a condition called water intoxication, which may be fatal. The danger in water intoxication is not that water itself becomes toxic. It is that the ingestion of too much water too fast dilutes sodium ions, potassium ions, and other salts in the bloodstream to concentrations that are not high enough to support brain, muscle, and heart functions. Military personnel, endurance athletes, and even desert hikers are susceptible to water intoxication if they drink water but do not replenish the salts lost in sweat. As this example shows, even the right substances in the wrong amounts can be dangerous!

Equivalents

Concentrations of ionic solutes are occasionally expressed in units called equivalents (Eq). One equivalent equals 1 mol of positive or negative charge. Thus, 1 mol/L of $Na^+(aq)$ is also 1 Eq/L because sodium has a 1+ charge. A 1 mol/L solution of $Ca^{2+}(aq)$ ions has a concentration of 2 Eq/L because calcium has a 2+ charge. Dilute solutions may be expressed in milliequivalents (mEq)—for example, human blood plasma has a total concentration of about 150 mEq/L. (For more information about the ions present in blood plasma, see Chapter 3, Section 3.3.)

Dilutions

When additional water is added to an aqueous solution, the concentration of that solution decreases. This is because the number of **moles of the solute does not change**, while the **volume of the solution increases**. We can set up an equality between the moles of the solute before the dilution (1) and the moles of the solute after the dilution (2).

$$\text{mol}_1 = \text{mol}_2$$

Since the moles of solute in a solution is equal to the molarity multiplied by the liters, we can set those equal.

$$M_1 \times L_1 = M_2 \times L_2$$

Finally, because the two sides of the equation are set equal to one another, the volume can be in any units we choose, as long as that unit is the same on both sides. Our equation for calculating the molarity of a diluted solution becomes:

$$M_1 \times V_1 = M_2 \times V_2$$

Suppose that you have $100.\ \text{mL}$ of a $2.0\ \text{M}$ solution of HCl. You dilute the solution by adding enough water to make the solution volume $500.\ \text{mL}$. The new molarity can easily be calculated by using the above equation and solving for M_2.

$$M_2 = \frac{M_1 \times V_1}{V_2} = \frac{2.0\ \text{M} \times 100.\ \text{mL}}{500.\ \text{mL}} = 0.40\ \text{M HCl}$$

The solution has been diluted by one-fifth since the new volume is five times as great as the original volume. Consequently, the molarity is one-fifth of its original value.

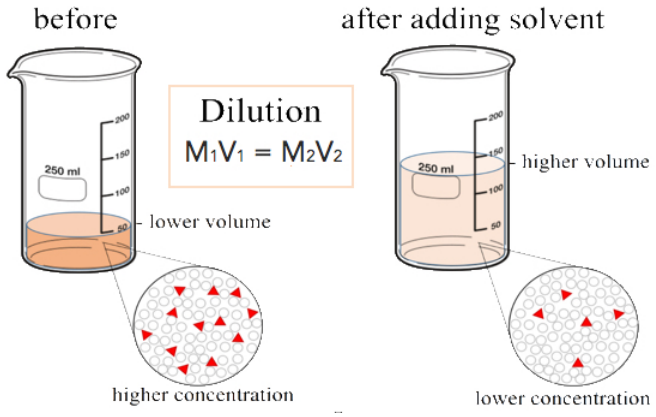


Figure 5.7.1: Figure 5.7.4: Diluting a solution by adding more solvent. Through the dilution process, the volume increases and the concentrations of the solutes decrease. As a consequence, there is more solution in the beaker after dilution, and the color of the solution becomes fainter. The inset shows that at the particular level (picometer to nanometer scale), there are less solute particles (red triangles) per volume. The content in the central box shows the dilution law, i.e. that the product of concentration and volume stays constant upon dilution. CC BY-SA 4.0.

Dilution Equations

Any units of concentration and volume can be used, as long as both concentrations and both volumes have the same unit. For example, if we are using M (molarity), then we can express the equation as follows:

$$\text{Molarity}_{\text{initial}} \times \text{volume}_{\text{initial}} = \text{Molarity}_{\text{final}} \times \text{volume}_{\text{final}} \text{ or}$$

$$M_1V_1 = M_2V_2$$

If we are using percent, the dilution equation is as follows:

$$\%_{\text{initial}} \times \text{volume}_{\text{initial}} = \%_{\text{final}} \times \text{volume}_{\text{final}} \text{ or}$$

$$\%_1V_1 = \%_2V_2$$

Example 5.7.8

A 125 mL sample of 0.900 M NaCl is diluted to 1,125 mL. What is the final concentration of the diluted solution?

Solution

Because the volume units are the same, and we are looking for the molarity of the final solution, we can use $(\text{concentration} \times \text{volume})_{\text{initial}} = (\text{concentration} \times \text{volume})_{\text{final}}$:

$$(0.900\ \text{M} \times 125\ \text{mL}) = (\text{concentration} \times 1{,}125\ \text{mL})$$

We solve by isolating the unknown concentration by itself on one side of the equation. Dividing by 1,125 mL gives

$$\text{concentration} = \frac{0.900\ \text{M} \times 125\ \text{mL}}{1,125\ \text{mL}} = 0.100\ \text{M}$$

as the final concentration.

Exercise 5.7.8

a. A nurse uses a syringe to inject 5.00 mL of 0.550 M heparin solution (heparin is an anticoagulant drug) into a 250 mL IV bag, for a final volume of 255 mL. What is the concentration of the resulting heparin solution?

b. A 0.885 M solution of KBr whose initial volume is 76.5 mL has more water added until its concentration is 0.500 M. What is the new volume of the solution?

Answer

a. 0.0108 M

b. 135.4 mL

Preparing IV Solutions

In a hospital emergency room, a physician orders an intravenous (IV) delivery of 100 mL of 0.5% KCl for a patient suffering from hypokalemia (low potassium levels). Does an aide run to a supply cabinet and take out an IV bag containing this concentration of KCl?

Not likely. It is more probable that the aide must make the proper solution from an IV bag of sterile solution and a more concentrated, sterile solution, called a *stock solution*, of KCl. The aide is expected to use a syringe to draw up some stock solution and inject it into the waiting IV bag and dilute it to the proper concentration. Thus the aide must perform a dilution calculation.



Figure 5.7.5:*Preparing IV Solution © Thinkstock. Medical personnel commonly must perform dilutions for IV solutions.*

If the stock solution is 10.0% KCl and the final volume and concentration need to be 100 mL and 0.50%, respectively, then it is an easy calculation to determine how much stock solution to use:

$$(10\%)V_1 = (0.50\%)(100\ \text{mL})$$

$$V_1 = 5\ \text{mL}$$

Of course, the addition of the stock solution affects the total volume of the diluted solution, but the final concentration is likely close enough even for medical purposes.

> Medical and pharmaceutical personnel are constantly dealing with dosages that require concentration measurements and dilutions. It is an important responsibility: calculating the *wrong* dose can be useless, harmful, or even fatal!

Key Takeaways

- Various concentration units are used to express the amounts of solute in a solution.
- Concentration units can be used as conversion factors in stoichiometry problems.
- New concentrations can be easily calculated if a solution is diluted.

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5.8: Limiting Reactant

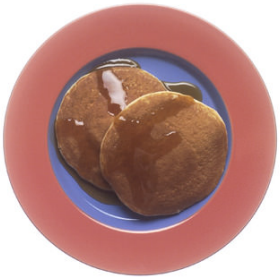


Figure 5.8.1 (Public Domain; Renee Comet and the National Cancer Institute; CK-12 Foundation - Christopher Auyeung via Commons Wikimedia, Pancakes [commons.wikimedia.org])

Don't you hate running out of cooking ingredients?

Cooking is a great example of everyday chemistry. In order to correctly follow a recipe, a cook needs to make sure that he has plenty of all the necessary ingredients in order to make his dish. Let us suppose that you are deciding to make some pancakes for a large group of people. The recipe on the box indicates that the following ingredients are needed for each batch of pancakes:

1 cup of pancake mix

$\frac{3}{4}$ cup milk

1 egg

1 tablespoon vegetable oil

Now you check the pantry and the refrigerator and see that you have the following ingredients available:

2 boxes of pancake mix (8 cups)

Half a gallon of milk (4 cups)

2 eggs

Full bottle of vegetable oil (about 3 cups)

The question that you must ask is: how many batches of pancakes can I make? The answer is two. Even though you have enough pancake mix, milk, and oil to make many more batches of pancakes, you are *limited* by the fact that you only have two eggs. As soon as you have made two batches of pancakes, you will be out of eggs and your "reaction" will be complete.

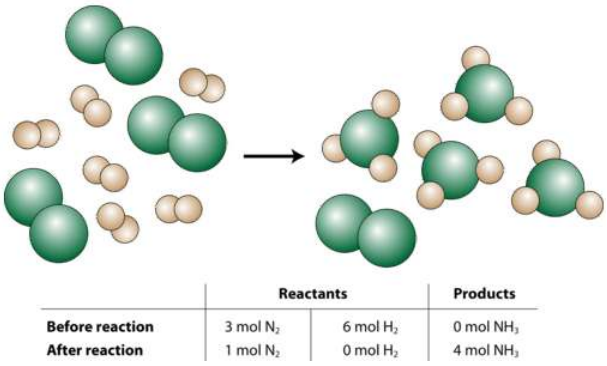
Limiting Reactant

For a chemist, the balanced chemical equation is the recipe that must be followed. As you have seen earlier, the Haber process is a reaction in which nitrogen gas is combined with hydrogen gas to form ammonia. The balanced equation is shown below.

$$N_2\,(g) + 3H_2\,(g) \rightarrow 2NH_3\,(g)$$

We know that the coefficients of the balanced equation indicate the mole ratio that is required for this reaction to occur. One mole of N_2 will react with three moles of H_2 to form two moles of NH_3.

Now let us suppose that a chemist were to react three moles of N_2 with six moles of H_2 (see figure below).



	Reactants		Products
Before reaction	3 mol N_2	6 mol H_2	0 mol NH_3
After reaction	1 mol N_2	0 mol H_2	4 mol NH_3

Figure 5.8.2: Reaction in presence of limiting reagent. (CC BY-NC 3.0; Christopher Auyeung via CK-12 Foundation)

So what happened in this reaction? The chemist started with 3 moles of $\mathbf{N_2}$. You may think of this as being 3 times as much as the "recipe" (the balanced equation) requires since the coefficient for the $\mathbf{N_2}$ is a 1. However, the 6 moles of $\mathbf{H_2}$ that the chemist started with is only two times as much as the "recipe" requires, since the coefficient for the $\mathbf{H_2}$ is a 3 and $\mathbf{3 \times 2 = 6}$. So, after the reaction is complete, the hydrogen gas will be completely used up; while there will be 1 mole of nitrogen gas left over. Finally, the reaction will produce 4 moles of $\mathbf{NH_3}$ because that is also two times as much as shown in the balanced equation. The overall reaction that occurred in words:

$$\mathbf{2\ mol\ N_2 + 6\ mol\ H_2 \rightarrow 4\ mol\ NH_3}$$

All the amounts are doubled from the original balanced equation.

The **limiting reactant** (or **limiting reagent**) is the reactant that determines the amount of product that can be formed in a chemical reaction. The reaction proceeds until the limiting reactant is completely used up. In our example above, the $\mathbf{H_2}$ is the limiting reactant. The **excess reactant** (or **excess reagent**) is the reactant that is initially present in a greater amount than will eventually be reacted. In other words, there is always excess reactant left over after the reaction is complete. In the above example, the $\mathbf{N_2}$ is the excess reactant.





Summary

- The amount of limiting reactant determines how much product will be formed in a chemical reaction.

Review

1. In the Haber reaction illustrated above, how do we know that hydrogen is the limiting reactant?
2. What if hydrogen were left over?
3. Which material would be limiting if no hydrogen or nitrogen were left over?

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5.9: Determining the Limiting Reactant



Figure 5.9.1 (Public Domain; Renee Comet and the National Cancer Institute via Wikipedia)

Who's coming for dinner?

You have ten people that show up for a dinner party. One of the guest brings twenty brownies for dessert. The decision about serving dessert is easy: two brownies are placed on every plate. If someone wants more brownies, they will have to wait until they go to the store. There are only enough brownies for everyone to have two.

Determining the Limiting Reactant

In the real world, amounts of reactants and products are typically measured by mass or by volume. It is first necessary to convert the given quantities of each reactant to moles in order to identify the limiting reactant.

Example 5.9.1: Determining the Limiting Reactant

Silver metal reacts with sulfur to form silver sulfide according to the following balanced equation:

$$2\text{Ag}\,(s) + \text{S}\,(s) \rightarrow \text{Ag}_2\text{S}\,(s)$$

What is the limiting reactant when $50.0\ \text{g Ag}$ is reacted with $10.0\ \text{g S}$?

Solution:

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

Known

- Given: $50.0\ \text{g Ag}$
- Given: $10.0\ \text{g S}$

Unknown

- limiting reactant

Use the atomic masses of **Ag** and **S** to determine the number of moles of each present. Then, use the balanced equation to calculate the number of moles of sulfur that would be needed to react with the number of moles of silver present. Compare this result to the actual number of moles of sulfur present.

Step 2: Solve.

First, calculate the number of moles of **Ag** and **S** present:

$$50.0\ \text{g Ag} \times \frac{1\ \text{mol Ag}}{107.87\ \text{g Ag}} = 0.464\ \text{mol Ag}$$

$$10.0\ \text{g S} \times \frac{1\ \text{mol S}}{32.07\ \text{g S}} = 0.312\ \text{mol S}$$

Second, find the moles of **S** that would be required to react with all of the given **Ag**:

$$0.464\ \text{mol Ag} \times \frac{1\ \text{mol S}}{2\ \text{mol Ag}} = 0.232\ \text{mol S (required)}$$

The amount of **S** actually present is 0.312 moles. The amount of **S** that is required to fully react with all of the **Ag** is 0.232 moles. Since there is more sulfur present than what is required to react, the sulfur is the excess reactant. Therefore, silver is the limiting reactant.

Step 3: Think about your result.

The balanced equation indicates that the necessary mole ratio of **Ag** to **S** is 2:1. Since there were not twice as many moles of **Ag** present in the original amounts, that makes silver the limiting reactant.

There is a very important point to consider about the preceding problem. Even though the mass of silver present in the reaction $(50.0\ \text{g})$ was greater than the mass of sulfur $(10.0\ \text{g})$, silver was the limiting reactant. This is because chemists must always convert to molar quantities and consider the

mole ratio from the balanced chemical equation.

There is one other component to be determined in a limiting reactant problem—the quantity of the excess reactant that will be left over after the reaction is complete. We will return to the sample problem, above, to answer this question below.

Example 5.9.2: Determining the Amount of Excess Reactant Left Over

What is the mass of excess reactant remaining when $50.0\ \text{g Ag}$ reacts with $10.0\ \text{g S}$?

$$2\text{Ag}\,(s) + \text{S}\,(s) \rightarrow \text{Ag}_2\text{S}\,(s)$$

Solution:

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

Known

- Excess reactant $= 0.312\ \text{mol S}$ (from Example 5.9.1)
- Amount of excess reactant needed $= 0.232\ \text{mol S}$ (from Example 5.9.1)

Unknown

- Mass of excess reactant remaining after the reaction = ? g

Subtract the amount (in moles) of the excess reactant that will react from the amount that is originally present. Convert moles to grams.

Step 2: Solve.

$$0.312\ \text{mol S} - 0.232\ \text{mol S} = 0.080\ \text{mol S (remaining after reaction)}$$

$$0.080\ \text{mol S} \times \frac{32.07\ \text{g S}}{1\ \text{mol S}} = 2.57\ \text{g S}$$

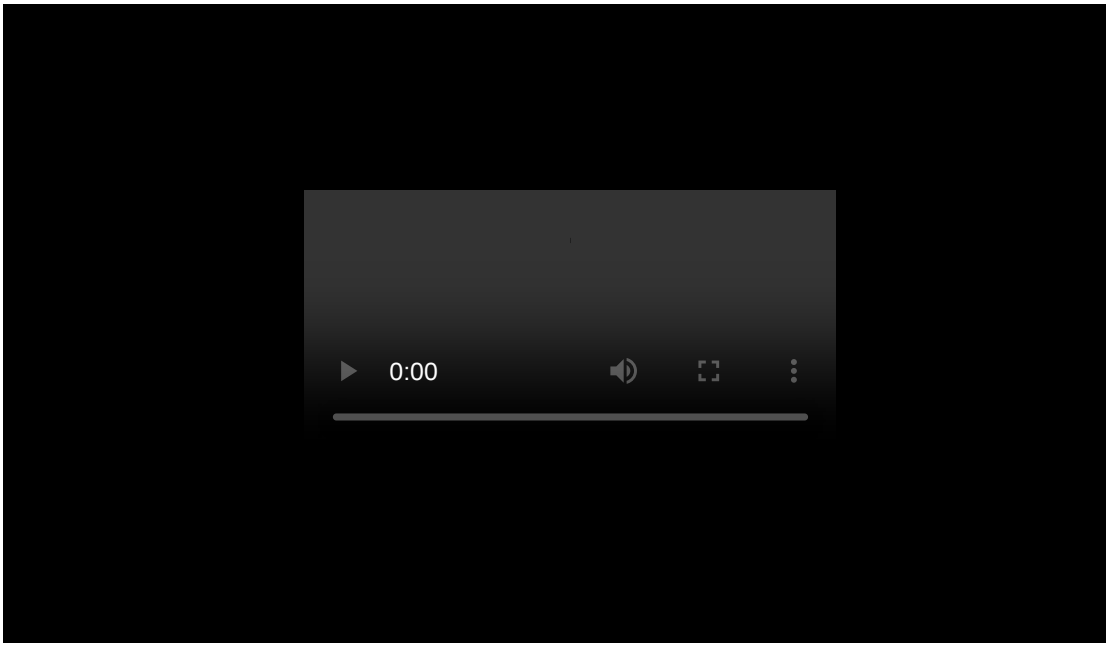
There are $2.57\ \text{g}$ of sulfur remaining when the reaction is complete.

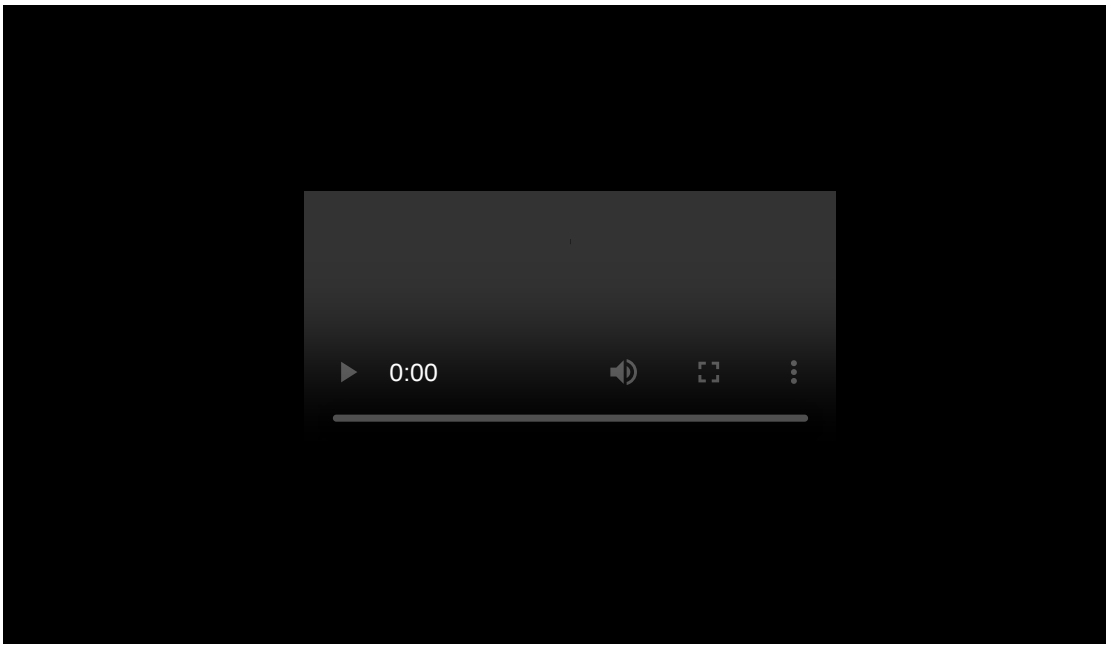
Step 3: Think about your result.

There were $10.0\ \text{g}$ of sulfur present before the reaction began. If $2.57\ \text{g}$ of sulfur remain after the reaction, then $7.43\ \text{g S}$ reacted.

$$7.43\ \text{g S} \times \frac{1\ \text{mol S}}{32.07\ \text{g S}} = 0.232\ \text{mol S}$$

This is the amount of sulfur that reacted. The problem is internally consistent.





Summary

- Determining the limiting reactant requires that all mass quantities first be converted to moles to evaluate the equation.

Review

1. Why do all mass values need to be converted to moles before determining the limiting reactant?
2. Silver metal reacts with sulfur to form silver sulfide according to the following balanced equation:

$$2\mathrm{Ag}\,(s) + \mathrm{S}\,(s) \rightarrow \mathrm{Ag_2S}\,(s)$$

   a. If 0.700 moles Ag is reacted with 10.0 g S, is sulfur or aluminum the limiting reactant?
   b. How many grams of Ag_2S will be produced?

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5.10: Theoretical Yield and Percent Yield



Figure 5.10.1 (Public Domain; Linda Bartlett and the National Cancer Institute via Wikipedia)

Can we save some money?

The world of pharmaceutical production is an expensive one. Many drugs have several steps in their synthesis and use costly chemicals. A great deal of research takes place to develop better ways to make drugs faster and more efficiently. Studying how much of a compound is produced in any given reaction is an important part of cost control.

Percent Yield

Chemical reactions in the real world do not always go exactly as planned on paper. In the course of an experiment, many things will contribute to the formation of less product than would be predicted. Besides spills and other experimental errors, there are often losses due to an incomplete reaction, undesirable side reactions, etc. Chemists need a measurement that indicates how successful a reaction has been. This measurement is called the percent yield.

To compute the percent yield, it is first necessary to determine how much of the product should be formed based on stoichiometry. This is called the **theoretical yield**, the maximum amount of product that could be formed from the given amounts of reactants. The **actual yield** is the amount of product that is actually formed when the reaction is carried out in the laboratory. The **percent yield** is the ratio of the actual yield to the theoretical yield, expressed as a percentage:

$$\text{Percent Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100\%$$

Percent yield is very important in the manufacture of products. Much time and money is spent improving the percent yield for chemical production. When complex chemicals are synthesized by many different reactions, one step with a low percent yield can quickly cause a large waste of reactants and unnecessary expense.

Typically, percent yields are understandably less than 100% because of the reasons previously indicated. However, percent yields greater than 100% are possible if the measured product of the reaction contains impurities that cause its mass to be greater than it actually would be if the product was pure. When a chemist synthesizes a desired chemical, he or she is always careful to purify the products of the reaction.

Example 5.10.1: Calculating the Theoretical Yield and the Percent Yield

Potassium chlorate decomposes upon slight heating in the presence of a catalyst, according to the reaction below.

$$2KClO_3\,(s) \rightarrow 2KCl\,(s) + 3O_2\,(g)$$

In a certain experiment, $40.0\ g\ KClO_3$ is heated until it completely decomposes. What is the theoretical yield of oxygen gas? The experiment is performed, the oxygen gas is collected, and its mass is found to be $14.9\ g$. What is the percent yield for the reaction?

Solution

First, we will calculate the theoretical yield based on the stoichiometry.

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

Known

- Molar mass $KClO_3 = 122.55$ g/mol
- Molar mass $O_2 = 32.00$ g/mol

Unknown

- theoretical yield O_2 = ? g

Apply stoichiometry to convert from the mass of a reactant to the mass of a product:

$$\text{g KClO}_3 \rightarrow \text{mol KClO}_3 \rightarrow \text{mol O}_2 \rightarrow \text{g O}_2$$

Step 2: Solve.

$$40.0\ \text{g KClO}_3 \times \frac{1\ \text{mol KClO}_3}{122.55\ \text{g KClO}_3} \times \frac{3\ \text{mol O}_2}{2\ \text{mol KClO}_3} \times \frac{32.00\ \text{g O}_2}{1\ \text{mol O}_2} = 15.7\ \text{g O}_2$$

The theoretical yield of O_2 is 15.7 g.

Step 3: Think about your result.

The mass of oxygen gas must be less than the 40.0 g of potassium chlorate that was decomposed.

Now we will use the actual yield and the theoretical yield to calculate the percent yield.

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

Known

- Actual yield $= 14.9$ g
- Theoretical yield $= 15.7$ g

Unknown

- Percent yield = ? %

$$\text{Percent Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100\%$$

Use the percent yield equation above.

Step 2: Solve.

$$\text{Percent Yield} = \frac{14.9\ \text{g}}{15.7\ \text{g}} \times 100\% = 94.9\%$$

Step 3: Think about your result.

Since the actual yield is slightly less than the theoretical yield, the percent yield is just under 100%.



Summary

- Theoretical yield is calculated based on the stoichiometry of the chemical equation.
- The actual yield is experimentally determined.
- The percent yield is determined by calculating the ratio of actual yield/theoretical yield.

Review

1. What do we need in order to calculate theoretical yield?
2. If I spill some of the product before I weigh it, how will that affect the actual yield?
3. How will spilling some of the product affect the percent yield?
4. I make a product and weigh it before it is dry. How will that affect the actual yield?

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5.11: Percent Error

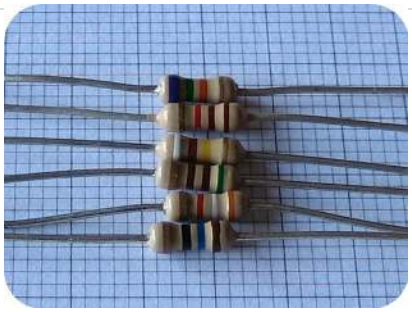


Figure 5.11.1 (Public Domain; Vald Kliper via Wikipedia)

How does an electrical circuit work?

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

Percent Error

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

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

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

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

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

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

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



Summary

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

Review

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

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CHAPTER OVERVIEW

6: Organic Chemistry

6.1: Organic Chemistry
6.2: Structures and Names of Alkanes
6.3: Branched-Chain Alkanes
6.4: Condensed Structural and Line-Angle Formulas
6.5: IUPAC Nomenclature
6.6: Constitutional Isomers
6.7: Physical Properties of Alkanes
6.8: Chemical Properties of Alkanes
6.9: Cycloalkanes
6.10: Alkenes- Structures and Names
6.11: Physical Properties of Alkenes
6.12: Chemical Properties of Alkenes
6.13: Polymers
6.14: Alkynes
6.15: Aromatic Compounds- Benzene
6.16: Structure and Nomenclature of Aromatic Compounds

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6.1: Organic Chemistry

Learning Objectives

- To recognize the composition and properties typical of organic and inorganic compounds.

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.

$$AgOCN + NH_4Cl \rightarrow AgCl + NH_4OCN$$

However, when heated, ammonium cyanate continues to react and rearranges into urea (NH_2CONH_2), a well-known organic material readily isolated from urine.

$$NH_4OCN \longrightarrow NH_2CONH_2$$

This observation 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.

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**.

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6.2: Structures and Names of Alkanes

Learning Objectives

- To identify and name simple (straight-chain) alkanes given formulas and write formulas for straight-chain alkanes given their names.

We begin our study of organic chemistry with the hydrocarbons, the simplest organic compounds, which are composed of carbon and hydrogen atoms only. As we noted, there are several different kinds of hydrocarbons. They are distinguished by the types of bonding between carbon atoms and the properties that result from that bonding. Hydrocarbons with only carbon-to-carbon single bonds (C–C) and existing as a continuous chain of carbon atoms also bonded to hydrogen atoms are called alkanes (or saturated hydrocarbons). *Saturated*, in this case, means that each carbon atom is bonded to four other atoms (hydrogen or carbon)—the most possible; there are no double or triple bonds in the molecules.

> 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).

We previously introduced the three simplest alkanes—methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) and they are shown again in Figure **6.2.1**.

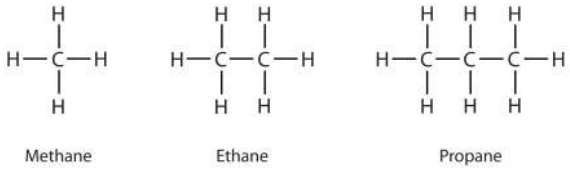


Figure **6.2.1**: The Three Simplest Alkanes

The flat representations shown do not accurately portray bond angles or molecular geometry. Methane has a tetrahedral shape that chemists often portray with wedges indicating bonds coming out toward you and dashed lines indicating bonds that go back away from you. An ordinary solid line indicates a bond in the plane of the page. Recall that the VSEPR theory correctly predicts a tetrahedral shape for the methane molecule (Figure **6.2.2**).

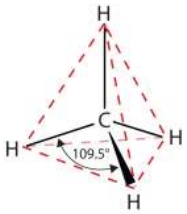


Figure **6.2.2**: The Tetrahedral Methane Molecule

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 **6.2.1**.

Table **6.2.1**: The First 10 Straight-Chain Alkanes

Name	Molecular Formula (C_nH_{2n+2})	Condensed Structural Formula	Number of Possible Isomers
methane	CH_4	CH_4	—
ethane	C_2H_6	CH_3CH_3	—
propane	C_3H_8	$CH_3CH_2CH_3$	—
butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2
pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	3
hexane	C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	5
heptane	C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	9
octane	C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	18
nonane	C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	35
decane	$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	75

Consider the series in Figure **6.2.3**. 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.

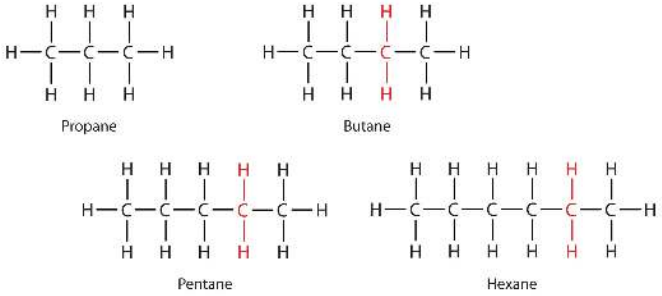


Figure **6.2.3**: Members of a Homologous Series. Each succeeding formula incorporates one carbon atom and two hydrogen atoms more than the previous formula.

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 $C_8H_{(2\times 8)+2} = C_8H_{18}$.

Key Takeaway

- Simple alkanes exist as a homologous series, in which adjacent members differ by a CH_2 unit.

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6.3: Branched-Chain Alkanes

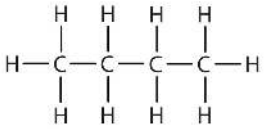
Learning Objectives

- To learn how alkane molecules can have branched chains and recognize compounds that are isomers.

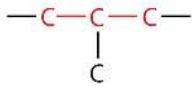
We can write the structure of butane (C_4H_{10}) by stringing four carbon atoms in a row,

–C–C–C–C–

and then adding enough hydrogen atoms to give each carbon atom four bonds:



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:



Now we add enough hydrogen atoms to give each carbon four bonds.

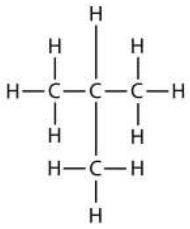


Figure **6.3.1**).

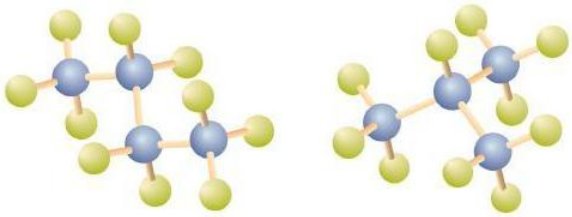
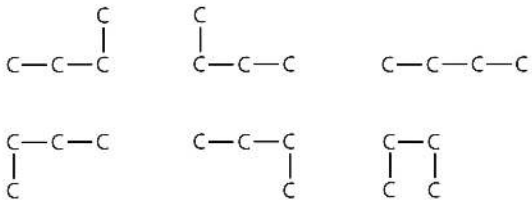


Figure **6.3.1**: Butane and Isobutane. The ball-and-stick models of these two compounds show them to be isomers; both have the molecular formula C_4H_{10}.

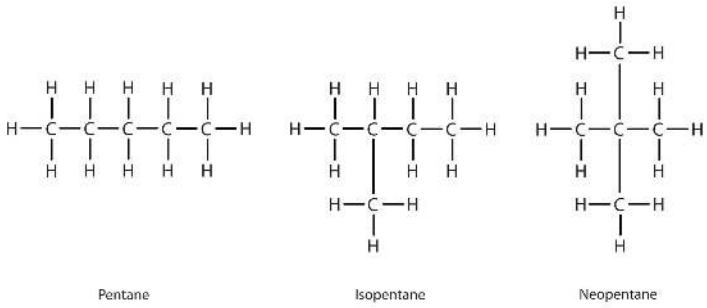
Notice that C_4H_{10} is depicted with a bent chain in Figure **6.3.1**. The four-carbon chain may be bent in various ways because the groups can rotate freely about the C–C bonds. However, this rotation does not change the identity of the compound. It is important to realize that bending a chain does *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 **6.3.1**.

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}. (Table 12.1.1 from the previous section has a column identifying the number of possible isomers for the first 10 straight-chain alkanes.) 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.



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.

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6.4: Condensed Structural and Line-Angle Formulas

Learning Objectives

- Write condensed structural formulas for alkanes given complete structural formulas.
- Draw line-angle formulas given structural formulas.

We use several kinds of formulas to describe organic compounds. A *molecular formula* shows only the kinds and numbers of atoms in a molecule. For example, the molecular formula C_4H_{10} tells us there are 4 carbon atoms and 10 hydrogen atoms in a molecule, but it doesn't distinguish between butane and isobutane. A structural formula shows all the carbon and hydrogen atoms and the bonds attaching them. Thus, structural formulas identify the specific isomers by showing the order of attachment of the various atoms.

Unfortunately, structural formulas are difficult to type/write and take up a lot of space. Chemists often use condensed structural formulas to alleviate these problems. 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, 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:



Parentheses in condensed structural formulas indicate that the enclosed grouping of atoms is attached to the adjacent carbon atom.

Key Takeaways

- 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.

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6.5: IUPAC Nomenclature

Learning Objectives

- To name alkanes by the IUPAC system and write formulas for alkanes given IUPAC names

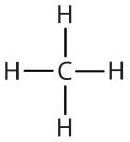
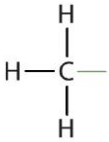
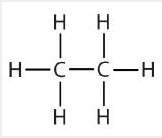
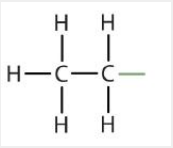
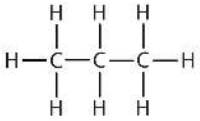
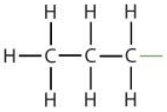
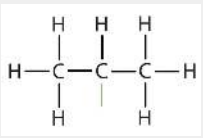
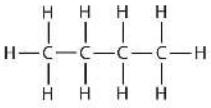
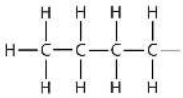
As noted in previously, the number of isomers increases rapidly as the number of carbon atoms increases. There are 3 pentanes, 5 hexanes, 9 heptanes, and 18 octanes. It would be difficult to assign unique individual names that we could remember. A systematic way of naming hydrocarbons and other organic 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. (Some of the names we used earlier, such as isobutane, isopentane, and neopentane, do not follow these rules and are called *common names*.) A stem name (Table **6.5.1**) 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. For now, we will consider only those substituents called alkyl groups.

Table **6.5.1**: Stems That Indicate the Number of Carbon Atoms in Organic Molecules

Stem	Number
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

An alkyl group is a group of atoms that results when one hydrogen atom is removed from an alkane. The group is named by replacing the *-ane* suffix of the parent hydrocarbon with *-yl*. For example, the $-CH_3$ group derived from methane (CH_4) results from subtracting one hydrogen atom and is called a *methyl group*. The alkyl groups we will use most frequently are listed in Table **6.5.2**. Alkyl groups are not independent molecules; they are parts of molecules that we consider as a unit to name compounds systematically.

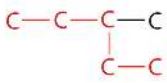
Table **6.5.2**: Common Alkyl Groups

Parent Alkane		Alkyl Group		Condensed Structural Formula
methane		methyl		$CH_3–$
ethane		ethyl		$CH_3CH_2–$
propane		propyl		$CH_3CH_2CH_2–$
		isopropyl		$(CH_3)_2CH–$
butane		butyl*		$CH_3CH_2CH_2CH_2–$

*There are four butyl groups, two derived from butane and two from isobutane. We will introduce the other three where appropriate.

Simplified IUPAC rules for naming alkanes are as follows (demonstrated in Example **6.5.1**).

1. **Name alkanes according to the LCC (longest continuous chain) of carbon atoms in the molecule (rather than the total number of carbon atoms).** This LCC, considered the parent chain, determines the base name, to which we add the suffix *-ane* to indicate that the molecule is an alkane.
2. **If the hydrocarbon is branched, number the carbon atoms of the LCC.** Numbers are assigned in the direction that gives the lowest numbers to the carbon atoms with attached substituents. Hyphens are used to separate numbers from the names of substituents; commas separate numbers from each other. (The LCC need not be written in a straight line; for example, the LCC in the following has five carbon atoms.)

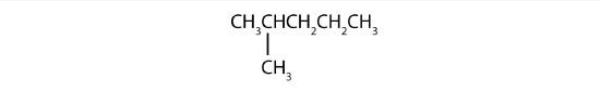
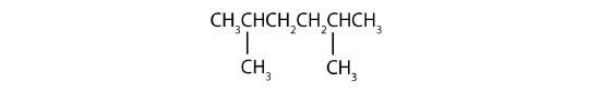
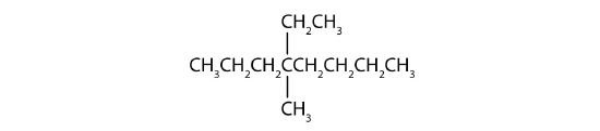


3. **Place the names of the substituent groups in alphabetical order before the name of the parent compound.** If the same alkyl group appears more than once, the numbers of all the carbon atoms to which it is attached are expressed. If the same group appears more than once on the same carbon atom, the number of that carbon atom is repeated as many times as the group appears. Moreover, the number of identical groups is indicated by the Greek prefixes *di-*, *tri-*, *tetra-*, and so on. These prefixes are *not* considered in determining the alphabetical order of the substituents. For example, ethyl is listed before dimethyl; the di- is simply ignored. The last alkyl group named is prefixed to the name of the parent alkane to form one word.

When these rules are followed, every unique compound receives its own exclusive name. The rules enable us to not only name a compound from a given structure but also draw a structure from a given name. The best way to learn how to use the IUPAC system is to put it to work, not just memorize the rules. It's easier than it looks.

Example 6.5.1

Name each compound.

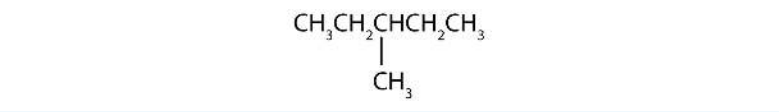
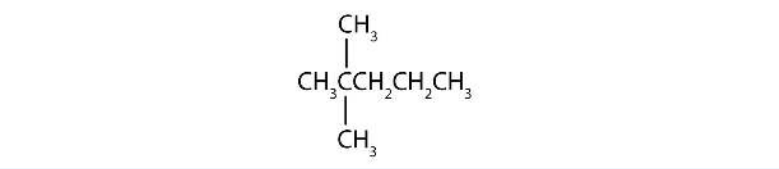
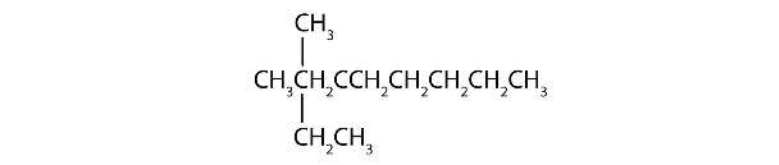
1. 
2. 
3. 

Solution

1. The LCC has five carbon atoms, and so the parent compound is pentane (rule 1). There is a methyl group (rule 2) attached to the second carbon atom of the pentane chain. The name is therefore 2-methylpentane.
2. The LCC has six carbon atoms, so the parent compound is hexne (rule 1). Methyl groups (rule 2) are attached to the second and fifth carbon atoms. The name is 2,5-dimethylhexane.
3. The LCC has eight carbon atoms, so the parent compound is octane (rule 1). There are methyl and ethyl groups (rule 2), both attached to the fourth carbon atom (counting from the *right* gives this carbon atom a lower number; rule 3). The correct name is thus 4-ethyl-4-methyloctane.

Exercise 6.5.1

Name each compound.

1. 
2. 
3. 

Example 6.5.2

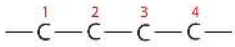
Draw the structure for each compound.

a. 2,3-dimethylbutane
b. 4-ethyl-2-methylheptane

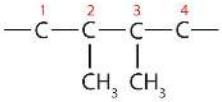
Solution a

In drawing structures, always start with the parent chain.

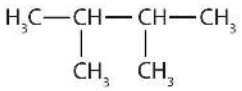
The parent chain is butane, indicating four carbon atoms in the LCC.



Then add the groups at their proper positions. You can number the parent chain from either direction as long as you are consistent; just don't change directions before the structure is done. The name indicates two methyl (CH_3) groups, one on the second carbon atom and one on the third.

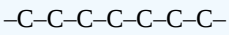


Finally, fill in all the hydrogen atoms, keeping in mind that each carbon atom must have four bonds.

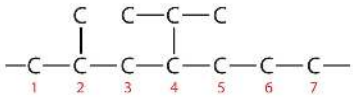


Solution b

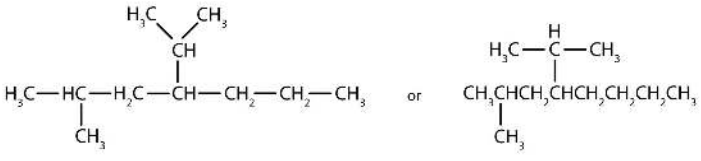
The parent chain is heptane in this case, indicating seven carbon atoms in the LCC.



Adding the groups at their proper positions gives



Filling in all the hydrogen atoms gives the following condensed structural formulas:



Note that the bonds (dashes) can be shown or not; sometimes they are needed for spacing.

Exercise 6.5.2

Draw the structure for each compound.

a. 4-ethyloctane
b. 3-ethyl-2-methylpentane
c. 3,3,5-trimethylheptane

Key Takeaway

- Alkanes have both common names and systematic names, specified by IUPAC.

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6.6: Constitutional Isomers

Learning Objective

- Introduction to constitutional isomers using alkanes

Evaluate the two molecules below (Figure **6.6.1**).

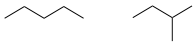


Figure **6.6.1**. Two alkanes for comparison

- How are they the same?
- How are they different?

Two molecules which have the same molecular formula but different structural formulas, or bonding arrangements, are known as **constitutional isomers.**

Pentane is an alkane with five carbon atoms. It has three constitutional isomers, shown below.

Figure **6.6.2**. Unbranched isomer of pentane



Figure **6.6.3**. Branched constitutional isomer of pentane



Figure **6.6.4**. Branched constitutional isomer of pentane

Practice Questions

1. Draw three constitutional isomers of heptane.

2. Circle the constitutional isomers of hexane in the figure below. Why are the remaining molecules not considered to be constitutional isomers of hexane?

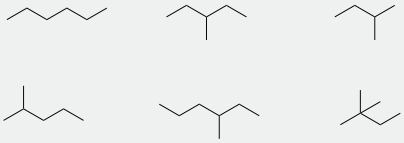


Figure **6.6.5**

3. Draw the constitutional isomer of hexane that is missing.

4. What is the minimum number of carbons in the chain of an alkane to be able to have a constitutional isomer?

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6.7: Physical Properties of Alkanes

Learning Objectives

- To identify the physical properties of alkanes and describe trends in these properties.

Because alkanes have relatively predictable physical properties and undergo relatively few chemical reactions other than combustion, they serve as a basis of comparison for the properties of many other organic compound families. Let's consider their physical properties first.

Table **6.7.1** describes some of the properties of some of the first 10 straight-chain alkanes. Because alkane molecules are nonpolar, they are insoluble in water, which is a polar solvent, but are soluble in nonpolar and slightly polar solvents. Consequently, alkanes themselves are commonly used as solvents for organic substances of low polarity, such as fats, oils, and waxes. Nearly all alkanes have densities less than 1.0 g/mL and are therefore less dense than water (the density of H_2O is 1.00 g/mL at 20°C). These properties explain why oil and grease do not mix with water but rather float on its surface.

Table **6.7.1**: Physical Properties of Some Alkanes

Molecular Name	Formula	Melting Point (°C)	Boiling Point (°C)	Density (20°C)*	Physical State (at 20°C)
methane	CH_4	–182	–164	0.668 g/L	gas
ethane	C_2H_6	–183	–89	1.265 g/L	gas
propane	C_3H_8	–190	–42	1.867 g/L	gas
butane	C_4H_{10}	–138	–1	2.493 g/L	gas
pentane	C_5H_{12}	–130	36	0.626 g/mL	liquid
hexane	C_6H_{14}	–95	69	0.659 g/mL	liquid
octane	C_8H_{18}	–57	125	0.703 g/mL	liquid
decane	$C_{10}H_{22}$	–30	174	0.730 g/mL	liquid

*Note the change in units going from gases (grams per liter) to liquids (grams per milliliter). Gas densities are at 1 atm pressure.



Figure **6.7.1**: Oil Spills. Crude oil coats the water's surface in the Gulf of Mexico after the *Deepwater Horizon* oil rig sank following an explosion. The leak was a mile below the surface, making it difficult to estimate the size of the spill. One liter of oil can create a slick 2.5 hectares (6.3 acres) in size. This and similar spills provide a reminder that hydrocarbons and water don't mix. Source: Photo courtesy of NASA Goddard / MODIS Rapid Response Team, NASA.gov, Topics, Earth Features, Oil Spill(opens in new window) [www.nasa.gov].

Looking Closer: Gas Densities and Fire Hazards

Table **6.7.1** indicates that the first four members of the alkane series are gases at ordinary temperatures. Natural gas is composed chiefly of methane, which has a density of about 0.67 g/L. The density of air is about 1.29 g/L. Because natural gas is less dense than air, it rises. When a natural-gas leak is detected and shut off in a room, the gas can be removed by opening an upper window. On the other hand, bottled gas can be either propane (density 1.88 g/L) or butanes (a mixture of butane and isobutane; density about 2.5 g/L). Both are much heavier than air (density 1.2 g/L). If bottled gas escapes into a building, it collects near the floor. This presents a much more serious fire hazard than a natural-gas leak because it is more difficult to rid the room of the heavier gas.

Also shown in Table **6.7.1** are the boiling points of the straight-chain alkanes increase with increasing molar mass. This general rule holds true for the straight-chain homologs of all organic compound families. Larger molecules have greater surface areas and consequently interact more strongly; more energy is therefore required to separate them. For a given molar mass, the boiling points of alkanes are relatively low because these nonpolar molecules have only weak dispersion forces to hold them together in the liquid state.

Looking Closer: An Alkane Basis for Properties of Other Compounds

An understanding of the physical properties of the alkanes is important in that petroleum and natural gas and the many products derived from them—gasoline, bottled gas, solvents, plastics, and more—are composed primarily of alkanes. This understanding is also vital because it is the basis for describing the properties of other organic and biological compound families. For example, large portions of the structures of lipids consist of nonpolar alkyl groups. Lipids include the dietary fats and fatlike compounds called phospholipids and sphingolipids that serve as structural components of living tissues. These compounds have both polar and nonpolar groups, enabling them to bridge the gap between water-soluble and water-insoluble phases. This characteristic is essential for the selective permeability of cell membranes.

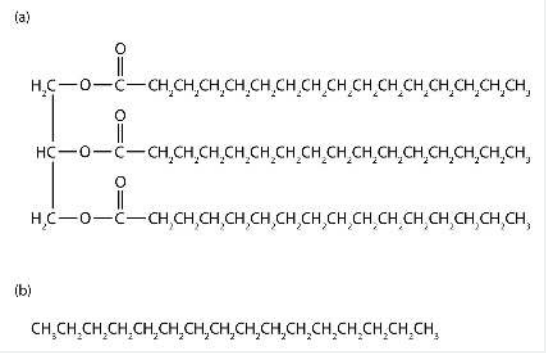


Figure **6.7.2**: Tripalmitin (a), a typical fat molecule, has long hydrocarbon chains typical of most lipids. Compare these chains to hexadecane (b), an alkane with 16 carbon atoms

Key Takeaway

- Alkanes are nonpolar compounds that are low boiling and insoluble in water.

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6.8: Chemical Properties of Alkanes

Learning Objectives

- To identify the main chemical properties of alkanes.

Alkane molecules are nonpolar and therefore generally do not react with ionic compounds such as most laboratory acids, bases, oxidizing agents, or reducing agents. Consider butane as an example:

$$\underset{\text{butane}}{CH_3CH_2CH_2CH_3} + OH^- \longrightarrow \text{no reaction}$$

$$+ H^+ \longrightarrow \text{no reaction}$$

$$+ MnO_4^- \longrightarrow \text{no reaction}$$

Butane plus O H superscript negative sign yields no reaction. There is also no reaction of butane with H superscript positive sign and Mn O subscript 4 superscript negative sign.

Neither positive ions nor negative ions are attracted to a nonpolar molecule. In fact, the alkanes undergo so few reactions that they are sometimes called *paraffins*, from the Latin *parum affinis*, meaning "little affinity."

Two important reactions that the alkanes do undergo are combustion and halogenation. Nothing happens when alkanes are merely mixed with oxygen (O_2) at room temperature, but when a flame or spark provides the activation energy, a highly exothermic combustion reaction proceeds vigorously. For methane (CH_4), the reaction is as follows:

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O + \text{heat}$$

If the reactants are adequately mixed and there is sufficient oxygen, the only products are carbon dioxide (CO_2), water (H_2O), and heat—heat for cooking foods, heating homes, and drying clothes. Because conditions are rarely ideal, however, other products are frequently formed. When the oxygen supply is limited, carbon monoxide (CO) is a by-product:

$$2\,CH_4 + 3\,O_2 \rightarrow 2\,CO + 4\,H_2O$$

This reaction is responsible for dozens of deaths each year from unventilated or improperly adjusted gas heaters. (Similar reactions with similar results occur with kerosene heaters.)

Alkanes also react with the halogens chlorine (Cl_2) and bromine (Br_2) in the presence of ultraviolet light or at high temperatures to yield chlorinated and brominated alkanes. For example, chlorine reacts with excess methane (CH_4) to give methyl chloride (CH_3Cl).

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

With more chlorine, a mixture of products is obtained: CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. Fluorine (F_2), the lightest halogen, combines explosively with most hydrocarbons. Iodine (I_2) is relatively unreactive. Fluorinated and iodinated alkanes are produced by indirect methods.

Key Takeaway

- Alkanes react with oxygen (combustion) and with halogens (halogenation).

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6.9: Cycloalkanes

Learning Objectives

- To name cycloalkanes given their formulas and write formulas for these compounds given their names.

The hydrocarbons we have encountered so far have been composed of molecules with open-ended chains of carbon atoms. When a chain contains three or more carbon atoms, the atoms can join to form *ring* or *cyclic* structures. The simplest of these cyclic hydrocarbons has the formula C_3H_6. Each carbon atom has two hydrogen atoms attached (Figure **6.9.1**) and is called cyclopropane.

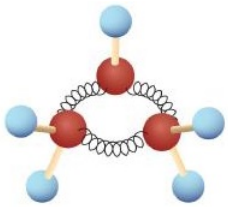
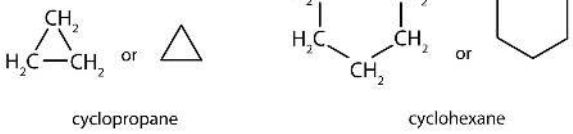


Figure **6.9.1**: Ball-and-Spring Model of Cyclopropane. The springs are bent to join the carbon atoms.

To Your Health: Cyclopropane as an Anesthetic

With its boiling point of −33°C, cyclopropane is a gas at room temperature. It is also a potent, quick-acting anesthetic with few undesirable side effects in the body. It is no longer used in surgery, however, because it forms explosive mixtures with air at nearly all concentrations.

The cycloalkanes—cyclic hydrocarbons with only single bonds—are named by adding the prefix *cyclo-* to the name of the open-chain compound having the same number of carbon atoms as there are in the ring. Thus the name for the cyclic compound C_4H_8 is cyclobutane. The carbon atoms in cyclic compounds can be represented by *line-angle formulas* that result in regular geometric figures. Keep in mind, however, that each corner of the geometric figure represents a carbon atom plus as many hydrogen atoms as needed to give each carbon atom four bonds.



Some cyclic compounds have substituent groups attached. Example **6.9.1** interprets the name of a cycloalkane with a single substituent group.

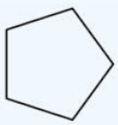
Example 6.9.1

Draw the structure for each compound.

a. cyclopentane
b. methylcyclobutane

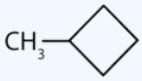
Solution a

The name *cyclopentane* indicates a cyclic (cyclo) alkane with five (pent-) carbon atoms. It can be represented as a pentagon.



Solution b

The name *methylcyclobutane* indicates a cyclic alkane with four (but-) carbon atoms in the cyclic part. It can be represented as a square with a CH_3 group attached.



? Exercise 6.9.1

Draw the structure for each compound.

a. cycloheptane
b. ethylcyclohexane

The properties of cyclic hydrocarbons are generally quite similar to those of the corresponding open-chain compounds. So cycloalkanes (with the exception of cyclopropane, which has a highly strained ring) act very much like noncyclic alkanes. Cyclic structures containing five or six carbon atoms, such as cyclopentane and cyclohexane, are particularly stable. We will see later that some carbohydrates (sugars) form five- or six-membered rings in solution.

The cyclopropane ring is strained because the C–C–C angles are 60°, and the preferred (tetrahedral) bond angle is 109.5°. (This strain is readily evident when you try to build a ball-and-stick model of cyclopropane; see Figure **6.9.1**.) Cyclopentane and cyclohexane rings have little strain because the C–C–C angles are near the preferred angles.

Key Takeaway

- Many organic compounds have cyclic structures.

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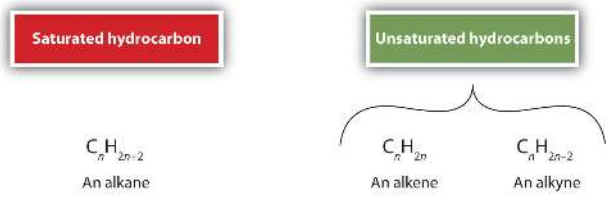
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6.10: Alkenes- Structures and Names

Learning Objectives

- To name alkenes given formulas and write formulas for alkenes given names.

As noted before, alkenes are hydrocarbons with carbon-to-carbon double bonds ($R_2C{=}CR_2$) and alkynes are hydrocarbons with carbon-to-carbon triple bonds (R–C≡C–R). Collectively, they are called unsaturated hydrocarbons because they have fewer hydrogen atoms than does an alkane with the same number of carbon atoms, as is indicated in the following general formulas:

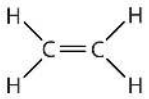


Some representative alkenes—their names, structures, and physical properties—are given in Table **6.10.1**.

Table **6.10.1**: Physical Properties of Some Selected Alkenes

IUPAC Name	Molecular Formula	Condensed Structural Formula	Melting Point (°C)	Boiling Point (°C)
ethene	C_2H_4	$CH_2{=}CH_2$	–169	–104
propene	C_3H_6	$CH_2{=}CHCH_3$	–185	–47
1-butene	C_4H_8	$CH_2{=}CHCH_2CH_3$	–185	–6
1-pentene	C_5H_{10}	$CH_2{=}CH(CH_2)_2CH_3$	–138	30
1-hexene	C_6H_{12}	$CH_2{=}CH(CH_2)_3CH_3$	–140	63
1-heptene	C_7H_{14}	$CH_2{=}CH(CH_2)_4CH_3$	–119	94
1-octene	C_8H_{16}	$CH_2{=}CH(CH_2)_5CH_3$	–102	121

We used only condensed structural formulas in Table **6.10.1**. Thus, $CH_2{=}CH_2$ stands for



The double bond is shared by the two carbons and does not involve the hydrogen atoms, although the condensed formula does not make this point obvious. Note that the molecular formula for ethene is C_2H_4, whereas that for ethane is C_2H_6.

The first two alkenes in Table **6.10.1**, ethene and propene, are most often called by their common names—ethylene and propylene, respectively (Figure **6.10.1**). Ethylene is a major commercial chemical. The US chemical industry produces about 25 billion kilograms of ethylene annually, more than any other synthetic organic chemical. More than half of this ethylene goes into the manufacture of polyethylene, one of the most familiar plastics. Propylene is also an important industrial chemical. It is converted to plastics, isopropyl alcohol, and a variety of other products.

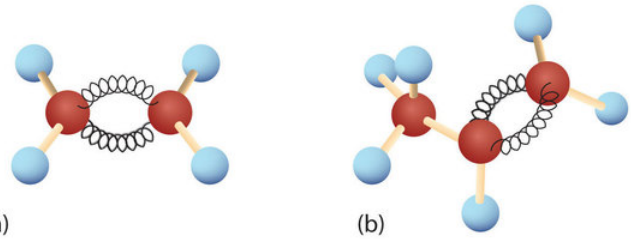
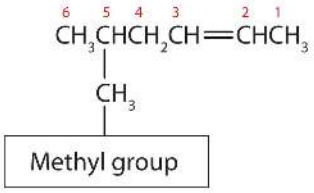


Figure **6.10.1**: Ethene and Propene. The ball-and-spring models of ethene/ethylene (a) and propene/propylene (b) show their respective shapes, especially bond angles.

Although there is only one alkene with the formula C_2H_4 (ethene) and only one with the formula C_3H_6 (propene), there are several alkenes with the formula C_4H_8.

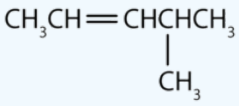
Here are some basic rules for naming alkenes from the International Union of Pure and Applied Chemistry (IUPAC):

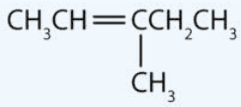
1. The longest chain of carbon atoms *containing the double bond* is considered the parent chain. It is named using the same stem as the alkane having the same number of carbon atoms but ends in *-ene* to identify it as an alkene. Thus the compound CH_2=$CHCH_3$ is *propene*.
2. If there are four or more carbon atoms in a chain, we must indicate the position of the double bond. The carbons atoms are numbered so that the first of the two that are doubly bonded is given the lower of the two possible numbers.The compound CH_3CH=$CHCH_2CH_3$, for example, has the double bond between the second and third carbon atoms. Its name is 2-pentene (not 3-pentene).
3. Substituent groups are named as with alkanes, and their position is indicated by a number. Thus, the structure below is 5-methyl-2-hexene. Note that the numbering of the parent chain is always done in such a way as to give the double bond the lowest number, even if that causes a substituent to have a higher number. *The double bond always has priority in numbering.*



Example 6.10.1

Name each compound.

a. 

b. 

Solution

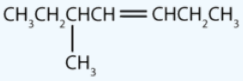
a. The longest chain containing the double bond has five carbon atoms, so the compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the fourth carbon atom (rule 3), so the compound's name is 4-methyl-2-pentene.

b. The longest chain containing the double bond has five carbon atoms, so the parent compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the third carbon atom (rule 3), so the compound's name is 3-methyl-2-pentene.

Exercise 6.10.1

Name each compound.

a. $CH_3CH_2CH_2CH_2CH_2CH{=}CHCH_3$

b. 

Answer

Just as there are cycloalkanes, there are *cycloalkenes*. These compounds are named like alkenes, but with the prefix *cyclo-* attached to the beginning of the parent alkene name.

Example 6.10.2

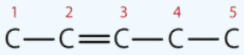
Draw the structure for each compound.

a. 3-methyl-2-pentene
b. cyclohexene

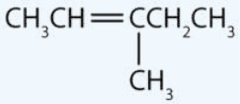
Solution

a.

First write the parent chain of five carbon atoms: C–C–C–C–C. Then add the double bond between the second and third carbon atoms:

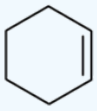


Now place the methyl group on the third carbon atom and add enough hydrogen atoms to give each carbon atom a total of four bonds.



b

First, consider what each of the three parts of the name means. *Cyclo* means a ring compound, *hex* means 6 carbon atoms, and *-ene* means a double bond.



Exercise 6.10.2

Draw the structure for each compound.

a. 2-ethyl-1-hexene
b. cyclopentene

Key Takeaway

- Alkenes are hydrocarbons with a carbon-to-carbon double bond.

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6.11: Physical Properties of Alkenes

Learning Objectives

- To identify the physical properties of alkenes and describe trends in these properties.

The physical properties of alkenes are similar to those of the alkanes. The table at the start of the chapter shows that the boiling points of straight-chain alkenes increase with increasing molar mass, just as with alkanes. For molecules with the same number of carbon atoms and the same general shape, the boiling points usually differ only slightly, just as we would expect for substances whose molar mass differs by only 2 u (equivalent to two hydrogen atoms). Like other hydrocarbons, the alkenes are insoluble in water but soluble in organic solvents.

Looking Closer: Environmental Note

Alkenes occur widely in nature. Ripening fruits and vegetables give off ethylene, which triggers further ripening. Fruit processors artificially introduce ethylene to hasten the ripening process; exposure to as little as 0.1 mg of ethylene for 24 h can ripen 1 kg of tomatoes. Unfortunately, this process does not exactly duplicate the ripening process, and tomatoes picked green and treated this way don't taste much like vine-ripened tomatoes fresh from the garden.



The bright red color of tomatoes is due to lycopene—a polyene.

Other alkenes that occur in nature include 1-octene, a constituent of lemon oil, and octadecene ($C_{18}H_{36}$) found in fish liver. Dienes (two double bonds) and polyenes (three or more double bonds) are also common. Butadiene (CH_2=$CHCH$=CH_2) is found in coffee. Lycopene and the carotenes are isomeric polyenes ($C_{40}H_{56}$) that give the attractive red, orange, and yellow colors to watermelons, tomatoes, carrots, and other fruits and vegetables. Vitamin A, essential to good vision, is derived from a carotene. The world would be a much less colorful place without alkenes.

Key Takeaway

- The physical properties of alkenes are much like those of the alkanes: their boiling points increase with increasing molar mass, and they are insoluble in water.

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6.12: Chemical Properties of Alkenes

Learning Objectives

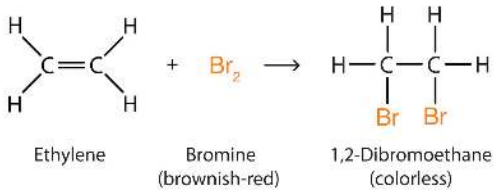
- To write equations for the addition reactions of alkenes with hydrogen, halogens, and water

Alkenes are valued mainly for addition reactions, in which one of the bonds in the double bond is broken. Each of the carbon atoms in the bond can then attach another atom or group while remaining joined to each other by a single bond. Perhaps the simplest addition reaction is hydrogenation—a reaction with hydrogen (H_2) in the presence of a catalyst such as nickel (Ni) or platinum (Pt).

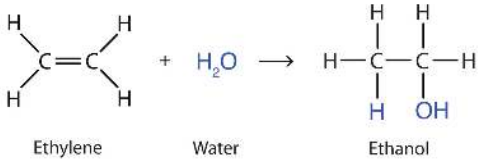


The product is an alkane having the same carbon skeleton as the alkene.

Alkenes also readily undergo halogenation—the addition of halogens. Indeed, the reaction with bromine (Br_2) can be used to test for alkenes. Bromine solutions are brownish red. When we add a Br_2 solution to an alkene, the color of the solution disappears because the alkene reacts with the bromine:



Another important addition reaction is that between an alkene and water to form an alcohol. This reaction, called hydration, requires a catalyst—usually a strong acid, such as sulfuric acid (H_2SO_4):



The hydration reaction is discussed later, where we deal with this reaction in the synthesis of alcohols.

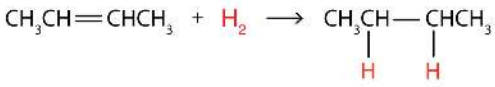
Example 6.12.1

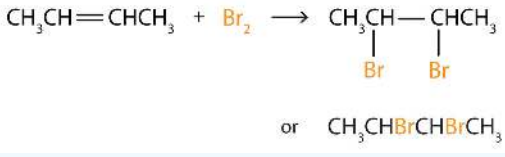
Write the equation for the reaction between $CH_3CH{=}CHCH_3$ and each substance.

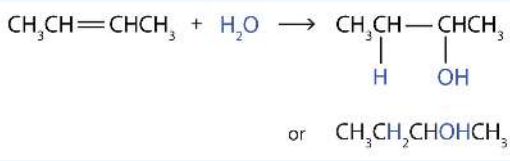
a. H_2 (Ni catalyst)
b. Br_2
c. H_2O (H_2SO_4 catalyst)

Solution

In each reaction, the reagent adds across the double bond.

a. 

b. 

c. 

? Exercise 6.12.1

Write the equation for each reaction.

a. $CH_3CH_2CH{=}CH_2$ with H_2 (Ni catalyst)
b. $CH_3CH{=}CH_2$ with Cl_2
c. $CH_3CH_2CH{=}CHCH_2CH_3$ with H_2O (H_2SO_4 catalyst)

Key Takeaway

- Alkenes undergo addition reactions, adding such substances as hydrogen, bromine, and water across the carbon-to-carbon double bond.

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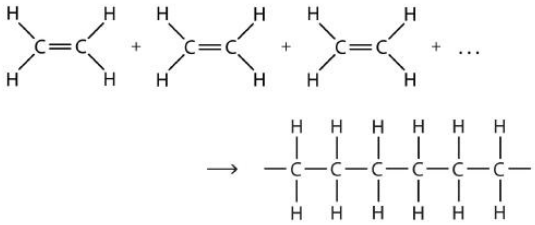
6.13: Polymers

Learning Objectives

- To draw structures for monomers that can undergo addition polymerization and for four-monomer-unit sections of an addition polymer.

The most important commercial reactions of alkenes are *polymerizations*, reactions in which small molecules, referred to in general as monomers (from the Greek *monos*, meaning “one,” and *meros*, meaning “parts”), are assembled into giant molecules referred to as polymers (from the Greek *poly*, meaning “many,” and *meros*, meaning “parts”). A polymer is as different from its monomer as a long strand of spaghetti is from a tiny speck of flour. For example, polyethylene, the familiar waxy material used to make plastic bags, is made from the monomer ethylene—a gas.

There are two general types of polymerization reactions: addition polymerization and condensation polymerization. In addition polymerization, the monomers add to one another in such a way that the polymer contains all the atoms of the starting monomers. Ethylene molecules are joined together in long chains. The polymerization can be represented by the reaction of a few monomer units:



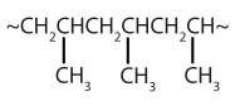
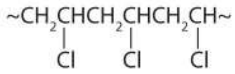
The bond lines extending at the ends in the formula of the product indicate that the structure extends for many units in each direction. Notice that all the atoms—two carbon atoms and four hydrogen atoms—of each monomer molecule are incorporated into the polymer structure. Because displays such as the one above are cumbersome, the polymerization is often abbreviated as follows:

$$n\mathrm{CH_2{=}CH_2} \rightarrow \text{-}\mathrm{CH_2CH_2}\text{-}_n$$

> Many natural materials—such as proteins, cellulose and starch, and complex silicate minerals—are polymers. Artificial fibers, films, plastics, semisolid resins, and rubbers are also polymers. More than half the compounds produced by the chemical industry are synthetic polymers.

Some common addition polymers are listed in Table **6.13.1**. Note that all the monomers have carbon-to-carbon double bonds. Many polymers are mundane (e.g., plastic bags, food wrap, toys, and tableware), but there are also polymers that conduct electricity, have amazing adhesive properties, or are stronger than steel but much lighter in weight.

Table **6.13.1***: Some Addition Polymers*

Monomer	Polymer	Polymer Name	Some Uses
$CH_2=CH_2$	$\sim CH_2CH_2CH_2CH_2CH_2CH_2\sim$	polyethylene	plastic bags, bottles, toys, electrical insulation
$CH_2=CHCH_3$		polypropylene	carpeting, bottles, luggage, exercise clothing
$CH_2=CHCl$		polyvinyl chloride	bags for intravenous solutions, pipes, tubing, floor coverings
$CF_2=CF_2$	$\sim CF_2CF_2CF_2CF_2CF_2CF_2\sim$	polytetrafluoroethylene	nonstick coatings, electrical insulation

Medical Uses of Polymers

An interesting use of polymers is the replacement of diseased, worn out, or missing parts in the body. For example, about a 250,000 hip joints and 500,000 knees are replaced in US hospitals each year. The artificial ball-and-socket hip joints are made of a special steel (the ball) and plastic (the socket). People crippled by arthritis or injuries gain freedom of movement and relief from pain. Patients with heart and circulatory problems can be helped by replacing worn out heart valves with parts based on synthetic polymers. These are only a few of the many biomedical uses of polymers.

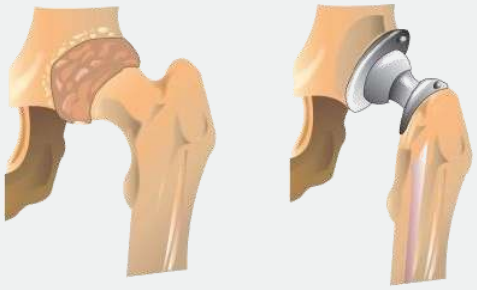


Figure **6.13.1**: Hip Joint Replacement. Synthetic polymers are an important part of a hip joint replacement. The hip is much like a ball-and-socket joint, and total hip replacements mimic this with a metal ball that fits in a plastic cup.

Key Takeaway

- Molecules having carbon-to-carbon double bonds can undergo addition polymerization.

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6.14: Alkynes

Learning Objectives

- Describe the general physical and chemical properties of alkynes.
- Name alkynes given formulas and write formulas for alkynes given names.

The simplest alkyne—a hydrocarbon with carbon-to-carbon triple bond—has the molecular formula C_2H_2 and is known by its common name—acetylene (Figure **6.14.1**). Its structure is H–C≡C–H.

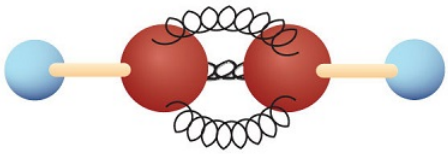


Figure **6.14.1**: Ball-and-Spring Model of Acetylene. Acetylene (ethyne) is the simplest member of the alkyne family.

Acetylene is used in oxyacetylene torches for cutting and welding metals. The flame from such a torch can be very hot. Most acetylene, however, is converted to chemical intermediates that are used to make vinyl and acrylic plastics, fibers, resins, and a variety of other products.

Alkynes are similar to alkenes in both physical and chemical properties. For example, alkynes undergo many of the typical addition reactions of alkenes. The International Union of Pure and Applied Chemistry (IUPAC) names for alkynes parallel those of alkenes, except that the family ending is *-yne* rather than *-ene*. The IUPAC name for acetylene is ethyne. The names of other alkynes are illustrated in the following exercises.

Key Takeaway

- Alkynes are hydrocarbons with carbon-to-carbon triple bonds and properties much like those of alkenes.

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6.15: Aromatic Compounds- Benzene

Learning Objectives

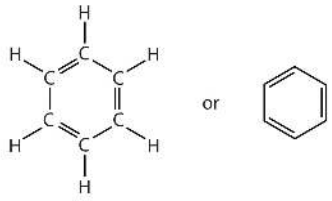
- To describe the bonding in benzene and the way typical reactions of benzene differ from those of the alkenes.

Next we consider a class of hydrocarbons with molecular formulas like those of unsaturated hydrocarbons, but which, unlike the alkenes, do not readily undergo addition reactions. These compounds comprise a distinct class, called aromatic hydrocarbons, with unique structures and properties. We start with the simplest of these compounds. Benzene (C_6H_6) is of great commercial importance, but it also has noteworthy health effects.

The formula C_6H_6 seems to indicate that benzene has a high degree of unsaturation. (Hexane, the saturated hydrocarbon with six carbon atoms has the formula C_6H_{14}—eight more hydrogen atoms than benzene.) However, despite the seeming low level of saturation, benzene is rather unreactive. It does not, for example, react readily with bromine, which, is a test for unsaturation.

Benzene is a liquid that smells like gasoline, boils at 80°C, and freezes at 5.5°C. It is the aromatic hydrocarbon produced in the largest volume. It was formerly used to decaffeinate coffee and was a significant component of many consumer products, such as paint strippers, rubber cements, and home dry-cleaning spot removers. It was removed from many product formulations in the 1950s, but others continued to use benzene in products until the 1970s when it was associated with leukemia deaths. Benzene is still important in industry as a precursor in the production of plastics (such as Styrofoam and nylon), drugs, detergents, synthetic rubber, pesticides, and dyes. It is used as a solvent for such things as cleaning and maintaining printing equipment and for adhesives such as those used to attach soles to shoes. Benzene is a natural constituent of petroleum products, but because it is a known carcinogen, its use as an additive in gasoline is now limited.

To explain the surprising properties of benzene, chemists suppose the molecule has a cyclic, hexagonal, planar structure of six carbon atoms with one hydrogen atom bonded to each. We can write a structure with alternate single and double bonds, either as a full structural formula or as a line-angle formula:



However, these structures do not explain the unique properties of benzene. Furthermore, experimental evidence indicates that all the carbon-to-carbon bonds in benzene are equivalent, and the molecule is unusually stable. Chemists often represent benzene as a hexagon with an inscribed circle:



The inner circle indicates that the valence electrons are shared equally by all six carbon atoms (that is, the electrons are *delocalized*, or spread out, over all the carbon atoms). It is understood that each corner of the hexagon is occupied by one carbon atom, and each carbon atom has one hydrogen atom attached to it. Any other atom or groups of atoms substituted for a hydrogen atom must be shown bonded to a particular corner of the hexagon. We use this modern symbolism, but many scientists still use the earlier structure with alternate double and single bonds.

To Your Health: Benzene and Us

Most of the benzene used commercially comes from petroleum. It is employed as a starting material for the production of detergents, drugs, dyes, insecticides, and plastics. Once widely used as an organic solvent, benzene is now known to have both short- and long-term toxic effects. The inhalation of large concentrations can cause nausea and even death due to respiratory or heart failure, while repeated exposure leads to a progressive disease in which the ability of the bone marrow to make new blood cells is eventually destroyed. This results in a condition called *aplastic anemia*, in which there is a decrease in the numbers of both the red and white blood cells.

Key Takeaway

- Aromatic hydrocarbons appear to be unsaturated, but they have a special type of bonding and do not undergo addition reactions.

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6.16: Structure and Nomenclature of Aromatic Compounds

Learning Objectives

- Recognize aromatic compounds from structural formulas.
- Name aromatic compounds given formulas.
- Write formulas for aromatic compounds given their names.

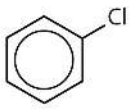
Historically, benzene-like substances were called aromatic hydrocarbons because they had distinctive aromas. Today, an aromatic compound is any compound that contains a benzene ring or has certain benzene-like properties (but not necessarily a strong aroma). You can recognize the aromatic compounds in this text by the presence of one or more benzene rings in their structure. Some representative aromatic compounds and their uses are listed in Table **6.16.1**, where the benzene ring is represented as C_6H_5.

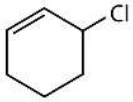
Table **6.16.1**: Some Representative Aromatic Compounds

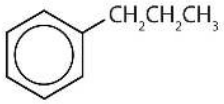
Name	Structure	Typical Uses
aniline	$C_6H_5–NH_2$	starting material for the synthesis of dyes, drugs, resins, varnishes, perfumes; solvent; vulcanizing rubber
benzoic acid	$C_6H_5–COOH$	food preservative; starting material for the synthesis of dyes and other organic compounds; curing of tobacco
bromobenzene	$C_6H_5–Br$	starting material for the synthesis of many other aromatic compounds; solvent; motor oil additive
nitrobenzene	$C_6H_5–NO_2$	starting material for the synthesis of aniline; solvent for cellulose nitrate; in soaps and shoe polish
phenol	$C_6H_5–OH$	disinfectant; starting material for the synthesis of resins, drugs, and other organic compounds
toluene	$C_6H_5–CH_3$	solvent; gasoline octane booster; starting material for the synthesis of benzoic acid, benzaldehyde, and many other organic compounds

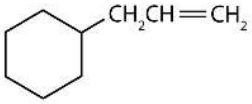
Example 6.16.1

Which compounds are aromatic?

1. 

2. 

3. 

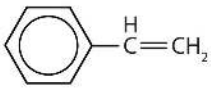
4. 

Solution

1. The compound has a benzene ring (with a chlorine atom substituted for one of the hydrogen atoms); it is aromatic.
2. The compound is cyclic, but it does not have a benzene ring; it is not aromatic.
3. The compound has a benzene ring (with a propyl group substituted for one of the hydrogen atoms); it is aromatic.
4. The compound is cyclic, but it does not have a benzene ring; it is not aromatic.

? Exercise 6.16.1

Which compounds are aromatic?

1. 

2. 

3. 

In the International Union of Pure and Applied Chemistry (IUPAC) system, aromatic hydrocarbons are named as derivatives of benzene. Figure 6.16.1 shows four examples. In these structures, it is immaterial whether the single substituent is written at the top, side, or bottom of the ring: a hexagon is symmetrical, and therefore all positions are equivalent.

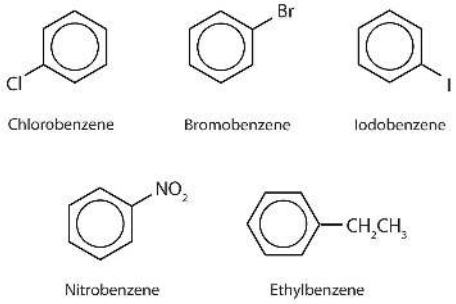


Figure 6.16.1: Some Benzene Derivatives. These compounds are named in the usual way with the group that replaces a hydrogen atom named as a substituent group: Cl as chloro, Br as bromo, I as iodo, NO_2 as nitro, and CH_3CH_2 as ethyl.

Although some compounds are referred to exclusively by IUPAC names, some are more frequently denoted by common names, as is indicated in Table 6.16.1.



When there is more than one substituent, the corners of the hexagon are no longer equivalent, so we must designate the relative positions. There are three possible disubstituted benzenes, and we can use numbers to distinguish them (Figure **6.16.2**). We start numbering at the carbon atom to which one of the groups is attached and count toward the carbon atom that bears the other substituent group by the shortest path.

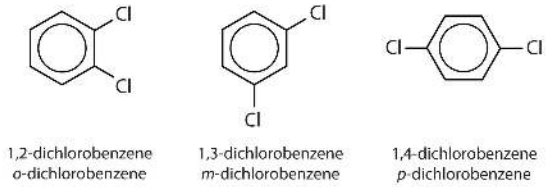
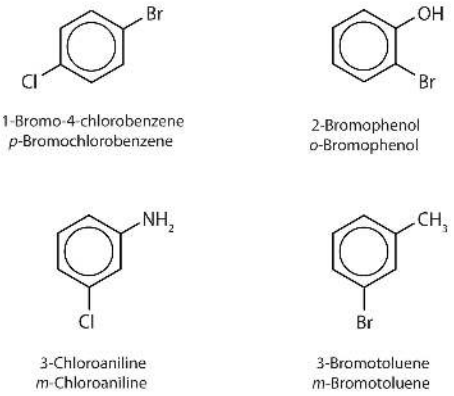


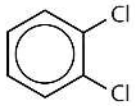
Figure **6.16.2**: The Three Isomeric Dichlorobenzenes

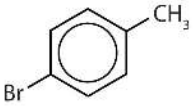
In Figure **6.16.2**, common names are also used: the prefix *ortho* (*o*-) for 1,2-disubstitution, *meta* (*m*-) for 1,3-disubstitution, and *para* (*p*-) for 1,4-disubstitution. The substituent names are listed in alphabetical order. The first substituent is given the lowest number. When a common name is used, the carbon atom that bears the group responsible for the name is given the number 1:

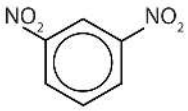


Example 6.16.2

Name each compound using both the common name and the IUPAC name.

1. 

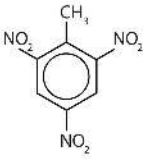
2. 

3. 

Solution

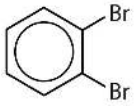
1. The benzene ring has two chlorine atoms (dichloro) in the first and second positions. The compound is *o*-dichlorobenzene or 1,2-dichlorobenzene.
2. The benzene ring has a methyl (CH_3) group. The compound is therefore named as a derivative of toluene. The bromine atom is on the fourth carbon atom, counting from the methyl group. The compound is *p*-bromotoluene or 4-bromotoluene.
3. The benzene ring has two nitro (NO_2) groups in the first and third positions. It is *m*-dinitrobenzene or 1,3-dinitrobenzene.

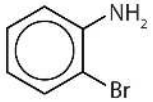
4. Note: The nitro (NO_2) group is a common substituent in aromatic compounds. Many nitro compounds are explosive, most notably 2,4,6-trinitrotoluene (TNT).

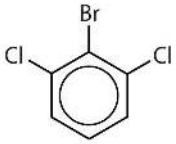


? Exercise 6.16.2

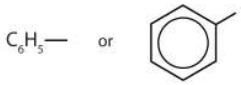
Name each compound using both the common name and the IUPAC name.

1. 

2. 

3. 

- Sometimes an aromatic group is found as a substituent bonded to a nonaromatic entity or to another aromatic ring. The group of atoms remaining when a hydrogen atom is removed from an aromatic compound is called an aryl group. The most common aryl group is derived from benzene (C_6H_6) by removing one hydrogen atom (C_6H_5) and is called a *phenyl* group, from *pheno*, an old name for benzene.



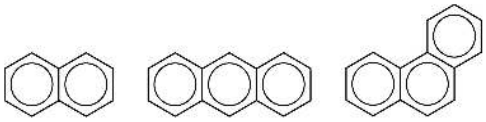
Phenyl group



2-Phenylheptane

Polycyclic Aromatic Hydrocarbons

Some common aromatic hydrocarbons consist of fused benzene rings—rings that share a common side. These compounds are called polycyclic aromatic hydrocarbons (PAHs).



Naphthalene Anthracene Phenanthrene

The three examples shown here are colorless, crystalline solids generally obtained from coal tar. Naphthalene has a pungent odor and is used in mothballs. Anthracene is used in the manufacture of certain dyes. Steroids, a large group of naturally occurring substances, contain the phenanthrene structure.

To Your Health: Polycyclic Aromatic Hydrocarbons and Cancer

The intense heating required for distilling coal tar results in the formation of PAHs. For many years, it has been known that workers in coal-tar refineries are susceptible to a type of skin cancer known as tar cancer. Investigations have shown that a number of PAHs

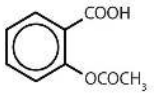
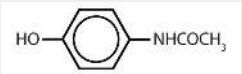
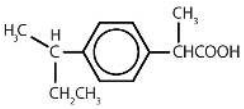
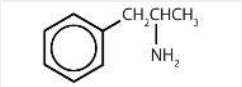
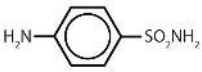
are carcinogens. One of the most active carcinogenic compounds, benzopyrene, occurs in coal tar and has also been isolated from cigarette smoke, automobile exhaust gases, and charcoal-broiled steaks. It is estimated that more than 1,000 t of benzopyrene are emitted into the air over the United States each year. Only a few milligrams of benzopyrene per kilogram of body weight are required to induce cancer in experimental animals.

Biologically Important Compounds with Benzene Rings

Substances containing the benzene ring are common in both animals and plants, although they are more abundant in the latter. Plants can synthesize the benzene ring from carbon dioxide, water, and inorganic materials. Animals cannot synthesize it, but they are dependent on certain aromatic compounds for survival and therefore must obtain them from food. Phenylalanine, tyrosine, and tryptophan (essential amino acids) and vitamins K, B_2 (riboflavin), and B_9 (folic acid) all contain the benzene ring. Many important drugs, a few of which are shown in Table **6.16.2**, also feature a benzene ring.

> So far we have studied only aromatic compounds with carbon-containing rings. However, many cyclic compounds have an element other than carbon atoms in the ring. These compounds, called *heterocyclic compounds*, are discussed later. Some of these are heterocyclic aromatic compounds.

Table **6.16.2**: Some Drugs That Contain a Benzene Ring

Name	Structure
aspirin	
acetaminophen	
ibuprofen	
amphetamine	
sulfanilamide	

Key Takeaway

- Aromatic compounds contain a benzene ring or have certain benzene-like properties; for our purposes, you can recognize aromatic compounds by the presence of one or more benzene rings in their structure.

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CHAPTER OVERVIEW

7: Chemistry in the Environment

7.1: Prelude to Solids, Liquids, and Gases
7.2: Solids and Liquids
7.3: Gases and Pressure
7.4: Gas Laws
7.5: Gay-Lussac's Law
7.6: Prelude to Acids and Bases
7.7: Arrhenius Definition of Acids and Bases
7.8: Brønsted-Lowry Definition of Acids and Bases
7.9: Water - Both an Acid and a Base
7.10: The Strengths of Acids and Bases
7.11: The pOH Concept
7.12: Titration Experiment
7.13: Titration Calculations
7.14: Buffers

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7.1: Prelude to Solids, Liquids, and Gases

We normally experience carbon dioxide (CO_2) as a gas, but if it were cooled down to about −78°C, it would become a solid. The everyday term for solid carbon dioxide is dry ice.

Why “dry” ice? Solid carbon dioxide is called dry ice because it converts from a solid to a gas directly, without going through the liquid phase, in a process called sublimation. Thus, there is no messy liquid phase to worry about. Although it is a novelty, dry ice has some potential dangers. Because it is so cold, it can freeze living tissues very quickly, so people handling dry ice should wear special protective gloves. The cold carbon dioxide gas is also heavier than air (because it is cold and more dense), so people in the presence of dry ice should be in a well-ventilated area.



Figure **7.1.1**: Dry ice. (CC BY SA 3.0 unported; ProjectManhattan).

Dry ice has several common uses. Because it is so cold, it is used as a refrigerant to keep other things cold or frozen (e.g., meats or ice cream). In the medical field, dry ice is used to preserve medical specimens, blood products, and drugs. It also has dermatological applications (e.g., freezing off warts). Organs for transplant are kept cool with dry ice until the recipient of the new organ is ready for surgery. In this respect, carbon dioxide is much like water—more than one phase of the same substance has significant uses in the real world.

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7.2: Solids and Liquids

Learning Objectives

- To describe the solid and liquid phases.

Solids and liquids are collectively called *condensed phases* because their particles are in virtual contact. The two states share little else, however.

Solids

In the solid state, the individual particles of a substance are in fixed positions with respect to each other because there is not enough thermal energy to overcome the intermolecular interactions between the particles. As a result, solids have a definite shape and volume. Most solids are hard, but some (like waxes) are relatively soft. Many solids composed of ions can also be quite brittle.



Figure **7.2.1**: Crystalline Arrangement of Quartz crystal cluster. Some large crystals look the way they do because of the regular arrangement of atoms (ions) in their crystal structure. from Wikipedia.

Solids usually have their constituent particles arranged in a regular, three-dimensional array of alternating positive and negative ions called a crystal. The effect of this regular arrangement of particles is sometimes visible macroscopically, as shown in Figure **7.2.1**. Some solids, especially those composed of large molecules, cannot easily organize their particles in such regular crystals and exist as amorphous (literally, “without form”) solids. Glass is one example of an amorphous solid.

Liquids

If the particles of a substance have enough energy to partially overcome intermolecular interactions, then the particles can move about each other while remaining in contact. This describes the liquid state. In a liquid, the particles are still in close contact, so liquids have a definite volume. However, because the particles can move about each other rather freely, a liquid has no definite shape and takes a shape dictated by its container.



Figure **7.2.2**: The formation of a spherical droplet of liquid water minimizes the surface area, which is the natural result of surface tension in liquids. from Wikipedia.

Gases

If the particles of a substance have enough energy to completely overcome intermolecular interactions, then the particles can separate from each other and move about randomly in space. Like liquids, gases have no definite shape, but unlike solids and liquids, gases have no definite volume either.

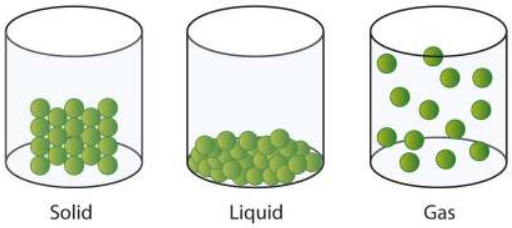


Figure 7.2.3: A Representation of the Solid, Liquid, and Gas States. A solid has definite volume and shape, a liquid has a definite volume but no definite shape, and a gas has neither a definite volume nor shape.

The change from solid to liquid usually does not significantly change the volume of a substance. However, the change from a liquid to a gas significantly increases the volume of a substance, by a factor of 1,000 or more. Figure 7.2.3 shows the differences among solids, liquids, and gases at the molecular level, while Table 7.2.1 lists the different characteristics of these states.

Table 7.2.1: Characteristics of the Three States of Matter

Characteristic	Solid	Liquid	Gas
shape	definite	indefinite	indefinite
volume	definite	definite	indefinite
relative intermolecular interaction strength	strong	moderate	weak
relative particle positions	in contact and fixed in place	in contact but not fixed	not in contact, random positions

✔ Example 7.2.1

What state or states of matter does each statement, describe?

a. This state has a definite volume.
b. This state has no definite shape.
c. This state allows the individual particles to move about while remaining in contact.

Solution

a. This statement describes either the liquid state or the solid state.
b. This statement describes either the liquid state or the gas state.
c. This statement describes the liquid state.

? Exercise 7.2.1

What state or states of matter does each statement describe?

a. This state has individual particles in a fixed position with regard to each other.
b. This state has individual particles far apart from each other in space.
c. This state has a definite shape.

Answer

a. solid
b. gas
c. solid

Looking Closer: Water, the Most Important Liquid

Earth is the only known body in our solar system that has liquid water existing freely on its surface. That is a good thing because life on Earth would not be possible without the presence of liquid water.

Water has several properties that make it a unique substance among substances. It is an excellent solvent; it dissolves many other substances and allows those substances to react when in solution. In fact, water is sometimes called the *universal solvent* because of this ability. Water has unusually high melting and boiling points (0°C and 100°C, respectively) for such a small molecule. The boiling points for similar-sized molecules, such as methane (BP = −162°C) and ammonia (BP = −33°C), are more than 100° lower. Though a liquid at normal temperatures, water molecules experience a relatively strong intermolecular interaction that allows them to maintain the liquid phase at higher temperatures than expected.

Unlike most substances, the solid form of water is less dense than its liquid form, which allows ice to float on water. The most energetically favorable configuration of H_2O molecules is one in which each molecule is hydrogen-bonded to four neighboring molecules. Owing to the thermal motions, this ideal is never achieved in the liquid, but when water freezes to ice, the molecules settle into exactly this kind of an arrangement in the ice crystal. This arrangement requires that the molecules be somewhat farther apart than would otherwise be the case; as a consequence, ice, in which hydrogen bonding is at its maximum, has a more open structure, and thus a lower density than water.

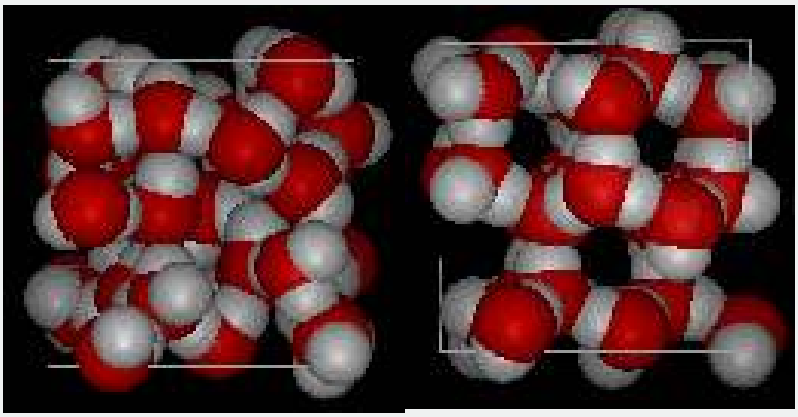


Figure **7.2.4**: Three-dimensional views of a typical local structure of liquid water (left) and ice (right).

Here are three-dimensional views of a typical local structure of water (left) and ice (right.) Notice the greater openness of the ice structure which is necessary to ensure the strongest degree of hydrogen bonding in a uniform, extended crystal lattice. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion. Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by “antifreeze” and why unprotected pipes in houses break if they are allowed to freeze.

Water also requires an unusually large amount of energy to change temperature. While 100 J of energy will change the temperature of 1 g of Fe by 230°C, this same amount of energy will change the temperature of 1 g of H_2O by only 100°C. Thus, water changes its temperature slowly as heat is added or removed. This has a major impact on weather, as storm systems like hurricanes can be impacted by the amount of heat that ocean water can store.

Water’s influence on the world around us is affected by these properties. Isn’t it fascinating that such a small molecule can have such a big impact?

Key Takeaway

- Solids and liquids are phases that have their own unique properties.

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7.3: Gases and Pressure

Learning Objectives

- To describe the gas phase.

The gas phase is unique among the three states of matter in that there are some simple models we can use to predict the physical behavior of all gases—independent of their identities. We cannot do this for the solid and liquid states. In fact, the development of this understanding of the behavior of gases represents the historical dividing point between alchemy and modern chemistry. Initial advances in the understanding of gas behavior were made in the mid 1600s by Robert Boyle, an English scientist who founded the Royal Society (one of the world's oldest scientific organizations).

How is it that we can model all gases independent of their chemical identity? The answer is in a group of statements called the kinetic theory of gases:

- Gases are composed of tiny particles that are separated by large distances.
- Gas particles are constantly moving, experiencing collisions with other gas particles and the walls of their container.
- The velocity of gas particles is related to the temperature of a gas.
- Gas particles do not experience any force of attraction or repulsion with each other.

Did you notice that none of these statements relates to the identity of the gas? This means that all gases should behave similarly. A gas that follows these statements perfectly is called an *ideal gas*. Most gases show slight deviations from these statements and are called *real gases*. However, the existence of real gases does not diminish the importance of the kinetic theory of gases.

One of the statements of the kinetic theory mentions collisions. As gas particles are constantly moving, they are also constantly colliding with each other and with the walls of their container. There are forces involved as gas particles bounce off the container walls (Figure **7.3.1**). The force generated by gas particles divided by the area of the container walls yields pressure. Pressure is a property we can measure for a gas, but we typically do not consider pressure for solids or liquids.

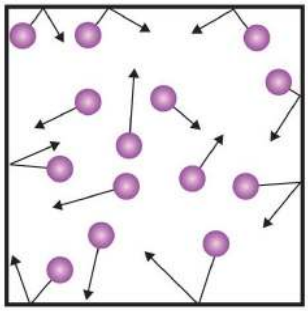


Figure **7.3.1**: Gas Pressure. Pressure is what results when gas particles rebound off the walls of their container.

The basic unit of pressure is the newton per square meter (N/m^2). This combined unit is redefined as a pascal (Pa). One pascal is not a very large amount of pressure. A more useful unit of pressure is the bar, which is 100,000 Pa (1 bar = 100,000 Pa). Other common units of pressure are the atmosphere (atm), which was originally defined as the average pressure of Earth's atmosphere at sea level; and mmHg (millimeters of mercury), which is the pressure generated by a column of mercury 1 mm high. The unit millimeters of mercury is also called a torr, named after the Italian scientist Evangelista Torricelli, who invented the barometer in the mid-1600s. A more precise definition of atmosphere, in terms of torr, is that there are exactly 760 torr in 1 atm. A bar equals 1.01325 atm. Given all the relationships between these pressure units, the ability to convert from one pressure unit to another is a useful skill.

Example 7.3.1: Converting Pressures

Write a conversion factor to determine how many atmospheres are in 1,547 mmHg.

Solution

Because 1 mmHg equals 1 torr, the given pressure is also equal to 1,547 torr. Because there are 760 torr in 1 atm, we can use this conversion factor to do the mathematical conversion:

$$1,547 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 2.04 \text{ atm}$$

Note how the torr units cancel algebraically.

? Exercise 7.3.1: Converting Pressures

Write a conversion factor to determine how many millimeters of mercury are in 9.65 atm.

Answer

$$9.65 \text{ atm} \times \frac{760 \text{ mmHg}}{1 \text{ atm}} = 7,334 \text{ mmHg}.$$

The kinetic theory also states that there is no interaction between individual gas particles. Although we know that there are, in fact, intermolecular interactions in real gases, the kinetic theory assumes that gas particles are so far apart that the individual particles don't "feel" each other. Thus, we can treat gas particles as tiny bits of matter whose identity isn't important to certain physical properties.

Key Takeaway

- The gas phase has certain general properties characteristic of that phase.

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7.4: Gas Laws

Learning Objectives

- To predict the properties of gases using the gas laws.

Experience has shown that several properties of a gas can be related to each other under certain conditions. The properties are pressure (*P*), volume (*V*), temperature (*T*, in kelvins), and amount of material expressed in moles (*n*). What we find is that a sample of gas cannot have any random values for these properties. Instead, only certain values, dictated by some simple mathematical relationships, will occur.

Boyle's Law

The first simple relationship, referred to as a gas law, is between the pressure of a gas and its volume. If the amount of gas in a sample and its temperature are kept constant, then as the pressure of a gas is increased, the volume of the gas decreases proportionately. Mathematically, this is written as

$$\mathrm{P} \propto \frac{1}{\mathrm{V}}$$

where the "∝" symbol means "is proportional to." This is one form of Boyle's law, which relates the pressure of a gas to its volume.

A more useful form of Boyle's law involves a change in conditions of a gas. For a given amount of gas at a constant temperature, if we know the initial pressure and volume of a gas sample and the pressure or volume changes, we can calculate what the new volume or pressure will be. That form of Boyle's law is written

$$P_i V_i = P_f V_f \tag{7.4.1}$$

where the subscript i refers to initial conditions and the subscript f refers to final conditions.

To use 7.4.1, you need to know any three of the variables so that you can algebraically calculate the fourth variable. Also, the pressure quantities must have the same units, as must the two volume quantities. If the two similar variables don't have the same variables, one value must be converted to the other value's unit.

Example 7.4.1: Increasing Pressure in a Gas

What happens to the volume of a gas if its pressure is increased? Assume all other conditions remain the same.

Solution

If the pressure of a gas is increased, the volume decreases in response.

Exercise 7.4.1: Increasing Volume in a Gas

What happens to the pressure of a gas if its volume is increased? Assume all other conditions remain the same.

Answer

If the volume of a gas is increased, the pressure decreases.

Example 7.4.2: Gas Compression

If a sample of gas has an initial pressure of 1.56 atm and an initial volume of 7.02 L, what is the final volume if the pressure is reduced to 0.987 atm? Assume that the amount and the temperature of the gas remain constant.

Solution

The key in problems like this is to be able to identify which quantities represent which variables from the relevant equation. The way the question is worded, you should be able to tell that 1.56 atm is P_i, 7.02 L is V_i, and 0.987 atm is P_f. What we are looking for is the final volume—V_f. Therefore, substituting these values into $P_iV_i = P_fV_f$:

$$(1.56 \text{ atm})(7.02 \text{ L}) = (0.987 \text{ atm}) \times V_f$$

The expression has atmospheres on both sides of the equation, so they cancel algebraically:

$$(1.56)(7.02 \text{ L}) = (0.987) \times V_f$$

Now we divide both sides of the expression by 0.987 to isolate V_f, the quantity we are seeking:

$$\frac{(1.56)(7.02 \text{ L})}{0.987} = \mathbf{V_f}$$

Performing the multiplication and division, we get the value of V_f, which is 11.1 L. The volume increases. This should make sense because the pressure decreases, so pressure and volume are inversely related.

Exercise 7.4.2

If a sample of gas has an initial pressure of 3.66 atm and an initial volume of 11.8 L, what is the final pressure if the volume is reduced to 5.09 L? Assume that the amount and the temperature of the gas remain constant.

Answer

8.48 atm

If the units of similar quantities are not the same, one of them must be converted to the other quantity's units for the calculation to work out properly. It does not matter which quantity is converted to a different unit; the only thing that matters is that the conversion and subsequent algebra are performed properly. The following example illustrates this process.

Example 7.4.3

If a sample of gas has an initial pressure of 1.56 atm and an initial volume of 7.02 L, what is the final volume if the pressure is changed to 1,775 torr? Does the answer make sense? Assume that the amount and the temperature of the gas remain constant.

Solution

This example is similar to Example **7.4.2**, except now the final pressure is expressed in torr. For the math to work out properly, one of the pressure values must be converted to the other unit. Let us change the initial pressure to torr:

$$1.56 \text{ atm} \times \frac{760 \text{ torr}}{1 \text{ atm}} = 1,190 \text{ torr}$$

Now we can use Boyle's law:

$$(1{,}190 \text{ torr})(7.02 \text{ L}) = (1{,}775 \text{ torr}) \times V_f$$

Torr cancels algebraically from both sides of the equation, leaving

$$(1{,}190)(7.02 \text{ L}) = (1{,}775) \times V_f$$

Now we divide both sides of the equation by 1,775 to isolate V_f on one side. Solving for the final volume,

$$\mathbf{V_f} = \frac{(1,190)(7.02 \text{ L})}{1,775} = 4.71 \text{ L}$$

Because the pressure increases, it makes sense that the volume decreases.

The answer for the final volume is essentially the same if we converted the 1,775 torr to atmospheres: $1,775 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 2.336 \text{ atm}$. Using Boyle's law: (1.56 atm)(7.02 L) = (2.335 atm) × V_f; $\mathbf{V_f} = \frac{(1.56 \text{ atm})(7.02 \text{ L})}{2.336 \text{ atm}} = 4.69 \text{ L}$.

Exercise 7.4.3

If a sample of gas has an initial pressure of 375 torr and an initial volume of 7.02 L, what is the final pressure if the volume is changed to 4,577 mL? Does the answer make sense? Assume that amount and the temperature of the gas remain constant.

Answer

575 torr

To Your Health: Breathing

Breathing certainly is a major contribution to your health! Without breathing, we could not survive. Curiously, the act of breathing itself is little more than an application of Boyle's law.

The lungs are a series of ever-narrowing tubes that end in a myriad of tiny sacs called alveoli. It is in the alveoli that oxygen from the air transfers to the bloodstream and carbon dioxide from the bloodstream transfers to the lungs for exhalation. For air to move in and out of the lungs, the pressure inside the lungs must change, forcing the lungs to change volume—just as predicted by Boyle's law.

The pressure change is caused by the diaphragm, a muscle that covers the bottom of the lungs. When the diaphragm moves down, it expands the size of our lungs. When this happens, the air pressure inside our lungs decreases slightly. This causes new air to rush in, and we inhale. The pressure decrease is slight—only 3 torr, or about 0.4% of an atmosphere. We inhale only 0.5–1.0 L of air per normal breath.

Exhaling air requires that we relax the diaphragm, which pushes against the lungs and slightly decreases the volume of the lungs. This slightly increases the pressure of the air in the lungs, and air is forced out; we exhale. Only 1–2 torr of extra pressure is needed to exhale. So with every breath, our own bodies are performing an experimental test of Boyle's law.

Charles's Law

Another simple gas law relates the volume of a gas to its temperature. Experiments indicate that as the temperature of a gas sample is increased, its volume increases as long as the pressure and the amount of gas remain constant. The way to write this mathematically is

$$V \propto T$$

At this point, the concept of temperature must be clarified. Although the Kelvin scale is the preferred temperature scale, the Celsius scale is also a common temperature scale used in science. The Celsius scale is based on the melting and boiling points of water and is actually the common temperature scale used by most countries around the world (except for the United States, which still uses the Fahrenheit scale). The value of a Celsius temperature is directly related to its Kelvin value by a simple expression:

$$\text{Kelvin temperature} = \text{Celsius temperature} + 273$$

Thus, it is easy to convert from one temperature scale to another.

The Kelvin scale is sometimes referred to as the absolute scale because the zero point on the Kelvin scale is at absolute zero, the coldest possible temperature. On the other temperature scales, absolute zero is −260°C or −459°F.

The expression relating a gas volume to its temperature begs the following question: to which temperature scale is the volume of a gas related? The answer is that gas volumes are directly related to the *Kelvin temperature*. Therefore, the temperature of a gas sample should always be expressed in (or converted to) a Kelvin temperature.

Example 7.4.4: Increasing Temperature

What happens to the volume of a gas if its temperature is decreased? Assume that all other conditions remain constant.

Solution

If the temperature of a gas sample is decreased, the volume decreases as well.

Exercise 7.4.4

What happens to the temperature of a gas if its volume is increased? Assume that all other conditions remain constant.

Answer

The temperature increases.

As with Boyle's law, the relationship between volume and temperature can be expressed in terms of initial and final values of volume and temperature, as follows:

$$\frac{V_i}{T_i} = \frac{V_f}{T_f}$$

where V_i and T_i are the initial volume and temperature, and V_f and T_f are the final volume and temperature. This is Charles's law. The restriction on its use is that the pressure of the gas and the amount of gas must remain constant. (Charles's law is sometimes referred to as Gay-Lussac's law, after the scientist who promoted Charles's work.)

Example 7.4.5

A gas sample at 20°C has an initial volume of 20.0 L. What is its volume if the temperature is changed to 60°C? Does the answer make sense? Assume that the pressure and the amount of the gas remain constant.

Solution

Although the temperatures are given in degrees Celsius, we must convert them to the kelvins before we can use Charles's law. Thus,

$$20°C + 273 = 293\ K = T_i \quad 60°C + 273 = 333\ K = T_f$$

Now we can substitute these values into Charles's law, along with the initial volume of 20.0 L:

$$\frac{20.0\ L}{293\ K} = \frac{V_f}{333\ K}$$

Multiplying the 333 K to the other side of the equation, we see that our temperature units will cancel:

$$\frac{(333\ K)(20.0\ L)}{293\ K} = V_f$$

Solving for the final volume, V_f = 22.7 L. So, as the temperature is increased, the volume increases. This makes sense because volume is directly proportional to the absolute temperature (as long as the pressure and the amount of the remain constant).

Exercise 7.4.5

A gas sample at 35°C has an initial volume of 5.06 L. What is its volume if the temperature is changed to −35°C? Does the answer make sense? Assume that the pressure and the amount of the gas remain constant.

Answer

3.91 L

Combined Gas Law

Other gas laws can be constructed, but we will focus on only two more. The combined gas law brings Boyle's and Charles's laws together to relate pressure, volume, and temperature changes of a gas sample:

Double subscripts: use braces to clarify

To apply this gas law, the amount of gas should remain constant. As with the other gas laws, the temperature must be expressed in kelvins, and the units on the similar quantities should be the same. Because of the dependence on three quantities at the same time, it is difficult to tell in advance what will happen to one property of a gas sample as two other properties change. The best way to know is to work it out mathematically.

Example 7.4.6

A sample of gas has P_i = 1.50 atm, V_i = 10.5 L, and T_i = 300 K. What is the final volume if P_f = 0.750 atm and T_f = 350 K?

Solution

Using the combined gas law, substitute for five of the quantities:

$$\frac{(1.50\ \text{atm})(10.5\ \text{L})}{300\ \text{K}} = \frac{(0.750\ \text{atm})(\text{V}_\text{f})}{350\ \text{K}}$$

We algebraically rearrange this expression to isolate V_f on one side of the equation:

$$\text{V}_\text{f} = \frac{(1.50\ \text{atm})(10.5\ \text{L})(350\ \text{K})}{(300\ \text{K})(0.750\ \text{atm})} = 24.5\ \text{L}$$

Note how all the units cancel except the unit for volume.

7.4.6 Exercise

A sample of gas has P_i = 0.768 atm, V_i = 10.5 L, and T_i = 300 K. What is the final pressure if V_f = 7.85 L and T_f = 250 K?

Answer

0.856 atm

Example 7.4.7

A balloon containing a sample of gas has a temperature of 22°C and a pressure of 1.09 atm in an airport in Cleveland. The balloon has a volume of 1,070 mL. The balloon is transported by plane to Denver, where the temperature is 11°C and the pressure is 655 torr. What is the new volume of the balloon?

Solution

The first task is to convert all quantities to the proper and consistent units. The temperatures must be expressed in kelvins, and the pressure units are different so one of the quantities must be converted. Let us convert the atmospheres to torr:

$$22°\text{C} + 273 = 295\ \text{K} = T_i$$

$$11°\text{C} + 273 = 284\ \text{K} = T_f$$

$$1.09\ \text{atm} \times \frac{760\ \text{torr}}{1\ \text{atm}} = 828\ \text{torr} = \text{P}_\text{i}$$

Now we can substitute the quantities into the combined has law:

$$\frac{(828\ \text{torr})(1,070\ \text{mL})}{295\ \text{K}} = \frac{(655\ \text{torr}) \times \text{V}_\text{f}}{284\ \text{K}}$$

To solve for V_f, we multiply the 284 K in the denominator of the right side into the numerator on the left, and we divide 655 torr in the numerator of the right side into the denominator on the left:

$$\frac{(828\ \text{torr})(1,070\ \text{mL})(284\ \text{K})}{(295\ \text{K})(655\ \text{torr})} = \text{V}_\text{f}$$

Notice that torr and kelvins cancel, as they are found in both the numerator and denominator. The only unit that remains is milliliters, which is a unit of volume. So V_f = 1,300 mL. The overall change is that the volume of the balloon has increased by 230 mL.

7.4.7 Exercise

A balloon used to lift weather instruments into the atmosphere contains gas having a volume of 1,150 L on the ground, where the pressure is 0.977 atm and the temperature is 18°C. Aloft, this gas has a pressure of 6.88 torr and a temperature of −15°C. What is the new volume of the gas?

Answer

110,038 L

The Ideal Gas Law

So far, the gas laws we have used have focused on changing one or more properties of the gas, such as its volume, pressure, or temperature. There is one gas law that relates all the independent properties of a gas under any particular condition, rather than a change in conditions. This gas law is called the ideal gas law. The formula of this law is as follows:

$$PV = nRT$$

In this equation, P is pressure, V is volume, n is amount of moles, and T is temperature. R is called the ideal gas law constant and is a proportionality constant that relates the values of pressure, volume, amount, and temperature of a gas sample. The variables in this equation do not have the subscripts i and f to indicate an initial condition and a final condition. The ideal gas law relates the four independent properties of a gas under *any* conditions.

The value of R depends on what units are used to express the other quantities. If volume is expressed in liters and pressure in atmospheres, then the proper value of R is as follows:

$$\mathrm{R = 0.08205\ \frac{L \cdot atm}{mol \cdot K}}$$

This may seem like a strange unit, but that is what is required for the units to work out algebraically.

Example 7.4.8

What is the volume in liters of 1.45 mol of N_2 gas at 298 K and 3.995 atm?

Solution

Using the ideal gas law where P = 3.995 atm, n = 1.45, and T = 298,

$$\mathrm{(3.995\ atm) \times V = (1.45\ mol)\left(0.08205\ \frac{L \cdot atm}{mol \cdot K}\right)(298\ K)}$$

On the right side, the moles and kelvins cancel. Also, because atmospheres appear in the numerator on both sides of the equation, they also cancel. The only remaining unit is liters, a unit of volume. So

$$3.995 \times V = (1.45)(0.08205)(298)\ \text{L}$$

Dividing both sides of the equation by 3.995 and evaluating, we get V = 8.87 L. Note that the conditions of the gas are not changing. Rather, the ideal gas law allows us to determine what the fourth property of a gas (here, volume) *must* be if three other properties (here, amount, pressure, and temperature) are known.

7.4.8 Exercise

What is the pressure of a sample of CO_2 gas if 0.557 mol is held in a 20.0 L container at 451 K?

Answer

1.03 atm

For convenience, scientists have selected 273 K (0°C) and 1.00 atm pressure as a set of standard conditions for gases. This combination of conditions is called standard temperature and pressure (STP). Under these conditions, 1 mol of any gas has about the same volume. We can use the ideal gas law to determine the volume of 1 mol of gas at STP:

$$(1.00\ \text{atm}) \times \text{V} = (1.00\ \text{mol}) \left(0.08205\ \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) (273\ \text{K})$$

This volume is 22.4 L. Because this volume is independent of the identity of a gas, the idea that 1 mol of gas has a volume of 22.4 L at STP makes a convenient conversion factor:

1 mol gas = 22.4 L (at STP)

Example 7.4.9

Cyclopropane (C_3H_6) is a gas that formerly was used as an anesthetic. How many moles of gas are there in a 100.0 L sample if the gas is at STP?

Solution

We can set up a simple, one-step conversion that relates moles and liters:

$$100.0\ \text{L}\ \text{C}_3\text{H}_6 \times \frac{1\ \text{mol}}{22.4\ \text{L}} = 4.46\ \text{mol}\ \text{C}_3\text{H}_6$$

There are almost 4.5 mol of gas in 100.0 L.

Note: Because of its flammability, cyclopropane is no longer used as an anesthetic gas.

7.4.9 Exercise

Freon is a trade name for a series of fluorine- and chlorine-containing gases that formerly were used in refrigeration systems. What volume does 8.75 mol of Freon have at STP?

Note: Many gases known as Freon are no longer used because their presence in the atmosphere destroys the ozone layer, which protects us from ultraviolet light from the sun.

Answer

196 L

Airbags

Airbags (Figure **7.4.3**) are a safety feature provided in most automobiles since the 1990s. The effective operation of an airbag requires that it be rapidly inflated with an appropriate amount (volume) of gas when the vehicle is involved in a collision. This requirement is satisfied in many automotive airbag systems through use of explosive chemical reactions, one common choice being the decomposition of sodium azide, NaN_3. When sensors in the vehicle detect a collision, an electrical current is passed through a carefully measured amount of NaN_3 to initiate its decomposition:

$$2\,\text{NaN}_3(s) \rightarrow 3\,\text{N}_2(g) + 2\,\text{Na}(s)$$

This reaction is very rapid, generating gaseous nitrogen that can deploy and fully inflate a typical airbag in a fraction of a second (~0.03–0.1 s). Among many engineering considerations, the amount of sodium azide used must be appropriate for generating enough nitrogen gas to fully inflate the air bag and ensure its proper function. For example, a small mass (~100 g) of NaN_3 will generate approximately 50 L of N_2.



Figure **7.4.3**: Airbags deploy upon impact to minimize serious injuries to passengers. (credit: Jon Seidman)

Dalton's Law of Partial Pressures

The ideal gas equation of state applies to mixtures just as to pure gases. It was in fact with a gas mixture, ordinary air, that Boyle, Gay-Lussac and Charles did their early experiments. The only new concept we need in order to deal with gas mixtures is the *partial pressure*, a concept invented by the famous English chemist John Dalton (1766-1844). Dalton reasoned that the low density and high compressibility of gases indicates that they consist mostly of empty space; from this it follows that when two or more different gases occupy the same volume, they behave entirely independently. The contribution that each component of a gaseous mixture makes to the total pressure of the gas is known as the *partial pressure* of that gas.

The definition of Dalton's Law of Partial Pressures that address this is:

The total pressure of a gas is the sum of the partial pressures of its components

which is expressed algebraically as

$$P_{total} = P_1 + P_2 + P_3 ... = \sum_i P_i$$

or, equivalently

$$P_{total} = \frac{RT}{V} \sum_i n_i$$

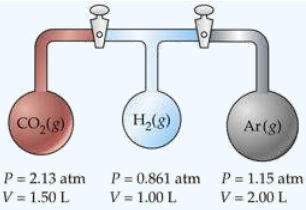
There is also a similar relationship based on *volume fractions*, known as *Amagat's law of partial volumes*. It is exactly analogous to Dalton's law, in that it states that the total volume of a mixture is just the sum of the partial volumes of its components. But there are two important differences: Amagat's law holds only for ideal gases which must all be at the same temperature and pressure. Dalton's law has neither of these restrictions. Although Amagat's law seems intuitively obvious, it sometimes proves useful in chemical engineering applications. We will make no use of it in this course.

Example 7.4.10

Three flasks having different volumes and containing different gases at various pressures are connected by stopcocks as shown. When the stopcocks are opened,

a. What will be the pressure in the system?
b. Which gas will be most abundant in the mixture?

Assume that the temperature is uniform and that the volume of the connecting tubes is negligible.



Solution

The trick here is to note that the total number of moles n_T and the temperature remain unchanged, so we can make use of Boyle's law PV = constant. We will work out the details for CO_2 only, denoted by subscripts *a*.

For CO_2,

$$P_aV_a = (2.13\ atm)(1.50\ L) = 3.20\ L \cdot atm$$

Adding the PV products for each separate container, we obtain

\[\sum_i P_i V_i = 6.36\; L \cdot atm = n_T RT \nonumber \]

We will call this sum P_1V_1. After the stopcocks have been opened and the gases mix, the new conditions are denoted by P_2V_2.

From Boyle's law (7.4.1),

$$P_1V_1 = P_2V_2 = 6.36\ L \cdot atm$$

$$V_2 = \sum_i V_i = 4.50\ L$$

Solving for the final pressure P_2 we obtain (6.36 L-atm)/(4.50 L) = **1.41 atm**.

For part *(b)*, note that the number of moles of each gas is $n = PV/RT$. The mole fraction of any one gas is $X_i = n_i / n_T$. For CO_2, this works out to (3.19/*RT*) / (6.36/*RT*) = 0.501. Because this exceeds 0.5, we know that this is the most abundant gas in the final mixture.

Dalton's law states that in a gas mixture (P_{total}) each gas will exert a pressure independent of the other gases (P_n) and each gas will behave as if it alone occupies the total volume. By extension, the partial pressure of each gas can be calculated by multiplying the total pressure (P_{total}) by the gas percentage (%).

$$P_{Total} = P_1 + P_2 + P_3 + P_4 + ... + P_n$$

or

$$P_n = \frac{n}{P_{Total}}$$

Table 7.4.1: Partial Pressures for the gases in air on a typical day

Gas	Partial Pressure (mm Hg)	Percentage (%)
Nitrogen, (N_2\)	P_{N_2} = 594	78
Oxygen, O_2	P_{O_2} = 160	21
Carbon Dioxide, CO_2	P_{CO_2} = 0.25	0.033
Water Vapor, H_2O	P_{H_2O} = 5.7	0.75
Other trace gases	P_{Other} = 0.05	0.22
Total air	P_{Total} = 760	1

Application of Dalton's Law: Collecting Gases over Water

A common laboratory method of collecting the gaseous product of a chemical reaction is to conduct it into an inverted tube or bottle filled with water, the opening of which is immersed in a larger container of water. This arrangement is called a *pneumatic trough*, and was widely used in the early days of chemistry. As the gas enters the bottle it displaces the water and becomes trapped in the upper part.

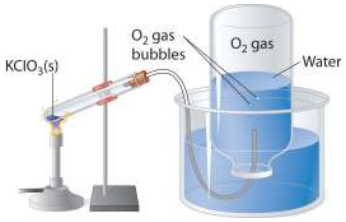


Figure **7.4.1**:An Apparatus for Collecting Gases by the Displacement of Water

The volume of the gas can be observed by means of a calibrated scale on the bottle, but what about its pressure? The total pressure confining the gas is just that of the atmosphere transmitting its force through the water. (An exact calculation would also have to take into account the height of the water column in the inverted tube.) But liquid water itself is always in equilibrium with its vapor, so the space in the top of the tube is a mixture of two gases: the gas being collected, and gaseous H_2O. The partial pressure of H_2O is known as the vapor pressure of water and it depends on the temperature. In order to determine the quantity of gas we have collected, we must use Dalton's Law to find the partial pressure of that gas.

Example 7.4.11

Oxygen gas was collected over water as shown above. The atmospheric pressure was 754 torr, the temperature was 22°C, and the volume of the gas was 155 mL. The vapor pressure of water at 22°C is 19.8 torr. Use this information to estimate the number of moles of O_2 produced.

Solution

From Dalton's law,

$$P_{O_2} = P_{total} - P_{H_2O} = 754 - 19.8 = 734\ torr = 0.966\ atm$$

Now use the Ideal Gas Law to convert to moles

$$n = \frac{PV}{RT} = \frac{(0.966\ atm)(0.155\ L)}{(0.082\ Latmmol^{-1}K^{-1})(295\ K)} = 0.00619\ mol$$

Henry’s Law

Henry's law is one of the gas laws formulated by William Henry in 1803. It states: "At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid." An equivalent way of stating the law is that the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid.

To explain this law, Henry derived the equation:

$$C = kP_{gas}$$

where

Henry’s Law tells us that the greater the pressure of gas above the surface of a liquid, the higher the concentration of the gas in the liquid. Also, Henry’s law tells us that gases diffuse from areas of high gas concentration to areas of low gas concentration.

Applicability of Henry's Law

- Henry's law only works if the molecules are at equilibrium.
- Henry's law does not work for gases at high pressures (e.g., $N_{2\,(g)}$ at high pressure becomes very soluble and harmful when in the blood supply).
- Henry's law does not work if there is a chemical reaction between the solute and solvent (e.g., $HCl_{(g)}$ reacts with water by a dissociation reaction to generate H_3O^+ and Cl^- ions).

Application of Henry's Law: Scuba diving

Our respiratory systems are designed to maintain the proper oxygen concentration in the blood when the partial pressure of O_2 is 0.21 atm, its normal sea-level value. Below the water surface, the pressure increases by 1 atm for each 10.3 m increase in depth; thus a scuba diver at 10.3 m experiences a total of 2 atm pressure pressing on the body. In order to prevent the lungs from collapsing, the air the diver breathes should also be at about the same pressure.

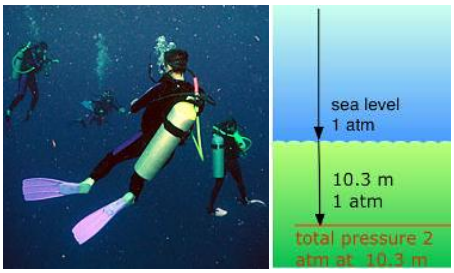


Figure **7.4.2**: Scuba Diving actively takes into account both Henry's and Dalton's Laws

But at a total pressure of 2 atm, the partial pressure of O_2 in ordinary air would be 0.42 atm; at a depth of 100 ft (about 30 m), the O_2 pressure of 0.8 atm would be far too high for health. For this reason, the air mixture in the pressurized tanks that scuba divers wear must contain a smaller fraction of O_2. This can be achieved most simply by raising the nitrogen content, but high partial pressures of N_2 can also be dangerous, resulting in a condition known as nitrogen narcosis. The preferred diluting agent for sustained deep diving is helium, which has very little tendency to dissolve in the blood even at high pressures.

Career Focus: Respiratory Therapist

Certain diseases—such as emphysema, lung cancer, and severe asthma—primarily affect the lungs. Respiratory therapists help patients with breathing-related problems. They can evaluate, help diagnose, and treat breathing disorders and even help provide emergency assistance in acute illness where breathing is compromised.

Most respiratory therapists must complete at least two years of college and earn an associate's degree, although therapists can assume more responsibility if they have a college degree. Therapists must also pass state or national certification exams. Once certified, respiratory therapists can work in hospitals, doctor's offices, nursing homes, or patient's homes. Therapists work with equipment such as oxygen tanks and respirators, may sometimes dispense medication to aid in breathing, perform tests, and educate patients in breathing exercises and other therapy.

Because respiratory therapists work directly with patients, the ability to work well with others is a must for this career. It is an important job because it deals with one of the most crucial functions of the body.

Key Takeaway

- The physical properties of gases are predictable using mathematical formulas known as gas laws.
- C is the solubility of a gas at a fixed temperature in a particular solvent (in units of M or mL gas/L)
- k is Henry's law constant (often in units of M/atm)
- P_{gas} is the partial pressure of the gas (often in units of Atm)

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7.5: Gay-Lussac's Law

Propane tanks are widely used with barbeque grills. However, it's not fun to find out half-way through grilling that you've run out of gas. You can buy gauges that measure the pressure inside the tank to see how much is left. The gauge measures pressure and will register a higher pressure on a hot day than it will on a cold day. So, you need to take the air temperature into account when you decide whether or not to refill the tank before your next cook-out.

Gay-Lussac's Law

When the temperature of a sample of gas in a rigid container is increased, the pressure of the gas increases as well. The increase in kinetic energy results in the molecules of gas striking the walls of the container with more force, resulting in a greater pressure. The French chemist Joseph Gay-Lussac (1778-1850) discovered the relationship between the pressure of a gas and its absolute temperature. **Gay-Lussac's Law** states that the pressure of a given mass of gas varies directly with the absolute temperature of the gas, when the volume is kept constant. Gay-Lussac's Law is very similar to Charles's Law, with the only difference being the type of container. Whereas the container in a Charles's Law experiment is flexible, it is rigid in a Gay-Lussac's Law experiment.



Figure **7.5.1**: *Joseph Gay-Lussac.* (CC BY-NC; CK-12)

The mathematical expressions for Gay-Lussac's Law are likewise similar to those of Charles's Law:

$$\frac{P}{T} \text{ and } \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

A graph of pressure vs. temperature also illustrates a direct relationship. As a gas is cooled at constant volume, its pressure continually decreases until the gas condenses to a liquid.

Example **7.5.1**

The gas in an aerosol can is under a pressure of $3.00\ \text{atm}$ at a temperature of $25°\text{C}$. It is dangerous to dispose of an aerosol can by incineration. What would the pressure in the aerosol can be at a temperature of $845°\text{C}$?

Solution

Known

- $P_1 = 3.00\ \text{atm}$
- $T_1 = 25°\text{C} = 298\ \text{K}$
- $T_2 = 845°\text{C} = 1118\ \text{K}$

Unknown

Use Gay-Lussac's Law to solve for the unknown pressure (P_2). The temperatures have first been converted to Kelvin.

Step 2: Solve.

First, rearrange the equation algebraically to solve for P_2.

$$P_2 = \frac{P_1 \times T_2}{T_1}$$

Now substitute the known quantities into the equation and solve.

$$P_2 = \frac{3.00\ \text{atm} \times 1118\ \text{K}}{298\ \text{K}} = 11.3\ \text{atm}$$

Step 3: Think about your result.

The pressure increases dramatically due to large increase in temperature.

Summary

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7.6: Prelude to Acids and Bases

One of the most concentrated acids in the body is stomach acid, which can be approximated as a 0.05 M hydrochloric acid solution. Special cells in the stomach wall secrete this acid, along with special enzymes, as part of the digestion process. In a laboratory, a 0.05 M solution of hydrochloric acid would dissolve some metals. How does the stomach survive the presence of such a reactive acid?

Actually, the stomach has several mechanisms for withstanding this chemical onslaught. First, the lining of the stomach is coated with a thin layer of mucus that contains some bicarbonate ions (HCO_3^-). These react with the hydrochloric acid to produce water, carbon dioxide, and harmless chloride ions. If any acid penetrates through the mucus, it can attack the surface layer of stomach cells, called the *gastric epithelium*. Cells in the gastric epithelium are being constantly shed, so damaged cells are quickly removed and replaced with healthy cells.



Figure **7.6.1**: Stomach with acidic digestive juices. (CC BY-SA 4.0; BruceBlaus).

However, if the gastric epithelium is destroyed faster than it can be replaced, the acid may reach the wall of the stomach, resulting in ulcers. If an ulcer grows large enough, it can expose blood vessels in the stomach wall, causing bleeding. In extreme situations, the loss of blood through a severe ulcer can threaten a person's health.

Ulcers can also result from the presence of a certain bacterium—*Helicobacter pylori*—in the stomach. The mechanism for this ulcer formation is not the same as that for ulcers caused by stomach acid and is not completely understood. However, there are two main treatments for ulcers: (1) *antacids* to react chemically with excess hydrochloric acid in the stomach and (2) *antibiotics* to destroy the *H. pylori* bacteria in the stomach.

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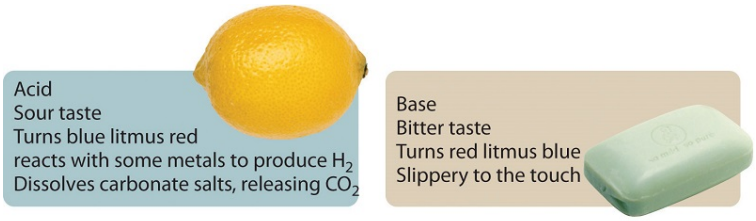
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7.7: Arrhenius Definition of Acids and Bases

Learning Objectives

- To recognize a compound as an Arrhenius acid or an Arrhenius base.
- To describe characteristics of acids and bases.
- To write equations of neutralization reactions.

One way to define a class of compounds is by describing the various characteristics its members have in common. In the case of the compounds known as acids, the common characteristics include a sour taste, the ability to change the color of the vegetable dye *litmus* to red, and the ability to dissolve certain metals and simultaneously produce hydrogen gas. For the compounds called bases, the common characteristics are a slippery texture, a bitter taste, and the ability to change the color of litmus to blue. Acids and bases also react with each other to form compounds generally known as salts.



Although we include their tastes among the common characteristics of acids and bases, we never advocate tasting an unknown chemical!

Chemists prefer, however, to have definitions for acids and bases in chemical terms. The Swedish chemist Svante Arrhenius developed the first chemical definitions of acids and bases in the late 1800s. Arrhenius defined an acid as a compound that increases the concentration of hydrogen ion (H^+) in aqueous solution. Many acids are simple compounds that release a hydrogen cation into solution when they dissolve. Similarly, Arrhenius defined a base as a compound that increases the concentration of hydroxide ion (OH^-) in aqueous solution. Many bases are ionic compounds that have the hydroxide ion as their anion, which is released when the base dissolves in water.

Table **7.7.1**: Formulas and Names for Some Acids and Bases

Acids		Bases	
Formula	Name	Formula	Name
HCl(aq)	hydrochloric acid	NaOH(aq)	sodium hydroxide
HBr(aq)	hydrobromic acid	KOH(aq)	potassium hydroxide
HI(aq)	hydriodic acid	$Mg(OH)_2$(aq)	magnesium hydroxide
H_2S(aq)	hydrosulfuric acid	$Ca(OH)_2$(aq)	calcium hydroxide
$HC_2H_3O_2$(aq)	acetic acid	NH_3(aq)	ammonia
HNO_3(aq)	nitric acid	$NaHCO_3$ (aq)	sodium bicarbonate
HNO_2(aq)	nitrous acid	$CaCO_3$ (aq)	calcium carbonate
H_2SO_4(aq)	sulfuric acid		
H_2SO_3(aq)	sulfurous acid		
$HClO_3$(aq)	chloric acid		
$HClO_4$(aq)	perchloric acid		
$HClO_2$(aq)	chlorous acid		
H_3PO_4(aq)	phosphoric acid		
H_3PO_3(aq)	phosphorous acid		
H_2CO_3(aq)	carbonic acid		

Many bases and their aqueous solutions are named using the normal rules of ionic compounds that were presented previously; that is, they are named as hydroxide compounds. For example, the base sodium hydroxide (NaOH) is both an ionic compound and an aqueous solution. However, aqueous solutions of acids have their own naming rules. The names of *binary acids* (compounds with hydrogen and one other element in their formula) are based on the root of the name of the other element preceded by the prefix *hydro-* and followed by the suffix *-ic acid*. Thus, an aqueous solution of HCl [designated "HCl(aq)"] is called hydrochloric acid, H_2S(aq) is called hydrosulfuric acid, and so forth. Acids composed of more than two elements (typically hydrogen and oxygen and some other element) have names based on the name of the other element, followed by the suffix *-ic acid* or *-ous acid*, depending on the number of oxygen atoms in the acid's formula. Other prefixes, like *per-* and *hypo-*, also appear in the names for some acids. Unfortunately, there is no strict rule for the number of oxygen atoms that are associated with the *-ic acid* suffix; the names of these acids are best memorized. Table **7.7.1** lists some acids and bases and their names. Note that acids have hydrogen written first, as if it were the cation, while most bases have the negative hydroxide ion, if it appears in the formula, written last.

> *The name oxygen comes from the Latin meaning "acid producer" because its discoverer, Antoine Lavoisier, thought it was the essential element in acids. Lavoisier was wrong, but it is too late to change the name now.*

Example 7.7.1

Name each substance.

a. HF(aq)
b. $Sr(OH)_2$(aq)

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Solution

a. This acid has only two elements in its formula, so its name includes the *hydro-* prefix. The stem of the other element's name, fluorine, is *fluor*, and we must also include the *-ic acid* ending. Its name is hydrofluoric acid.

b. This base is named as an ionic compound between the strontium ion and the hydroxide ion: strontium hydroxide.

? Exercise 7.7.1

Name each substance.

a. $H_2Se(aq)$

b. $Ba(OH)_2(aq)$

Answer

a. hydroselenic acid

b. barium hydroxide

Notice that one base listed in Table 7.7.1—ammonia—does not have hydroxide as part of its formula. How does this compound increase the amount of hydroxide ion in aqueous solution? Instead of dissociating into hydroxide ions, ammonia molecules react with water molecules by taking a hydrogen ion from the water molecule to produce an ammonium ion and a hydroxide ion:

$$NH_{3(aq)} + H_2O_{(\ell)} \rightarrow NH^+_{4(aq)} + OH^-_{(aq)} \tag{7.7.1}$$

Because this reaction of ammonia with water causes an increase in the concentration of hydroxide ions in solution, ammonia satisfies the Arrhenius definition of a base. Many other nitrogen-containing compounds are bases because they too react with water to produce hydroxide ions in aqueous solution.

Neutralization

As we noted previously, acids and bases react chemically with each other to form *salts*. A salt is a general chemical term for any ionic compound formed from an acid and a base. In reactions where the acid is a hydrogen ion containing compound and the base is a hydroxide ion containing compound, water is also a product. The general reaction is as follows:

$$\text{acid} + \text{base} \rightarrow \text{water} + \text{salt}$$

The reaction of acid and base to make water and a salt is called **neutralization**. Like any chemical equation, a neutralization chemical equation must be properly balanced. For example, the neutralization reaction between sodium hydroxide and hydrochloric acid is as follows:

$$NaOH(aq) + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(\ell)} \tag{7.7.2}$$

with coefficients all understood to be one. The neutralization reaction between sodium hydroxide and sulfuric acid is as follows:

$$2NaOH_{(aq)} + H_2SO_{4(aq)} \rightarrow Na_2SO_{4(aq)} + 2H_2O_{(\ell)} \tag{7.7.3}$$

Once a neutralization reaction is properly balanced, we can use it to perform stoichiometry calculations, such as the ones we practiced earlier.

There are a number of examples of acid-base chemistry in everyday life. One example is the use of baking soda, or sodium bicarbonate in baking. $NaHCO_3$ is a base. When it reacts with an acid such as lemon juice, buttermilk, or sour cream in a batter, bubbles of carbon dioxide gas are formed from decomposition of the resulting carbonic acid, and the batter "rises." Baking powder is a combination of sodium bicarbonate, and one or more acid salts that react when the two chemicals come in contact with water in the batter.

$$HCO^-_3(aq) + H^+(aq) \rightarrow H_2CO_3(aq) \tag{7.7.4}$$

$$H_2CO_3(aq) \rightarrow CO_2(g) + H_2O(l)$$

Example 7.7.2

Nitric acid [$HNO_3(aq)$] can be neutralized by calcium hydroxide [$Ca(OH)_2(aq)$].

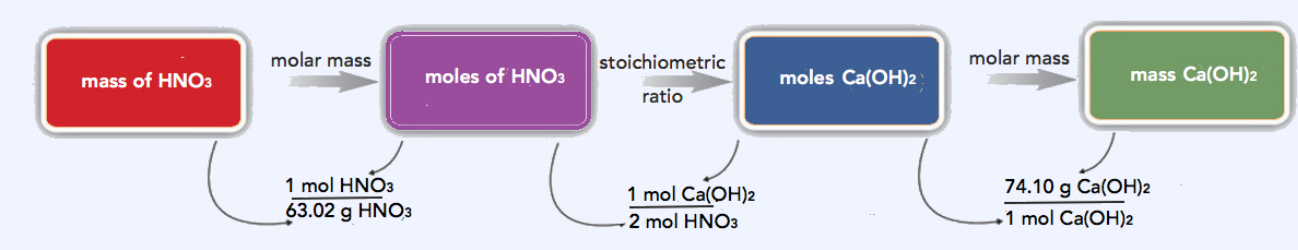
a. Write a balanced chemical equation for the reaction between these two compounds and identify the salt it produces.
b. For one reaction, 16.8 g of HNO_3 is present initially. How many grams of $Ca(OH)_2$ are needed to neutralize that much HNO_3?
c. In a second reaction, 805 mL of 0.672 M $Ca(OH)_2$ is present initially. What volume of 0.432 M HNO_3 solution is necessary to neutralize the $Ca(OH)_2$ solution?

Solution

a. Because there are two OH^- ions in the formula for $Ca(OH)_2$, we need two moles of HNO_3 to provide H^+ ions. The balanced chemical equation is as follows: $Ca(OH)_2(aq) + 2HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + 2H_2O(\ell)$

The salt formed is calcium nitrate.

b. This calculation is much like the calculations we did in Chapter 6. First we convert the mass of HNO_3 to moles using its molar mass of 1.01 + 14.01 + 3(16.00) = 63.02 g/mol; then we use the balanced chemical equation to determine the related number of moles of $Ca(OH)_2$ needed to neutralize it; and then we convert that number of moles of $Ca(OH)_2$ to the mass of $Ca(OH)_2$ using its molar mass of 40.08 + 2(1.01) + 2(16.00) = 74.10 g/mol.



$$16.8\ \text{g HNO}_3 \times \frac{1\ \text{mol HNO}_3}{63.02\ \text{g HNO}_3} \times \frac{1\ \text{mol Ca(OH)}_2}{2\ \text{mol HNO}_3} \times \frac{74.10\ \text{g Ca(OH)}_2}{1\ \text{mol Ca(OH)}_2} = 9.88\ \text{g Ca(OH)}_2\ \text{needed}$$

c. Having concentration information allows us to employ the skills we developed in Chapter 9. We have two alternative solutions: the multi-step process and the combined one-line process (found at the bottom).

First, we use the concentration and volume data to determine the number of moles of $Ca(OH)_2$ present. Recognizing that 805 mL = 0.805 L,

$$0.672\ \text{M Ca(OH)}_2 = \frac{\text{mol Ca(OH)}_2}{0.805\ \text{L soln}}$$

$$0.672\ \text{M CaOH)}_2 \times (0.805\ \text{L soln}) = \text{mol Ca(OH)}_2 = 0.541\ \text{mol Ca(OH)}_2$$

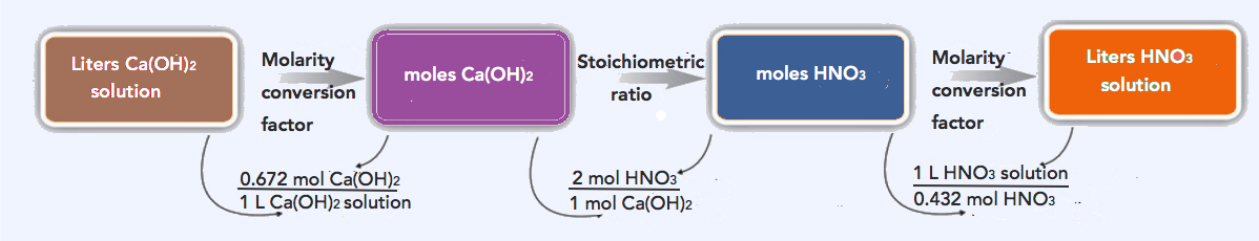
We combine this information with the proper ratio from the balanced chemical equation to determine the number of moles of HNO_3 needed:

$$0.541\ \text{mol Ca(OH)}_2 \times \frac{2\ \text{mol HNO}_3}{1\ \text{mol Ca(OH)}_2} = 1.08\ \text{mol HNO}_3$$

Now, using the definition of molarity one more time, we determine the volume of acid solution needed:

$$0.432\ \text{M HNO}_3 = \frac{1.08\ \text{mol HNO}_3}{\text{volume of HNO}_3}$$

$$\text{volume of HNO}_3 = \frac{1.08\ \text{mol HNO}_3}{0.432\ \text{M HNO}_3} = 2.50\ \text{L} = 2.50 \times 10^3\ \text{mL HNO}_3$$



$$0.805\ \text{L Ca(OH)}_2\ \text{soln} \times \frac{0.672\ \text{mol Ca(OH)}_2}{1\ \text{L Ca(OH)}_2\ \text{soln}} \times \frac{2\ \text{mol HNO}_3}{1\ \text{mol Ca(OH)}_2} \times \frac{1\ \text{L HNO}_3\ \text{soln}}{0.432\ \text{mol HNO}_3} = 2.50\ \text{L HNO}_3\ \text{soln needed}$$

? Exercise 7.7.2

Hydrocyanic acid [HCN(aq)] can be neutralized by potassium hydroxide [KOH(aq)].

a. Write a balanced chemical equation for the reaction between these two compounds and identify the salt it produces.
b. For one reaction, 37.5 g of HCN is present initially. How many grams of KOH are needed to neutralize that much HCN?
c. In a second reaction, 43.0 mL of 0.0663 M KOH is present initially. What volume of 0.107 M HCN solution is necessary to neutralize the KOH solution?

Answer

a. KOH(aq) + HCN(aq) → KCN(aq) + $H_2O(\ell)$ KCN is the salt.

b. 77.8 g

c. 0.0266 L or 26.6 mL

Hydrocyanic acid (HCN) is one exception to the acid-naming rules that specify using the prefix *hydro-* for binary acids (acids composed of hydrogen and only one other element).

Stomach Antacids

Our stomachs contain a solution of roughly 0.03 *M* HCl, which helps us digest the food we eat. The burning sensation associated with heartburn is a result of the acid of the stomach leaking through the muscular valve at the top of the stomach into the lower reaches of the esophagus. The lining of the esophagus is not protected from the corrosive effects of stomach acid the way the lining of the stomach is, and the results can be very painful. When we have heartburn, it feels better if we reduce the excess acid in the esophagus by taking an antacid. As you may have guessed, antacids are bases. One of the most common antacids is calcium carbonate, $CaCO_3$. The reaction,

$$CaCO_3(s) + 2HCl(aq) \rightleftharpoons CaCl_2(aq) + H_2O(l) + CO_2(g)$$

not only neutralizes stomach acid, it also produces $CO_2(g)$, which may result in a satisfying belch.

Milk of Magnesia is a suspension of the sparingly soluble base magnesium hydroxide, $Mg(OH)_2$. It works according to the reaction:

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

The hydroxide ions generated in this equilibrium then go on to react with the hydronium ions from the stomach acid, so that :

$$H_3O^+ + OH^- \rightleftharpoons 2H_2O(l)$$

This reaction does not produce carbon dioxide, but magnesium-containing antacids can have a laxative effect. Several antacids have aluminum hydroxide, $Al(OH)_3$, as an active ingredient. The aluminum hydroxide tends to cause constipation, and some antacids use aluminum hydroxide in concert with magnesium hydroxide to balance the side effects of the two substances.

Example 7.7.3

Assume that the stomach of someone suffering from acid indigestion contains 75 mL of 0.20 M HCl. How many Tums tablets are required to neutralize 90% of the stomach acid, if each tablet contains 500 mg of $CaCO_3$? (Neutralizing all of the stomach acid is not desirable because that would completely shut down digestion.)

Solution

A. Write the balanced chemical equation for the reaction and then decide whether the reaction will go to completion.
B. Calculate the number of moles of acid present. Multiply the number of moles by the percentage to obtain the quantity of acid that must be neutralized. Using mole ratios, calculate the number of moles of base required to neutralize the acid.
C. Calculate the number of moles of base contained in one tablet by dividing the mass of base by the corresponding molar mass. Calculate the number of tablets required by dividing the moles of base by the moles contained in one tablet.

A. We first write the balanced chemical equation for the reaction:

$$2HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + H_2CO_3(aq)$$

Each carbonate ion can react with 2 mol of H^+ to produce H_2CO_3, which rapidly decomposes to H_2O and CO_2. Because HCl is a strong acid and CO_3^{2-} is a weak base, the reaction will go to completion.

B. Next we need to determine the number of moles of HCl present:

$$75\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.20\ mol\ HCl}{\cancel{L}}\right) = 0.015\ mol\ HCl$$

Because we want to neutralize only 90% of the acid present, we multiply the number of moles of HCl by 0.90:

$$(0.015\ mol\ HCl)(0.90) = 0.014\ mol\ HCl$$

We know from the stoichiometry of the reaction that each mole of $CaCO_3$ reacts with 2 mol of HCl, so we need

$$moles\ CaCO_3 = 0.014\ \cancel{mol\ HCl}\left(\frac{1\ mol\ CaCO_3}{2\ \cancel{mol\ HCl}}\right) = 0.0070\ mol\ CaCO_3$$

C. Each Tums tablet contains

$$\left(\frac{500\ \cancel{mg\ CaCO_3}}{1\ Tums\ tablet}\right)\left(\frac{1\ \cancel{g}}{1000\ \cancel{mg\ CaCO_3}}\right)\left(\frac{1\ mol\ CaCO_3}{100.1\ \cancel{g}}\right) = 0.00500\ mol\ CaCO_3$$

Thus we need $\dfrac{0.0070\ \cancel{mol\ CaCO_3}}{0.00500\ \cancel{mol\ CaCO_3}} = 1.4$ Tums tablets.

7.7.3 Exercise

Assume that as a result of overeating, a person's stomach contains 300 mL of 0.25 M HCl. How many Rolaids tablets must be consumed to neutralize 95% of the acid, if each tablet contains 400 mg of $NaAl(OH)_2CO_3$? The neutralization reaction can be written as follows:

$$NaAl(OH)_2CO_3(s) + 4HCl(aq) \rightarrow AlCl_3(aq) + NaCl(aq) + CO_2(g) + 3H_2O(l)$$

Answer

6.4 tablets

Key Takeaway

- An Arrhenius acid increases the H^+ ion concentration in water, while an Arrhenius base increases the OH^- ion concentration in water.

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7.8: Brønsted-Lowry Definition of Acids and Bases

Learning Objectives

1. Recognize a compound as a Brønsted-Lowry acid or a Brønsted-Lowry base.
2. Illustrate the proton transfer process that defines a Brønsted-Lowry acid-base reaction.

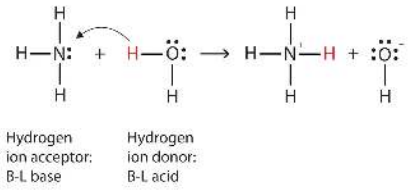
Ammonia (NH_3) increases the hydroxide ion concentration in aqueous solution by reacting with water rather than releasing hydroxide ions directly. In fact, the Arrhenius definitions of an acid and a base focus on hydrogen ions and hydroxide ions. Are there more fundamental definitions for acids and bases?

In 1923, the Danish scientist Johannes Brønsted and the English scientist Thomas Lowry independently proposed new definitions for acids and bases. Rather than considering both hydrogen and hydroxide ions, they focused on the hydrogen ion only. A Brønsted-Lowry acid is a compound that supplies a hydrogen ion in a reaction. A Brønsted-Lowry base, conversely, is a compound that accepts a hydrogen ion in a reaction. Thus, the Brønsted-Lowry definitions of an acid and a base focus on the movement of hydrogen ions in a reaction, rather than on the production of hydrogen ions and hydroxide ions in an aqueous solution.

Let us use the reaction of ammonia in water to demonstrate the Brønsted-Lowry definitions of an acid and a base. Ammonia and water molecules are reactants, while the ammonium ion and the hydroxide ion are products:

$$NH_3(aq) + H_2O(\ell) \rightarrow NH_4^+(aq) + OH^-(aq) \tag{7.8.1}$$

What has happened in this reaction is that the original water molecule has donated a hydrogen ion to the original ammonia molecule, which in turn has accepted the hydrogen ion. We can illustrate this as follows:



Because the water molecule donates a hydrogen ion to the ammonia, it is the Brønsted-Lowry acid, while the ammonia molecule—which accepts the hydrogen ion—is the Brønsted-Lowry base. Thus, ammonia acts as a base in both the Arrhenius sense and the Brønsted-Lowry sense.

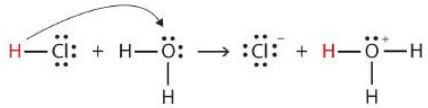
Is an Arrhenius acid like hydrochloric acid still an acid in the Brønsted-Lowry sense? Yes, but it requires us to understand what really happens when HCl is dissolved in water. Recall that the hydrogen *atom* is a single proton surrounded by a single electron. To make the hydrogen *ion*, we remove the electron, leaving a bare proton. Do we *really* have bare protons floating around in aqueous solution? No, we do not. What really happens is that the H^+ ion attaches itself to H_2O to make H_3O^+, which is called the *hydronium ion*. For most purposes, H^+ and H_3O^+ represent the same species, but writing H_3O^+ instead of H^+ shows that we understand that there are no bare protons floating around in solution. Rather, these protons are actually attached to solvent molecules.

> A proton in aqueous solution may be surrounded by more than one water molecule, leading to formulas like $H_5O_2^+$ or $H_9O_4^+$ rather than H_3O^+. It is simpler, however, to use H_3O^+.

With this in mind, how do we define HCl as an acid in the Brønsted-Lowry sense? Consider what happens when HCl is dissolved in H_2O:

$$HCl(g) + H_2O(\ell) \rightarrow H_3O^+(aq) + Cl^-(aq) \tag{7.8.2}$$

We can depict this process using Lewis electron dot diagrams:



Now we see that a hydrogen ion is transferred from the HCl molecule to the H_2O molecule to make chloride ions and hydronium ions. As the hydrogen ion donor, **HCl acts as a Brønsted-Lowry acid**; as a hydrogen ion acceptor, **H_2O is a Brønsted-Lowry base**. So HCl is an acid not just in the Arrhenius sense but also in the Brønsted-Lowry sense. Moreover, by the Brønsted-Lowry definitions, H_2O is a base in the formation of aqueous HCl. So the Brønsted-Lowry definitions of an acid and a base classify the dissolving of HCl in water as a reaction between an acid and a base—although the Arrhenius definition would not have labeled H_2O a base in this circumstance.

All Arrhenius acids and bases are Brønsted-Lowry acids and bases as well. However, not all Brønsted-Lowry acids and bases are Arrhenius acids and bases.

✔ Example 7.8.1

Aniline ($C_6H_5NH_2$) is slightly soluble in water. It has a nitrogen atom that can accept a hydrogen ion from a water molecule just like the nitrogen atom in ammonia does. Write the chemical equation for this reaction and identify the Brønsted-Lowry acid and base.

Solution

$C_6H_5NH_2$ and H_2O are the reactants. When $C_6H_5NH_2$ accepts a proton from H_2O, it gains an extra H and a positive charge and leaves an OH^- ion behind. The reaction is as follows:

$$C_6H_5NH_2(aq) + H_2O(\ell) \rightarrow C_6H_5NH_3^+(aq) + OH^-(aq)$$

Because $C_6H_5NH_2$ accepts a proton, it is the Brønsted-Lowry base. The H_2O molecule, because it donates a proton, is the Brønsted-Lowry acid.

? Exercise 7.8.1

Caffeine ($C_8H_{10}N_4O_2$) is a stimulant found in coffees and teas. When dissolved in water, it can accept a proton from a water molecule. Write the chemical equation for this process and identify the Brønsted-Lowry acid and base.

Answer

$C_8H_{10}N_4O_2(aq) + H_2O(\ell) \rightarrow C_8H_{11}N_4O_2^+(aq) + OH^-(aq)$

B-L base B-L acid

The Brønsted-Lowry definitions of an acid and a base can be applied to chemical reactions that occur in solvents other than water. The following example illustrates.

✔ Example 7.8.2

Sodium amide ($NaNH_2$) dissolves in methanol (CH_3OH) and separates into sodium ions and amide ions (NH_2^-). The amide ions react with methanol to make ammonia and the methoxide ion (CH_3O^-). Write a balanced chemical equation for this process and identify the Brønsted-Lowry acid and base.

Solution

The equation for the reaction is between NH_2^- and CH_3OH to make NH_3 and CH_3O^- is as follows:

$$NH_2^-(solv) + CH_3OH(\ell) \rightarrow NH_3(solv) + CH_3O^-(solv)$$

The label *(solv)* indicates that the species are dissolved in some solvent, in contrast to *(aq)*, which specifies an aqueous (H_2O) solution. In this reaction, we see that the NH_2^- ion accepts a proton from a CH_3OH molecule to make an NH_3 molecule. Thus, as the proton acceptor, NH_2^- is the Brønsted-Lowry base. As the proton donor, CH_3OH is the Brønsted-Lowry acid.

? Exercise 7.8.2

Pyridinium chloride (C_5H_5NHCl) dissolves in ethanol (C_2H_5OH) and separates into pyridinium ions ($C_5H_5NH^+$) and chloride ions. The pyridinium ion can transfer a hydrogen ion to a solvent molecule. Write a balanced chemical equation for this process and identify the Brønsted-Lowry acid and base.

Answer

$C_5H_5NH^+(solv) + C_2H_5OH(\ell) \rightarrow C_5H_5N(solv) + C_2H_5OH_2^+(solv)$

B-L acid B-L base

Application in Everyday Life

Many people like to put lemon juice or vinegar, both of which are acids, on cooked fish (Figure 7.8.1). It turns out that fish have volatile amines (bases) in their systems, which are neutralized by the acids to yield involatile ammonium salts. This reduces the odor of the fish, and also adds a "sour" taste that we seem to enjoy.



$CH_3COOH + NH_2CH_2CH_2CH_2CH_2NH_2 \longrightarrow CH_3COO^- + NH_3^+CH_2CH_2CH_2CH_2NH_2$

Acetic acid + Putrescine → Acetate ion + Putrescinium ion

Figure 7.8.1: A neutralization reaction takes place between citric acid or acetic acid (proton donors) in lemons or vinegar and putrescine (proton acceptor) in the flesh of fish. (CC BY 4.0; OpenStax)

Pickling is a method used to preserve vegetables using a naturally produced acidic environment. The vegetable, such as a cucumber, is placed in a sealed jar submerged in a brine solution. The brine solution favors the growth of beneficial bacteria and suppresses the growth of harmful bacteria. The beneficial bacteria feed on starches in the cucumber and produce lactic acid as a waste product in a process called fermentation. The lactic acid eventually increases the acidity of the brine to a level that kills any harmful bacteria, which require a basic environment. Without the harmful bacteria consuming the cucumbers they are able to last much longer than if they were unprotected. A byproduct of the pickling process changes the flavor of the vegetables with the acid making them taste sour.

To Your Health: Brønsted-Lowry Acid-Base Reactions in Pharmaceuticals

There are many interesting applications of Brønsted-Lowry acid-base reactions in the pharmaceutical industry. For example, drugs often need to be water soluble for maximum effectiveness. However, many complex organic compounds are not soluble or are only slightly soluble in water. Fortunately, those drugs that contain proton-accepting nitrogen atoms (and there are a lot of them) can be

reacted with dilute hydrochloric acid [HCl(aq)]. The nitrogen atoms—acting as Brønsted-Lowry bases—accept the hydrogen ions from the acid to make an ion, which is usually much more soluble in water. The modified drug molecules can then be isolated as chloride salts:

\[\mathrm{RN(sl\: aq) + H^+(aq) \rightarrow RNH^+(aq) \xrightarrow{Cl^-(aq)} RNHCl(s)} \label{Eq3} \]

where RN represents some organic compound containing nitrogen. The label *(sl aq)* means "slightly aqueous," indicating that the compound RN is only slightly soluble. Drugs that are modified in this way are called *hydrochloride salts*. Examples include the powerful painkiller codeine, which is commonly administered as codeine hydrochloride. Acids other than hydrochloric acid are also used. Hydrobromic acid, for example, gives *hydrobromide salts*. Dextromethorphan, an ingredient in many cough medicines, is dispensed as dextromethorphan hydrobromide. The accompanying figure shows another medication (lidocaine) as a hydrochloride salt.



Figure used with permission from Wikipedia.

Conjugate Acid-Base Pairs

According to the Bronsted-Lowry theory of acids and bases, an acid is a proton donor and a base is a proton acceptor. Once an acid has given up a proton, the part that remains is called the acid's **conjugate base**. This species is a base because it can accept a proton (to re-form the acid). The conjugate base of HF (first example below) is fluoride ion, F^-.

$$\text{Acid} = H^+ + \text{Conjugate base of Acid}^-$$

$$HF \rightleftharpoons H^+ + F^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$NH_4^+ \rightleftharpoons H^+ + NH_3$$

Similarly, the part of the base that remains after a base accepts a proton is called the base's **conjugate acid**. This species is an acid because it can give up a proton (and thus re-form the base). The conjugate acid of fluoride ion, F^- (first example below) is HF.

$$H^+ + \text{Base} = \text{Conjugate acid of Base}^+$$

$$H^+ + F^- \rightleftharpoons HF$$

$$H^+ + OH^- \rightleftharpoons H_2O$$

$$H^+ + H_2O \rightleftharpoons H_3O^+$$

$$H^+ + NH_3 \rightleftharpoons NH_4^+$$

To summarize, the conjugate base of HF is fluoride ion, F^-, and the conjugate acid of fluoride ion, F^-, is HF. The HF/F- pair is referred to as a conjugate acid-base pair. The difference in the formulas of a conjugate acid-base pair (example: HF and F^-) is H^+. The table below lists conjugate acid-base pairs for your reference so that you can figure out the strategy of identifying them. For any given acid or base, you should be able to give its conjugate base or conjugate acid. The formula of an acid's conjugate base is generated by **removing a proton** (H^+) from the acid formula. The formula of the base's conjugate acid is formed by **adding a proton** (H^+) to the formula of the base.

Table **7.8.1**. Conjugate acid-base pairs.

Conjugate Acid	Conjugate Base
H_3O^+	H_2O
H_2O	OH^-
H_2SO_4	HSO_4^-
HSO_4^-	SO_4^{2-}
NH_4^+	NH_3
NH_3	NH_2^-
CH_3COOH	CH_3COO^-
$CH_3NH_3^+$	CH_3NH_2

Example 7.8.3 : Conjugate Pairs

Write the formula of the conjugate base of (a) HCl and (b) HCO_3^-.

Write the formula of the conjugate acid of (c) CH_3NH_2 and (d) OH^-.

Solution:

A conjugate base is formed by removing a proton (H^+). A conjugate acid is formed by accepting a proton (H^+).

a. After HCl donates a proton, a Cl^- ion is produced, and so Cl^- is the conjugate base.
b. After hydrogen carbonate ion, HCO_3^-, donates a proton, its conjugate base, CO_3^{2-} is produced.
c. After accepting a proton (H^+), CH_3NH_2 is converted to $CH_3NH_3^+$, its conjugate acid.
d. After accepting a proton (H^+), OH^- is converted to H_2O, its conjugate acid.

7.8.3Exercise : Conjugate Pairs

Write the formula of the conjugate base of (a) HNO_2 and (b) H_2CO_3.

Write the formula of the conjugate acid of (c) C_6H5NH_2 and (d) HCO_3^-.

Answer

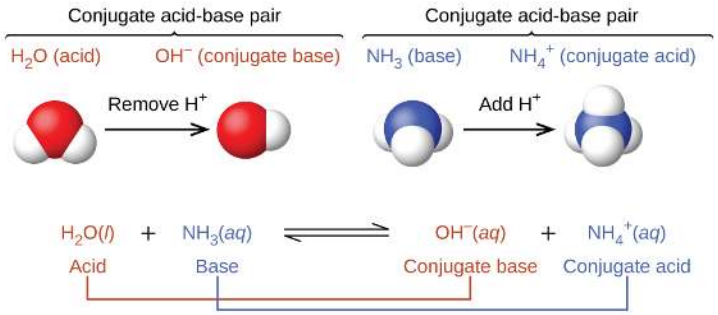
a. NO_2^- is the conjugate base of HNO_2.

b. HCO_3^- is the conjugate base of H_2CO_3

c. $C_6H5NH_3^+$ is the conjugate acid of C_6H5NH_2.

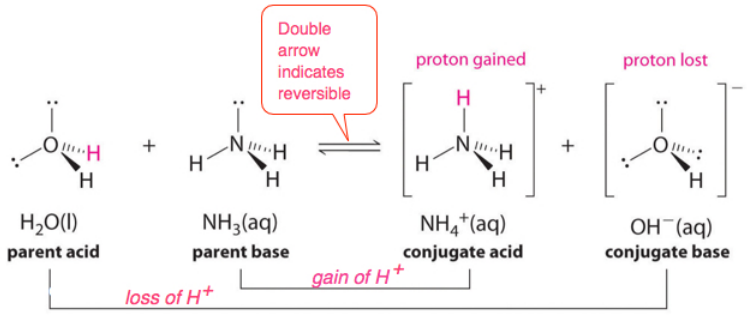
d. H_2CO_3 is the conjugate acid of HCO_3^-

In the reaction of ammonia with water to give ammonium ions and hydroxide ions, ammonia acts as a base by accepting a proton from a water molecule, which in this case means that water is acting as an acid. In the reverse reaction, an ammonium ion acts as an acid by donating a proton to a hydroxide ion, and the hydroxide ion acts as a base. The **conjugate acid–base pairs** for this reaction are $\boldsymbol{NH_4^+/NH_3}$ and $\boldsymbol{H_2O/OH^-}$. This means that the conjugate acid of the base NH_3 is NH_4^+ while the conjugate base of the acid NH_4^+ is NH_3. Similarly, the conjugate base of the acid H_2O is OH^-, and the conjugate acid of the base OH^- is H_2O.



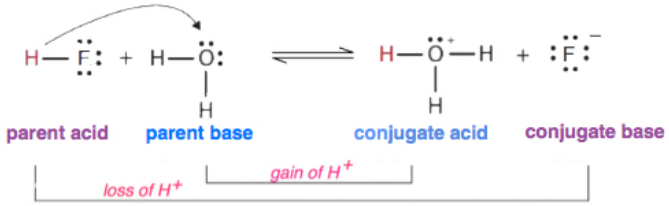
This figure has three parts in two rows. In the first row, two diagrams of acid-base pairs are shown. On the left, a space filling model of H subscript 2 O is shown with a red O atom at the center and two smaller white H atoms attached in a bent shape. Above this model is the label “H subscript 2 O (acid)” in purple. An arrow points right, which is labeled “Remove H superscript plus.” To the right is another space filling model with a single red O atom to which a single smaller white H atom is attached. The label in purple above this model reads, “O H superscript negative (conjugate base).” Above both of these red and white models is an upward pointing bracket that is labeled “Conjugate acid-base pair.” To the right is a space filling model with a central blue N atom to which three smaller white H atoms are attached in a triangular pyramid arrangement. A label in green above reads “N H subscript 3 (base).” An arrow labeled “Add H superscript plus” points right. To the right of the arrow is another space filling model with a blue central N atom and four smaller white H atoms in a tetrahedral arrangement. The green label above reads “N H subscript 3 superscript plus (conjugate acid).” Above both of these blue and white models is an upward pointing bracket that is labeled “Conjugate acid-base pair.” The second row of the figure shows the chemical reaction, H subscript 2 O (l) is shown in purple, and is labeled below in purple as “acid,” plus N H subscript 3 (a q) in green, labeled below in green as “base,” followed by a double sided arrow arrow and O H superscript negative (a q) in purple, labeled in purple as “conjugate base,” plus N H subscript 4 superscript plus (a q)” in green, which is labeled in green as “conjugate acid.” The acid on the left side of the equation is connected to the conjugate base on the right with a purple line. Similarly, the base on the left is connected to the conjugate acid on the right side.

In the **forward** reaction, the parent acid is H_2O and and the parent base is NH_3 (shown in the illustration below). The acid H_2O loses a proton (H^+) to form its conjugate base OH^-. The base NH_3 gains a proton, to produce its conjugate acid NH_4^+. In the **reverse** reaction, the acid NH_4^+ loses a proton (H^+) to form its conjugate base NH_3. The base OH^- gains a proton, to produce its conjugate acid H_2O.



When hydrogen fluoride (HF) dissolves in water and ionizes, protons are transferred from hydrogen fluoride (parent acid) molecules to water (parent base) molecules, yielding hydronium ions (conjugate acid of water) and fluoride ions (conjugate base of HF):

$$HF + H_2O \rightleftharpoons H_3O^+ + F^-$$



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Example 7.8.3

Identify the conjugate acid-base pairs in this equilibrium.

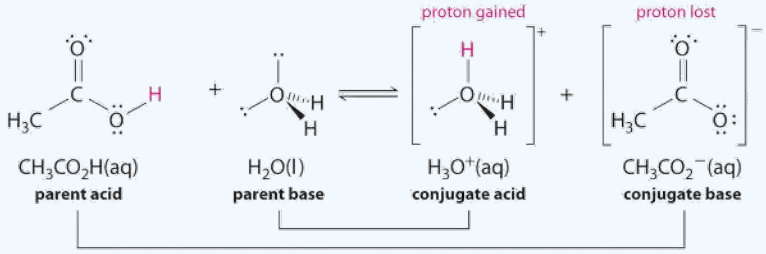
$$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$$

Solution

Similarly, in the reaction of acetic acid with water, acetic acid **donates** a proton to water, which acts as the base. In the reverse reaction, H_3O^+ is the acid that donates a proton to the acetate ion, which acts as the base.

Once again, we have two conjugate acid–base pairs:

- the parent acid and its conjugate base ($CH_3CO_2H/CH_3CO_2^-$) and
- the parent base and its conjugate acid (H_3O^+/H_2O).



Example 7.8.4

Identify the conjugate acid-base pairs in this equilibrium.

$$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$$

Solution

One pair is H_2O and OH^-, where H_2O has one more H^+ and is the conjugate acid, while OH^- has one less H^+ and is the conjugate base.

The other pair consists of $(CH_3)_3N$ and $(CH_3)_3NH^+$, where $(CH_3)_3NH^+$ is the conjugate acid (it has an additional proton) and $(CH_3)_3N$ is the conjugate base.

Exercise 7.8.4

Identify the conjugate acid-base pairs in this equilibrium.

$$NH_2^- + H_2O \rightleftharpoons NH_3 + OH^-$$

Answer:

H_2O (acid) and OH^- (base); NH_2^- (base) and NH_3 (acid)

The use of conjugate acid-base pairs allows us to make a very simple statement about relative strengths of acids and bases. *The stronger an acid, the weaker its conjugate base*, and, conversely, *the stronger a base, the weaker its conjugate acid.*

Key Takeaways

- A Brønsted-Lowry acid is a proton donor, and a Brønsted-Lowry base is a proton acceptor.
- Brønsted-Lowry acid-base reactions are essentially proton transfer reactions.

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7.9: Water - Both an Acid and a Base

Learning Objectives

- To write chemical equations for water acting as an acid and as a base.

Water (H_2O) is an interesting compound in many respects. Here, we will consider its ability to behave as an acid or a base.

In some circumstances, a water molecule will accept a proton and thus act as a **Brønsted-Lowry base**. We saw an example in the dissolving of HCl in H_2O:

$$\mathrm{HCl} + \mathrm{H_2O}(\ell) \rightarrow \mathrm{H_3O^+(aq)} + \mathrm{Cl^-(aq)} \tag{7.9.1}$$

In other circumstances, a water molecule can donate a proton and thus act as a **Brønsted-Lowry acid**. For example, in the presence of the amide ion (see Example 4 in Section 10.2), a water molecule donates a proton, making ammonia as a product:

$$H_2O(\ell) + NH_2^-(aq) \rightarrow OH^-(aq) + NH_3(aq) \tag{7.9.2}$$

In this case, NH_2^- is a Brønsted-Lowry base (the proton acceptor).

So, depending on the circumstances, H_2O can act as either a Brønsted-Lowry acid or a Brønsted-Lowry base. Water is not the only substance that can react as an acid in some cases or a base in others, but it is certainly the most common example—and the most important one. A substance that can either donate or accept a proton, depending on the circumstances, is called an **amphiprotic** compound.

A water molecule can act as an acid or a base even in a sample of pure water. About 6 in every 100 million (6 in 10^8) water molecules undergo the following reaction:

$$H_2O(\ell) + H_2O(\ell) \rightarrow H_3O^+(aq) + OH^-(aq) \tag{7.9.3}$$

This process is called the **autoionization of water** (Figure 7.9.1) and occurs in every sample of water, whether it is pure or part of a solution. Autoionization occurs to some extent in any amphiprotic liquid. (For comparison, liquid ammonia undergoes autoionization as well, but only about 1 molecule in a million billion (1 in 10^{15}) reacts with another ammonia molecule.)

Note

It is rare to truly have pure water. Water exposed to air will usually be slightly acidic because dissolved carbon dioxide gas, or carbonic acid, decreases the pH slightly below 7. Alternatively, dissolved minerals, like calcium carbonate (limestone), can make water slightly basic.

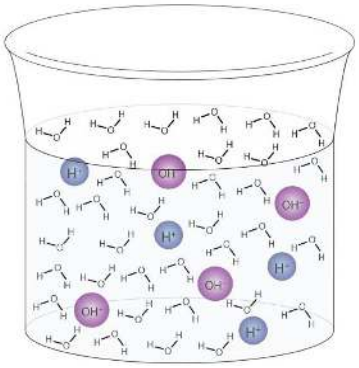


Figure 7.9.1 Autoionization. A small fraction of water molecules—approximately 6 in 100 million—ionize spontaneously into hydronium ions and hydroxide ions. This picture necessarily overrepresents the amount of autoionization that really occurs in pure water.

Example 7.9.1

Identify water as either a Brønsted-Lowry acid or a Brønsted-Lowry base.

1. $H_2O(\ell) + NO_2^-(aq) \rightarrow HNO_2(aq) + OH^-(aq)$
2. $HC_2H_3O_2(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + C_2H_3O_2^-(aq)$

Solution

1. In this reaction, the water molecule donates a proton to the NO_2^- ion, making $OH^-(aq)$. As the proton donor, H_2O acts as a Brønsted-Lowry acid.
2. In this reaction, the water molecule accepts a proton from $HC_2H_3O_2$, becoming $H_3O^+(aq)$. As the proton acceptor, H_2O is a Brønsted-Lowry base.

Exercise 7.9.2

Identify water as either a Brønsted-Lowry acid or a Brønsted-Lowry base.

1. $HCOOH(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + HCOO^-(aq)$
2. $H_2O(\ell) + PO_4^{3-}(aq) \rightarrow OH^-(aq) + HPO_4^{2-}(aq)$

Answer

1. H_2O acts as the proton acceptor (Brønsted-Lowry base)
2. H_2O acts as the proton donor (Brønsted-Lowry acid)

Key Takeaway

- Water molecules can act as both an acid and a base, depending on the conditions.

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7.10: The Strengths of Acids and Bases

Learning Objectives

- Describe the difference between strong and weak acids and bases.
- Describe how a chemical reaction reaches chemical equilibrium.
- Define the pH scale and use it to describe acids and bases.

Acids and bases do not all demonstrate the same degree of chemical activity in solution. Different acids and bases have different strengths.

Strong and Weak Acids

Let us consider the strengths of acids first. A small number of acids ionize completely in aqueous solution. For example, when HCl dissolves in water, every molecule of HCl separates into a hydronium ion and a chloride ion:

$$\mathrm{HCl\,(g) + H_2O\,(l) \xrightarrow{\sim 100\,\%} H_3O^+\,(aq) + Cl^-\,(aq)} \tag{7.10.1}$$

HCl(aq) is one example of a **strong acid**, which is a compound that is essentially **100% ionized** in aqueous solution. There are very few strong acids. The important ones are listed in Table **7.10.1**.

Table **7.10.1**: Strong Acids and Bases (All in Aqueous Solution)

Acids	Bases
HCl	LiOH
HBr	NaOH
HI	KOH
HNO_3	$Mg(OH)_2$
H_2SO_4	$Ca(OH)_2$
$HClO_4$	

By analogy, a strong base is a compound that is essentially 100% ionized in aqueous solution. As with acids, there are only a few strong bases, which are also listed in Table **7.10.1**.

If an acid is **not listed** in Table **7.10.1**, it is likely a **weak acid**, which is a compound that is not 100% ionized in aqueous solution. Similarly, a weak base is a compound that is not 100% ionized in aqueous solution. For example, acetic acid ($\mathrm{HC_2H_3O_2}$) is a weak acid. The ionization reaction for acetic acid is as follows:

$$\mathrm{HC_2H_3O_2\,(aq) + H_2O(\ell) \rightarrow H_3O^+\,(aq) + C_2H_3O_2^-\,(aq)} \tag{7.10.2}$$

Depending on the concentration of $HC_2H_3O_2$, the ionization reaction may occur only for 1%–5% of the acetic acid molecules.

Looking Closer: Household Acids and Bases

Many household products are acids or bases. For example, the owner of a swimming pool may use muriatic acid to clean the pool. Muriatic acid is another name for hydrochloric acid [$\mathrm{HCl\,(aq)}$]. Vinegar has already been mentioned as a dilute solution of acetic acid [$\mathrm{HC_2H_3O_2\,(aq)}$]. In a medicine chest, one may find a bottle of vitamin C tablets; the chemical name of vitamin C is ascorbic acid ($\mathrm{HC_6H_7O_6}$).

One of the more familiar household bases is ammonia (NH_3), which is found in numerous cleaning products. As we mentioned previously, ammonia is a base because it increases the hydroxide ion concentration by reacting with water:

$$\mathrm{NH_3\,(aq) + H_2O(\ell) \rightarrow NH_4^+\,(aq) + OH^-\,(aq)} \tag{7.10.3}$$

Many soaps are also slightly basic because they contain compounds that act as Brønsted-Lowry bases, accepting protons from water and forming excess hydroxide ions. This is one reason that soap solutions are slippery.



Figure 7.10.1: (left) Bottles of alkaline drain cleaners containing sodium hydroxide can dissolve greases and hair. (right) Chemical burns caused by sodium hydroxide solution photographed 44 hours after exposure. Figures used with permission from Wikipedia.

Perhaps the most dangerous household chemical is the lye-based drain cleaner. Lye is a common name for sodium hydroxide, although it is also used as a synonym for potassium hydroxide. Lye is an extremely caustic chemical that can react with grease, hair, food particles, and other substances that may build up and form a clog in a pipe. Unfortunately, lye can also attack tissues and other substances in our bodies. Thus, when we use lye-based drain cleaners, we must be very careful not to touch any of the solid drain cleaner or spill the water it was poured into. Safer, nonlye drain cleaners use peroxide compounds to react on the materials in the clog and clear the drain.

Chemical Equilibrium in Weak Acids and Bases

The behavior of **weak acids and bases** illustrates a key concept in chemistry. Does the chemical reaction describing the ionization of a weak acid or base just stop when the acid or base is done ionizing? Actually, no. Rather, the reverse process—the reformation of the molecular form of the acid or base—occurs, ultimately at the same rate as the ionization process. For example, the ionization of the weak acid $\mathbf{HC_2H_3O_2\,(aq)}$ is as follows:

$$\mathbf{HC_2H_3O_2\,(aq) + H_2O(\ell) \rightarrow H_3O^+\,(aq) + C_2H_3O_2^-\,(aq)} \tag{7.10.4}$$

The reverse process also begins to occur:

$$\mathbf{H_3O^+\,(aq) + C_2H_3O_2^-\,(aq) \rightarrow HC_2H_3O_2\,(aq) + H_2O(\ell)} \tag{7.10.5}$$

Eventually, there is a balance between the two opposing processes, and no additional change occurs. The chemical reaction is better represented at this point with a double arrow:

$$\mathbf{HC_2H_3O_2\,(aq) + H_2O(\ell) \rightleftharpoons H_3O^+\,(aq) + C_2H_3O_2^-\,(aq)} \tag{7.10.6}$$

The $\rightleftharpoons$ implies that **both the forward and reverse reactions** are occurring, and their effects cancel each other out. A process at this point is considered to be at **chemical equilibrium** (or equilibrium). It is important to note that the processes do not stop. They balance out each other so that there is no further net change; that is, chemical equilibrium is a *dynamic equilibrium*.

✔ Example 7.10.1: Partial Ionization

Write the equilibrium chemical equation for the partial ionization of each weak acid or base.

a. $HNO_2(aq)$
b. $C_5H_5N(aq)$

Solution

a. $HNO_2(aq) + H_2O(\ell) \leftrightarrows NO_2^-(aq) + H_3O^+(aq)$
b. $C_5H_5N(aq) + H_2O(\ell) \leftrightarrows C_5H_5NH^+(aq) + OH^-(aq)$

? Exercise 7.10.1

Write the equilibrium chemical equation for the partial ionization of each weak acid or base.

a. $HF_{(aq)}$
b. $AgOH_{(aq)}$
c. $CH_3NH_2(aq)$

Answer

a. $HF(aq) + H_2O(\ell) \leftrightarrows F^-(aq) + H_3O^+(aq)$

b. $AgOH(aq) \leftrightarrows Ag^+(aq) + OH^-(aq)$

c. $CH_3NH_2(aq) + H_2O(\ell) \leftrightarrows CH_3NH_3^+(aq) + OH^-(aq)$

Acid Ionization Constant, K_a

The ionization for a general weak acid, **HA**, can be written as follows:

$$\mathrm{HA}\,(aq) \rightleftharpoons \mathrm{H^+}\,(aq) + \mathrm{A^-}\,(aq)$$

Because the acid is weak, an equilibrium expression can be written. An **acid ionization constant** (K_a) is the equilibrium constant for the ionization of an acid.

$$K_a = \frac{[\mathrm{H^+}]\,[\mathrm{A^-}]}{[\mathrm{HA}]}$$

The acid ionization represents the fraction of the original acid that has been ionized in solution. Therefore, the numerical value of K_a is a reflection of the strength of the acid. Weak acids with relatively higher K_a values are stronger than acids with relatively lower K_a values. Because strong acids are essentially 100% ionized, the concentration of the acid in the denominator is nearly zero and the K_a value approaches infinity. For this reason, K_a values are generally reported for weak acids only.

The table below is a listing of acid ionization constants for several acids. Note that polyprotic acids have a distinct ionization constant for each ionization step, with each successive ionization constant being smaller than the previous one.

Table 7.10.2: Acid Ionization Constants at 25°C

Name of Acid	Ionization Equation	K_a
Sulfuric acid	$\mathrm{H_2SO_4 \rightleftharpoons H^+ + HSO_4^-}$ $\mathrm{HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}}$	very large 1.3×10^{-2}
Hydrofluoric acid	$\mathrm{HF \rightleftharpoons H^+ + F^-}$	7.1×10^{-4}
Nitrous acid	$\mathrm{HNO_2 \rightleftharpoons H^+ + NO_2^-}$	4.5×10^{-4}
Benzoic acid	$\mathrm{C_6H_5COOH \rightleftharpoons H^+ + C_6H_5COO^-}$	6.5×10^{-5}
Acetic acid	$\mathrm{CH_3COOH \rightleftharpoons H^+ + CH_3COO^-}$	1.8×10^{-5}
Carbonic acid	$\mathrm{H_2CO_3 \rightleftharpoons H^+ + HCO_3^-}$ $\mathrm{HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}}$	4.2×10^{-7} 4.8×10^{-11}

Hydrofluoric acid $HF_{(aq)}$ reacts directly with glass (very few chemicals react with glass). Hydrofluoric acid is used in glass etching.

Strong and Weak Bases and Base Ionization Constant, K_b

As with acids, bases can either be strong or weak, depending on their extent of ionization. A **strong base** is a base, which ionizes completely in an aqueous solution. The most common strong bases are soluble metal hydroxide compounds such as potassium

hydroxide. Some metal hydroxides are not as strong simply because they are not as soluble. Calcium hydroxide is only slightly soluble in water, but the portion that does dissolve also dissociates into ions.

A **weak base** is a base that ionizes only slightly in an aqueous solution. Recall that a base can be defined as a substance, which accepts a hydrogen ion from another substance. When a weak base such as ammonia is dissolved in water, it accepts an H^+ ion from water, forming the hydroxide ion and the conjugate acid of the base, the ammonium ion.

$$NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$$

The equilibrium greatly favors the reactants and the extent of ionization of the ammonia molecule is very small.

An equilibrium expression can be written for the reactions of weak bases with water. Because the concentration of water is extremely large and virtually constant, the water is not included in the expression. A **base ionization constant** (K_b) is the equilibrium constant for the ionization of a base. For ammonia the expression is:

$$K_b = \frac{[NH_4^+]\,[OH^-]}{[NH_3]}$$

The numerical value of K_b is a reflection of the strength of the base. Weak bases with relatively higher K_b values are stronger than bases with relatively lower K_b values. Table 7.10.3 is a listing of base ionization constants for several weak bases.

Table 7.10.3: Base Ionization Constants at 25°C

Name of Base	Ionization Equation	K_b
Methylamine	$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$	5.6×10^{-4}
Ammonia	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}
Pyridine	$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$	1.7×10^{-9}
Acetate ion	$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$	5.6×10^{-10}
Fluoride ion	$F^- + H_2O \rightleftharpoons HF + OH^-$	1.4×10^{-11}
Urea	$H_2NCONH_2 + H_2O \rightleftharpoons H_2NCONH_3^+ + OH^-$	1.5×10^{-14}

The Ion-Product of Water

As we have already seen, H_2O can act as an acid or a base. Within any given sample of water, some H_2O molecules are acting as acids, and other H_2O molecules are acting as bases. The chemical equation is as follows:

$$\underbrace{H_2O}_{\text{acid}} + \underbrace{H_2O}_{\text{base}} \rightleftharpoons H_3O^+ + OH^- \tag{7.10.7}$$

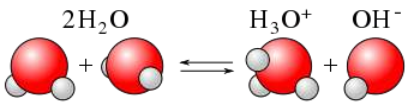


Figure 7.10.2: Autoionization of water, giving hydroxide and hydronium ions.

Similar to a weak acid, the autoionization of water is an equilibrium process, and is more properly written as follows:

$$H_2O(\ell) + H_2O(\ell) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq) \tag{7.10.8}$$

We often use the simplified form of the reaction:

$$H_2O\,(l) \rightleftharpoons H^+\,(aq) + OH^-\,(aq)$$

The equilibrium constant for the autoionization of water is referred to as the ion-product for water and is given the symbol Kw.

$$K_w = [H^+][OH^-]$$

The **ion-product of water (*Kw*)** is the mathematical product of the concentration of hydrogen ions and hydroxide ions. Note that H_2O is not included in the ion-product expression because it is a pure liquid. The value of Kw is very small, in accordance with a

reaction that favors the reactants. At 25°C, the experimentally determined value of K_w in pure water is 1.0×10^{-14}.

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

In a sample of pure water, the concentrations of hydrogen and hydroxide ions are equal to one another. Pure water or any other aqueous solution in which this ratio holds is said to be **neutral.** To find the molarity of each ion, the square root of Kw is taken.

$$[H^+] = [OH^-] = 1.0\times10^{-7}$$

The product of these two concentrations is 1.0×10^{-14}

$$[H^+]\times[OH^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

- For acids, the concentration of H^+ or $[H^+]$) is greater than 1.0×10^{-7} M
- For bases, the concentration of OH^- or $[OH^-]$ is greater than 1.0×10^{-7} M.

Aqueous HCl is an example of acidic solution. Hydrogen chloride (HCl) ionizes to produce H^+ and Cl^- ions upon dissolving in water. This **increases the concentration of H^+ ions** in the solution. According to **Le Chatelier's principle**, the equilibrium represented by

$$H_2O\,(l) \rightleftharpoons H^+\,(aq) + OH^-\,(aq)$$

$$HCl\,(g) \longrightarrow H^+\,(aq) + Cl^-\,(aq)$$

is **forced to the left**, towards the reactant. As a result, the **concentration of the hydroxide ion decreases**.

Now, consider KOH (aq), a **basic solution**. Solid potassium hydroxide (KOH) dissociates in water to yield potassium ions and hydroxide ions.

$$KOH(s) \rightarrow K^+(aq) + OH^-(aq)$$

The **increase in concentration of the OH^- ions** will cause a decrease in the concentration of the H^+ ions.

No matter whether the aqueous solution is an acid, a base, or neutral:and the ion-product of $[H^+][OH^-]$ remains constant.

- For acidic solutions, $[H^+]$) is greater than $[OH^-]$.
- For basic solutions, [OH−] is greater than $[H^+]$.
- For neutral solutions, $[H_3O^+] = [OH-] = 1.0\times10^{-7}$M

This means that if you know $[H^+]$ for a solution, you can calculate what $[OH^-]$) has to be for the product to equal 1.0×10^{-14}, or if you know $[OH^-]$), you can calculate $[H^+]$. This also implies that as one concentration goes up, the other must go down to compensate so that their product always equals the value of K_w.

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \tag{7.10.9}$$

Example 7.10.2

Hydrochloric acid (HCl) is a strong acid, meaning it is 100% ionized in solution. What is the $[H^+]$ and the $[OH^-]$ in a solution of 2.0×10^{-3} M HCl?

Solution

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

Known

- $[HCl] = 2.0\times10^{-3}$ M
- $Kw = 1.0\times10^{-14}$

Unknown

- $[H^+]$=?M
- $[OH^-]$=?M

Because HCl is 100% ionized, the concentration of H+ ions in solution will be equal to the original concentration of HCl. Each HCl molecule that was originally present ionizes into one H+ ion and one Cl− ion. The concentration of OH− can then be determined from the [H+] and Kw.

Step 2: Solve.

$$[H^+]=2.0\times10^{-3}\,M$$

$$Kw = [H^+][OH^-] = 1.0\times10^{-14}$$

$$[OH^-] = Kw/[H^+] = 1.0\times10^{-14}/2.0\times10^{-3} = 5.0\times10^{-12}\,M$$

Step 3: Think about your result.

The $[H^+]$ is much higher than the $[OH^-]$ because the solution is acidic. As with other equilibrium constants, the unit for Kw is customarily omitted.

7.10.2 Exercise

Sodium hydroxide (NaOH) is a strong base. What is the $[H^+]$ and the $[OH^-]$ in a 0.001 M NaOH solution at 25 °C?

Answer

$[OH^-]$ = 0.001M or 1 x 10^{-3}M; $[H^+]=1\times10^{-11}$M.

The pH Scale

One qualitative measure of the strength of an acid or a base solution is the pH scale, which is based on the concentration of the hydronium (or hydrogen) ion in aqueous solution.

$$pH = -\log[H^+]$$

or

$$pH = -\log[H_3O^+]$$

Figure **7.10.3** illustrates this relationship, along with some examples of various solutions. Because hydrogen ion concentrations are generally less than one (for example $1.3 \times 10^{-3}\ M$), the log of the number will be a negative number. To make pH even easier to work with, pH is defined as the ***negative* log of** $[H_3O^+]$, which will give a positive value for pH.

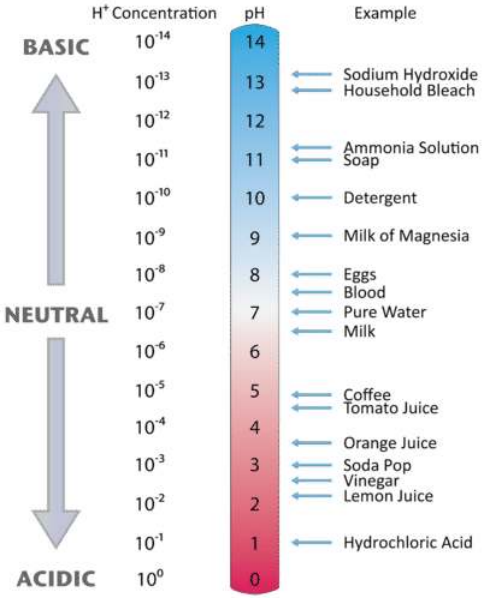


Figure **7.10.3**: The relationship between $[H^+]$ and pH *values for several common materials.*

https://chem.libretexts.org/@go/page/270504

A neutral (neither acidic nor basic) solution has a pH of 7. A pH below 7 means that a solution is acidic, with lower values of pH corresponding to increasingly acidic solutions. A pH greater than 7 indicates a basic solution, with higher values of pH corresponding to increasingly basic solutions. Thus, given the pH of several solutions, you can state which ones are acidic, which ones are basic, and which are more acidic or basic than others. These are summarized in Table \(\PageIndex{4}.

Table **7.10.4**: Acidic, Basic and Neutral pH Values

Acidic, Basic and Neutral pH Values

Classification	Relative Ion Concentrations	pH at 25 °C
acidic	$[H^+] > [OH^-]$	pH < 7
neutral	$[H^+] = [OH^-]$	pH = 7
basic	$[H^+] < [OH^-]$	pH > 7

Example 7.10.3

Find the pH, given the $[H^+]$ of the following:

a. 1×10^{-3} M
b. 2.5×10^{-11} M
c. 4.7×10^{-9} M

Solution

pH = - log $[H_3O^+]$

Substitute the known quantity into the equation and solve. Use a scientific calculator for b and c.

a. pH = - log $[\underline{1} \times 10^{-3}]$ = 3.$\underline{0}$ (1 decimal place since 1 has 1 significant figure)
b. pH = - log $[\underline{2.5} \times 10^{-11}]$ = 10.$\underline{60}$ (2 decimal places since 2.5 has 2 significant figures)
c. pH = - log $[\underline{4.7} \times 10^{-9}]$ = 8.$\underline{33}$ (2 decimal places since 4.7 has 2 significant figures)

Note on significant figures:

Because the number(s) before the decimal point in the pH value relate to the power on 10, the number of digits *after* the decimal point (underlined) is what determines the number of significant figures in the final answer.

7.10.3 Exercise

Find the pH, given $[H^+]$ of the following:

a. 5.8×10^{-4} M
b. 1.0×10^{-7} M

Answer

a. 3.24

b. 7.00

Table **7.10.5** lists the pH of several common solutions. The most acidic among the listed solutions is battery acid with the lowest pH value (0.3). The most basic is 1M NaOH solution with the highest pH value of 14.0. Notice that some biological fluids (stomach acid and urine) are nowhere near neutral. You may also notice that many food products are slightly acidic. They are acidic because they contain solutions of weak acids. If the acid components of these foods were strong acids, the food would likely be inedible.

Table **7.10.5**: The pH Values of Some Common Solutions

Solution	pH
battery acid	0.3
stomach acid	1–2
lemon or lime juice	2.1
vinegar	2.8–3.0
Coca-Cola	3
wine	2.8–3.8
beer	4–5
coffee	5
milk	6
urine	6
pure H_2O	7
(human) blood	7.3–7.5
sea water	8
antacid (milk of magnesia)	10.5
NH_3 (1 M)	11.6
bleach	12.6
NaOH (1 M)	14.0

Example 7.10.4

Label each solution as acidic, basic, or neutral based only on the stated ***pH***.

a. milk of magnesia, pH = 10.5
b. pure water, pH = 7
c. wine, pH = 3.0

Solution

a. With a pH greater than 7, milk of magnesia is basic. (Milk of magnesia is largely $Mg(OH)_2$.)
b. Pure water, with a pH of 7, is neutral.
c. With a pH of less than 7, wine is acidic.

7.10.4 Exercise

Identify each substance as acidic, basic, or neutral based only on the stated ***pH***.

a. human blood with ***pH*** = 7.4
b. household ammonia with ***pH*** = 11.0
c. cherries with ***pH*** = 3.6

Answer

a. slightly basic

b. basic

c. acidic

Acid Rain

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved CO_2 which forms carbonic acid:

$$\mathrm{H_2O\,(l) + CO_2\,(g) \longrightarrow H_2CO_3\,(aq)} \tag{7.10.10}$$

$$\mathrm{H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq)} \tag{7.10.11}$$

Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including CO_2, SO_2, SO_3, NO, and NO_2 being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:

$$\mathrm{H_2O\,(l) + SO_3\,(g) \longrightarrow H_2SO_4\,(aq)} \tag{7.10.12}$$

$$\mathrm{H_2SO_4\,(aq) \longrightarrow H^+\,(aq) + HSO_4^-\,(aq)} \tag{7.10.13}$$

Carbon dioxide is naturally present in the atmosphere because we and most other organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or when we burn wood or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also stems from burning fossil fuels, which have traces of sulfur, and from the process of "roasting" ores of metal sulfides in metal-refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (Figure **7.10.4**). Regulations limiting the amount of sulfur and nitrogen oxides that can be released into the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.



(a) (b)

Figure **7.10.4**: (a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also is corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by "Eden, Janine and Jim"/Flickr)

Two photos are shown. Photograph a on the left shows the upper portion of trees against a bright blue sky. The tops of several trees at the center of the photograph have bare branches and appear to be dead. Image b shows a statue of a man that appears to from the revolutionary war era in either marble or limestone.

Key Takeaways

- Acids and bases can be strong or weak depending on the extent of ionization in solution.
- Most chemical reactions reach equilibrium at which point there is no net change.
- The ion-product of $[H^+][OH^-]$ in an aqueous solution remains constant.
- A ***p*H** value is simply the *negative* of the logarithm of the H^+ ion concentration ($-\log[H^+]$).
- The pH scale is used to succinctly communicate the acidity or basicity of a solution.
- A solution is **acidic** if pH < 7.
- A solution is **basic** if pH > 7.
- A solution is **neutral** if pH = 7.

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7.11: The pOH Concept

Soap Lake has a long history as a healing place. Indian tribes would put aside their rivalries when they came to the lake to enjoy the high mineral content of the water. In the days before good antibiotics, thousands of visitors would come and enjoy the soothing waters of the lake. Soap Lake is alkaline, with water quality though to be similar to that of the moons of the planet Jupiter.

The pOH Concept

As with the hydrogen-ion concentration, the concentration of the hydroxide ion can be expressed logarithmically by the pOH. The **pOH** of a solution is the negative logarithm of the hydroxide-ion concentration:

$$\text{pOH} = -\log\left[\text{OH}^-\right]$$

The pH of a solution can be related to the pOH. Consider a solution with a pH $= 4.0$. The $[\text{H}^+]$ of the solution would be 1.0×10^{-4} M. Dividing K_w by this yields a $[\text{OH}^-]$ of 1.0×10^{-10} M. Finally the pOH of the solution equals $-\log\left(1.0 \times 10^{-10}\right) = 10$. This example illustrates the following relationship.

$$\text{pH} + \text{pOH} = 14$$

The pOH scale is similar to the pH scale in that a pOH of 7 is indicative of a neutral solution. A basic solution has a pOH less than 7, while an acidic solution has a pOH of greater than 7. The pOH is convenient to use when finding the hydroxide ion concentration from a solution with a known pH.

Example 7.11.1

Find the hydroxide concentration of a solution with a pH of 4.42.

Solution

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

Known

- pH $= 4.42$
- pH + pOH $= 14$

Unknown

First, the pOH is calculated, followed by the $[\text{OH}^-]$.

Step 2: Solve.

$$\text{pOH} = 14 - \text{pH} = 14 - 4.42 = 9.58$$
$$\left[\text{OH}^-\right] = 10^{-\text{pOH}} = 10^{-9.58} = 2.6 \times 10^{-10}\ \text{M}$$

Step 3: Think about your result.

The pH is that of an acidic solution, and the resulting hydroxide-ion concentration is less than 1×10^{-7} M. The answer has two significant figures because the given pH has two decimal places.

The diagram below shows all of the interrelationships between $[\text{H}^+]$, $[\text{OH}^-]$, pH, and pOH.

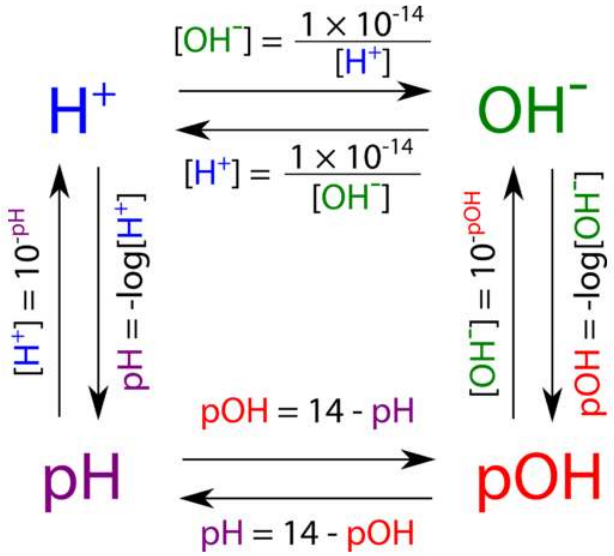


Figure 7.11.1: Relationships between hydrogen ion concentration, hydroxide ion concentration, pH and pOH. (CC BY-NC; CK-12)

Summary

- The pOH of a solution is the negative logarithm of the hydroxide-ion concentration.
- Calculations involving pOH are described.

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7.12: Titration Experiment

A large amount of current research involves the development of biodiesel fuels. Often this material can be made from used vegetable oils. The vegetable oil is treated with lye to create the biofuel. In the oils is a variable amount of acid that needs to be determined, so that the workers will know how much lye to add to make the final fuel. Before the lye is added, the native vegetable oil is titrated to find out how much free acid is present. Then, the amount of lye added can be adjusted to take into account the amount needed to neutralize these free acids.

Titration Experiment

In the neutralization of hydrochloric acid by sodium hydroxide, the mole ratio of acid to base is 1:1.

$$\mathrm{HCl}\,(aq) + \mathrm{NaOH}\,(aq) \rightarrow \mathrm{NaCl}\,(aq) + \mathrm{H_2O}\,(l)$$

One mole of HCl would be fully neutralized by one mole of NaOH. If instead the hydrochloric acid was reacted with barium hydroxide, the mole ratio would be 2:1.

$$2\mathrm{HCl}\,(aq) + \mathrm{Ba(OH)_2}\,(aq) \rightarrow \mathrm{BaCl_2}\,(aq) + 2\mathrm{H_2O}\,(l)$$

Now two moles of HCl would be required to neutralize one mole of $\mathrm{Ba(OH)_2}$. The mole ratio ensures that the number of moles of $\mathrm{H^+}$ ions supplied by the acid is equal to the number of $\mathrm{OH^-}$ ions supplied by the base. This must be the case for neutralization to occur. The **equivalence point** is the point in a neutralization reaction where the number of moles of hydrogen ions is equal to the number of moles of hydroxide ions.

In the laboratory, it is useful to have an experiment where the unknown concentration of an acid or a base can be determined. This can be accomplished by performing a controlled neutralization reaction. A **titration** is an experiment where a volume of a solution of known concentration is added to a volume of another solution in order to determine its concentration. Many titrations are acid-base neutralization reactions, though other types of titrations can also be performed.

In order to perform an acid-base titration, the chemist must have a way to visually detect that the neutralization reaction has occurred. An **indicator** is a substance that has a distinctly different color when in an acidic or basic solution. A commonly used indicator for strong acid-strong base titrations is phenolphthalein. Solutions in which a few drops of phenolphthalein have been added turn from colorless to brilliant pink as the solution turns from acidic to basic. The steps in a titration reaction are outlined below.

1. A measured volume of an acid of unknown concentration is added to an Erlenmeyer flask.
2. Several drops of an indicator are added to the acid and mixed by swirling the flask.
3. A buret is filled with a base solution of known molarity.
4. The stopcock of the buret is opened and base is slowly added to the acid, while the flask is constantly swirled to ensure mixing. The stopcock is closed at the exact point at which the indicator just changes color.

The **standard solution** is the solution in a titration whose concentration is known. In the titration described above, the base solution is the standard solution. It is very important in a titration to add the solution from the buret slowly, so that the point at which the indicator changes color can be found accurately. The **end point** of a titration is the point at which the indicator changes color. When phenolphthalein is the indicator, the end point will be signified by a faint pink color.



Figure 7.12.1: Phenolphthalein in basic solution. (CC BY-NC; CK-12)

Summary

- The equivalence point is the point in a neutralization reaction where the number of moles of hydrogen ions is equal to the number of moles of hydroxide ions.
- A titration is an experiment where a volume of a solution of known concentration is added to a volume of another solution in order to determine its concentration. (Many titrations are acid-base neutralization reactions.)
- An indicator is a substance that has a distinctly different color when in an acidic or basic solution.
- The process for carrying out a titration is described.

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7.13: Titration Calculations

The manufacture of soap requires a number of chemistry techniques. One necessary piece of information is the saponification number. This is the amount of base needed to hydrolyze a certain amount of fat to produce the free fatty acids that are an essential part of the final product. The fat is heated with a known amount of base (usually **NaOH** or **KOH**). After hydrolysis is complete, the leftover base is titrated to determine how much was needed to hydrolyze the fat sample.

Titration Calculations

At the equivalence point in a neutralization, the moles of acid are equal to the moles of base.

$$\text{moles acid} = \text{moles base}$$

Recall that the molarity (**M**) of a solution is defined as the moles of the solute divided by the liters of solution (**L**). So the moles of solute are therefore equal to the molarity of a solution multiplied by the volume in liters.

$$\text{moles solute} = \text{M} \times \text{L}$$

We can then set the moles of acid equal to the moles of base.

$$\text{M}_A \times \text{V}_A = \text{M}_B \times \text{V}_B$$

M_A is the molarity of the acid, while M_B is the molarity of the base. V_A and V_B are the volumes of the acid and base, respectively.

Suppose that a titration is performed and $20.70\ \text{mL}$ of $0.500\ \text{M NaOH}$ is required to reach the end point when titrated against $15.00\ \text{mL}$ of **HCl** of unknown concentration. The above equation can be used to solve for the molarity of the acid.

$$\text{M}_A = \frac{\text{M}_B \times \text{V}_B}{\text{V}_A} = \frac{0.500\ \text{M} \times 20.70\ \text{mL}}{15.00\ \text{mL}} = 0.690\ \text{M}$$

The higher molarity of the acid compared to the base in this case means that a smaller volume of the acid is required to reach the equivalence point.

The above equation works only for neutralizations in which there is a 1:1 ratio between the acid and the base. The example below demonstrates the technique to solve a titration problem for a titration of sulfuric acid with sodium hydroxide.

Example **7.13.1**

In a titration of sulfuric acid against sodium hydroxide, $32.20\ \text{mL}$ of $0.250\ \text{M NaOH}$ is required to neutralize $26.60\ \text{mL}$ of H_2SO_4. Calculate the molarity of the sulfuric acid.

$$\text{H}_2\text{SO}_4\,(aq) + 2\text{NaOH}\,(aq) \rightarrow \text{Na}_2\text{SO}_4\,(aq) + 2\text{H}_2\text{O}\,(l)$$

Solution

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

- Molarity $\text{NaOH} = 0.250\ \text{M}$
- Volume $\text{NaOH} = 32.20\ \text{mL}$
- Volume $\text{H}_2\text{SO}_4 = 26.60\ \text{mL}$

Unknown

First determine the moles of **NaOH** in the reaction. From the mole ratio, calculate the moles of H_2SO_4 that reacted. Finally, divide the moles of H_2SO_4 by its volume to get the molarity.

Step 2: Solve.

$$\text{mol NaOH} = \text{M} \times \text{L} = 0.250\ \text{M} \times 0.03220\ \text{L} = 8.05 \times 10^{-3}\ \text{mol NaOH}$$

$$8.05 \times 10^{-3}\ \text{mol NaOH} \times \frac{1\ \text{mol H}_2\text{SO}_4}{2\ \text{mol NaOH}} = 4.03 \times 10^{-3}\ \text{mol H}_2\text{SO}_4$$

$$\frac{4.03 \times 10^{-3}\ \text{mol H}_2\text{SO}_4}{0.02660\ \text{L}} = 0.151\ \text{M H}_2\text{SO}_4$$

Step 3: Think about your result.

The volume of H_2SO_4 required is smaller than the volume of $NaOH$ because of the two hydrogen ions contributed by each molecule.

Summary

- The process of calculating concentration from titration data is described and illustrated.

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7.14: Buffers

Learning Objectives

- To define *buffer* and describe how it reacts with an acid or a base.

Weak acids are relatively common, even in the foods we eat. But we occasionally come across a strong acid or base, such as stomach acid, that has a strongly acidic pH of 1–2. By definition, strong acids and bases can produce a relatively large amount of hydrogen or hydroxide ions and, as a consequence, have a marked chemical activity. In addition, very small amounts of strong acids and bases can change the pH of a solution very quickly. If 1 mL of stomach acid [which we will approximate as 0.05 M HCl(aq)] is added to the bloodstream, and if no correcting mechanism is present, the pH of the blood would go from about 7.4 to about 4.9—a pH that is not conducive to continued living. Fortunately, the body has a mechanism for minimizing such dramatic pH changes.

The mechanism involves a **buffer**, a solution that resists dramatic changes in pH. A *buffer* (or *buffered*) solution is one that resists a change in its pH when H^+ or OH^- ions are added or removed owing to some other reaction taking place in the same solution. Buffers do so by being composed of certain pairs of solutes: either a **weak acid plus its conjugate base** or a **weak base plus its conjugate acid**.

For example, a buffer can be composed of dissolved **acetic acid ($HC_2H_3O_2$, a weak acid) and sodium acetate** ($NaC_2H_3O_2$). Sodium acetate is a salt that dissociates into sodium ions and acetate ions in solution. For as long as acetic acid and acetate ions are present in significant amounts a solution, this can resist dramatic pH changes. Another example of a buffer is a solution containing **ammonia (NH_3, a weak base) and ammonium chloride** (NH_4Cl). Ammonium acetate is also a salt that dissociates into ammonium ions and chloride ions in solution. The presence of ammonium ions with ammonia molecules satisfies the requisite condition for a buffer solution.

How Buffers Work

The essential component of a buffer system is a **conjugate acid-base pair** whose concentration is fairly high in relation to the concentrations of added H^+ or OH^- it is expected to buffer against. Let us use an acetic acid–sodium acetate buffer to demonstrate how buffers work. If a strong base—a source of OH^-(aq) ions—is added to the buffer solution, those hydroxide ions will react with the acetic acid in an acid-base reaction:

$$HC_2H_3O_2\,(aq) + OH^-\,(aq) \longrightarrow H_2O(\ell) + C_2H_3O_2^-\,(aq) \tag{7.14.1}$$

Rather than changing the pH dramatically by making the solution basic, the added hydroxide ions react to make water, and the pH does not change much.

> Many people are aware of the concept of buffers from *buffered aspirin*, which is aspirin that also has magnesium carbonate, calcium carbonate, magnesium oxide, or some other salt. The salt acts like a base, while aspirin is itself a weak acid.

If a strong acid—a source of H^+ ions—is added to the buffer solution, the H^+ ions will react with the anion from the salt. Because $HC_2H_3O_2$ is a weak acid, it is not ionized much. This means that if lots of hydrogen ions and acetate ions (from sodium acetate) are present in the same solution, they will come together to make acetic acid:

$$H^+\,(aq) + C_2H_3O_2^-\,(aq) \longrightarrow HC_2H_3O_2\,(aq) \tag{7.14.2}$$

Rather than changing the pH dramatically and making the solution acidic, the added hydrogen ions react to make molecules of a weak acid. Figure 7.14.1 illustrates both actions of a buffer.

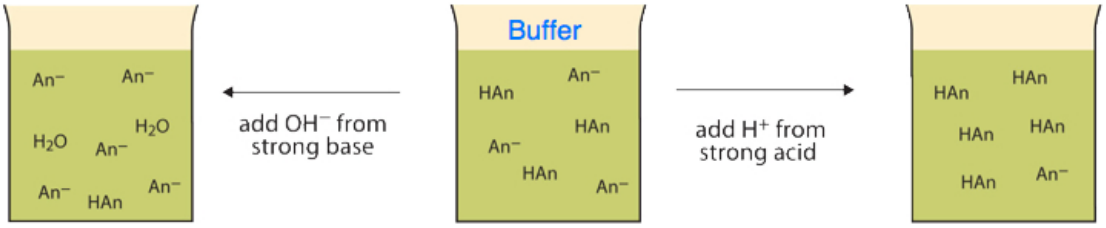


Figure **7.14.1**: The Action of Buffers. Buffers can react with both strong acids (top) and strong bases (bottom) to minimize large changes in pH.

A simple buffer system might be a 0.2 *M* solution of sodium acetate; the conjugate pair here is acetic acid HAc and its conjugate base, the acetate ion Ac^-. The idea is that this conjugate pair "pool" will be available to gobble up any small ($\leq 10^{-3}$ *M*) addition of H+ or OH^- that may result from other processes going on in the solution.

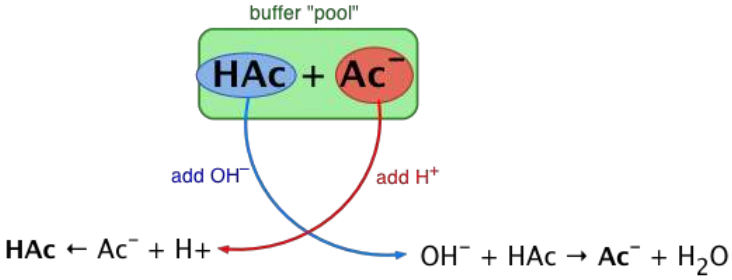


Figure **7.14.2**: How HAc/Ac buffer works

Buffers work well only for limited amounts of added strong acid or base. Once either solute is all reacted, the solution is no longer a buffer, and rapid changes in pH may occur. We say that a buffer has a certain capacity. Buffers that have more solute dissolved in them to start with have larger capacities, as might be expected.

Buffers made from weak bases and salts of weak bases act similarly. For example, in a buffer containing NH_3 and NH_4Cl, ammonia molecules can react with any excess hydrogen ions introduced by strong acids:

$$NH_{3(aq)} + H^+_{(aq)} \rightarrow NH^+_{4(aq)} \tag{7.14.3}$$

while the ammonium ion [NH_4^+(aq)] can react with any hydroxide ions introduced by strong bases:

$$NH^+_{4(aq)} + OH^-_{(aq)} \rightarrow NH_{3(aq)} + H_2O_{(\ell)} \tag{7.14.4}$$

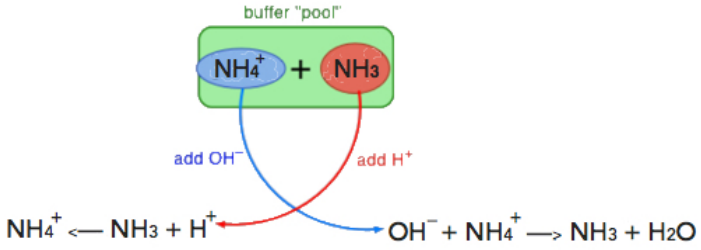


Figure **7.14.3**: How NH_4^+/NH_3 buffer works

Example 7.14.1

Which solute combinations can make a buffer solution? Assume all are aqueous solutions.

a. $HCHO_2$ and $NaCHO_2$
b. HCl and NaCl
c. CH_3NH_2 and CH_3NH_3Cl

d. NH_3 and NaOH

Solution

a. Formic acid ($HCHO_2$) is a weak acid, while $NaCHO_2$ is a salt supplying —formate ion (CHO_2^-), the conjugate base of $HCHO_2$. The combination of these two solutes would make a buffer solution.
b. Hydrochloric acid (HCl) is a strong acid, not a weak acid, so the combination of these two solutes would not make a buffer solution.
c. Methylamine (CH_3NH_2) is like ammonia, a weak base. The compound CH_3NH_3Cl is a salt supplying $CH_3NH_3^+$, the conjugate acid of CH_3NH_2. The combination of these two solutes would make a buffer solution.
d. Ammonia (NH_3) is a weak base, but NaOH is a strong base. The combination of these two solutes would not make a buffer solution.

? Exercise 7.14.1

Which solute combinations can make a buffer solution? Assume all are aqueous solutions.

a. $NaHCO_3$ and NaCl
b. H_3PO_4 and NaH_2PO_4
c. NH_3 and $(NH_4)_3PO_4$
d. NaOH and NaCl

Answer

b. H_3PO_4 (weak acid) and $H_2PO_4^-$ (conjugate base of H_3PO_4) make a buffer.

c. NH_3 (weak base) and NH_4^+ (conjugate acid of NH_3) make a buffer

✓ Food and Drink App: The Acid That Eases Pain

Although medicines are not exactly "food and drink," we do ingest them, so let's take a look at an acid that is probably the most common medicine: acetylsalicylic acid, also known as aspirin. Aspirin is well known as a pain reliever and antipyretic (fever reducer).

The structure of aspirin is shown in the accompanying figure. The acid part is circled; it is the H atom in that part that can be donated as aspirin acts as a Brønsted-Lowry acid. Because it is not given in Table 10.5.1, acetylsalicylic acid is a weak acid. However, it is still an acid, and given that some people consume relatively large amounts of aspirin daily, its acidic nature can cause problems in the stomach lining, despite the stomach's defenses against its own stomach acid.

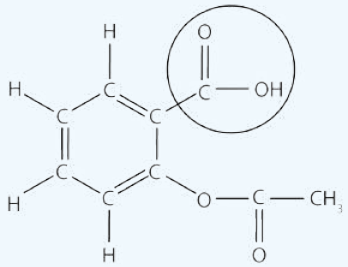


Figure 7.14.4 The Molecular Structure of Aspirin. The circled atoms are the acid part of the molecule.

Because the acid properties of aspirin may be problematic, many aspirin brands offer a "buffered aspirin" form of the medicine. In these cases, the aspirin also contains a buffering agent-usually MgO-that regulates the acidity of the aspirin to minimize its acidic side effects.

As useful and common as aspirin is, it was formally marketed as a drug starting in 1899. The US Food and Drug Administration (FDA), the governmental agency charged with overseeing and approving drugs in the United States, wasn't formed until 1906. Some have argued that if the FDA had been formed before aspirin was introduced, aspirin may never have gotten approval due to its potential for side effects-gastrointestinal bleeding, ringing in the ears, Reye's syndrome (a liver

problem), and some allergic reactions. However, recently aspirin has been touted for its effects in lessening heart attacks and strokes, so it is likely that aspirin is here to stay.

Buffer solutions are essential components of all living organisms.

- Our blood is buffered to maintain a pH of 7.4 that must remain unchanged as metabolically-generated CO_2 (carbonic acid) is added and then removed by our lungs.
- Buffers in the oceans, in natural waters such as lakes and streams, and within soils help maintain their environmental stability against acid rain and increases in atmospheric CO_2.
- Many industrial processes, such as brewing, require buffer control, as do research studies in biochemistry and physiology that involve enzymes, are active only within certain pH ranges.

The pH in living systems (Figure \(\PageIndex{1}\)) is maintained by buffer systems.

Table 7.3.2: pH in Living Systems

Compartment	pH
Gastric Acid	1
Lysosomes	4.5
Granules of Chromaffin Cells	5.5
Human Skin	5.5
Urine	6
Neutral H_2O at 37 °C	6.81
Cytosol	7.2
Cerebrospinal Fluid	7.3
Blood	7.43-7.45
Mitochondrial Matrix	7.5
Pancreas Secretions	8.1

Human blood has a buffering system to minimize extreme changes in pH. One buffer in blood is based on the presence of HCO_3^- and H_2CO_3 [H_2CO_3 is another way to write CO_2(aq)]. With this buffer present, even if some stomach acid were to find its way directly into the bloodstream, the change in the pH of blood would be minimal. Inside many of the body's cells, there is a buffering system based on phosphate ions.

Medicine: The Buffer System in Blood

The normal pH of human blood is about 7.4. The carbonate buffer system in the blood uses the following equilibrium reaction:

$$\mathbf{CO_2}(g) + \mathbf{2\,H_2O}(l) \rightleftharpoons \mathbf{H_2CO_3}(aq) \rightleftharpoons \mathbf{HCO_3^-}(aq) + \mathbf{H_3O^+}(aq)$$

The concentration of carbonic acid, H_2CO_3 is approximately 0.0012 *M*, and the concentration of the hydrogen carbonate ion, $\mathbf{HCO_3^-}$, is around 0.024 *M*. Using the Henderson-Hasselbalch equation and the pK_a of carbonic acid at body temperature, we can calculate the pH of blood:

$$\mathbf{pH} = \mathbf{p}K_\mathbf{a} + \log\frac{[\mathbf{base}]}{[\mathbf{acid}]} = 6.1 + \log\frac{0.024}{0.0012} = 7.4$$

The fact that the H_2CO_3 concentration is significantly lower than that of the $\mathbf{HCO_3^-}$ ion may seem unusual, but this imbalance is due to the fact that most of the by-products of our metabolism that enter our bloodstream are acidic. Therefore, there must be a larger proportion of base than acid, so that the capacity of the buffer will not be exceeded.

Lactic acid is produced in our muscles when we exercise. As the lactic acid enters the bloodstream, it is neutralized by the HCO_3^- ion, producing H_2CO_3. An enzyme then accelerates the breakdown of the excess carbonic acid to carbon dioxide and water, which can be eliminated by breathing. In fact, in addition to the regulating effects of the carbonate buffering system on the pH of blood, the body uses breathing to regulate blood pH. If the pH of the blood decreases too far, an increase in breathing removes CO_2 from the blood through the lungs driving the equilibrium reaction such that $[H_3O^+]$ is lowered. If the blood is too alkaline, a lower breath rate increases CO_2 concentration in the blood, driving the equilibrium reaction the other way, increasing $[H^+]$ and restoring an appropriate pH.

Career Focus: Blood Bank Technology Specialist

At this point in this text, you should have the idea that the chemistry of blood is fairly complex. Because of this, people who work with blood must be specially trained to work with it properly.

A blood bank technology specialist is trained to perform routine and special tests on blood samples from blood banks or transfusion centers. This specialist measures the pH of blood, types it (according to the blood's ABO+/− type, Rh factors, and other typing schemes), tests it for the presence or absence of various diseases, and uses the blood to determine if a patient has any of several medical problems, such as anemia. A blood bank technology specialist may also interview and prepare donors to give blood and may actually collect the blood donation.

Blood bank technology specialists are well trained. Typically, they require a college degree with at least a year of special training in blood biology and chemistry. In the United States, training must conform to standards established by the American Association of Blood Banks.

Key Takeaway

- A buffer is a solution that resists sudden changes in pH.

Concept Review Exercise

1. Explain how a buffer prevents large changes in pH.

Answer

1. A buffer has components that react with both strong acids and strong bases to resist sudden changes in pH.

Exercises

1. Describe a buffer. What two related chemical components are required to make a buffer?
2. Can a buffer be made by combining a strong acid with a strong base? Why or why not?
3. Which solute combinations can make a buffer? Assume all are aqueous solutions.
    1. HCl and NaCl
    2. HNO_2 and $NaNO_2$
    3. NH_4NO_3 and HNO_3
    4. NH_4NO_3 and NH_3
4. Which solute combinations can make a buffer? Assume all are aqueous solutions.
    1. H_3PO_4 and Na_3PO_4
    2. $NaHCO_3$ and Na_2CO_3
    3. $NaNO_3$ and $Ca(NO_3)_2$
    4. HN_3 and NH_3
5. For each combination in Exercise 3 that is a buffer, write the chemical equations for the reactions of the buffer components when a strong acid and a strong base is added.
6. For each combination in Exercise 4 that is a buffer, write the chemical equations for the reaction of the buffer components when a strong acid and a strong base is added.
7. The complete phosphate buffer system is based on four substances: H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}. What different buffer solutions can be made from these substances?

8. Explain why NaBr cannot be a component in either an acidic or a basic buffer.
9. Explain why $Mg(NO_3)_2$ cannot be a component in either an acidic or a basic buffer.

Answers

1. A buffer resists sudden changes in pH. It has a weak acid or base and a salt of that weak acid or base.
2. No. Combining a strong acid and a strong base will produce salt and water. Excess strong acid or strong base will not act as a buffer.
3. 1. not a buffer
   2. buffer
   3. not a buffer
   4. buffer

4. 1. not a buffer

2. buffer

3. not a buffer

4. not buffer

5. 3b: strong acid: $H^+ + NO_2^- \rightarrow HNO_2$; strong base: $OH^- + HNO_2 \rightarrow H_2O + NO_2^-$; 3d: strong acid: $H^+ + NH_3 \rightarrow NH_4^+$; strong base: $OH^- + NH_4^+ \rightarrow H_2O + NH_3$
6. 4b: strong acid: $H^+ + CO_3^{2-} \rightarrow HCO3^-$; strong base: $OH^- + HCO_3^- \rightarrow H_2O + CO_3^{2-}$;
7. Buffers can be made by combining H_3PO_4 and $H_2PO_4^-$, $H_2PO_4^-$ and HPO_4^{2-}, and HPO_4^{2-} and PO_4^{3-}.
8. NaBr splits up into two ions in solution, Na^+ and Br^-. Na^+ will not react with any added base knowing that NaOH is a strong base. Br- will not react with any added acid knowing that HBr is a strong acid. Because NaBr will not react with any added base or acid, it does not resist change in pH and is not a buffer.
9. $Mg(NO_3)_2$ includes two types of ions, Mg^{2+} and NO_3^-. $Mg(OH)_2$ is strong base and completely dissociates (100% falls apart), so Mg^{2+} will not react with any added base (0% combines with OH^-). HNO_3 is strong acid and completely dissociates (100% falls apart), so NO_3^- will not react with any added acid (0% combines with H^+). Because $Mg(NO_3)_2$ will not react with any added base or acid, it does not resist change in pH and is not a buffer.

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CHAPTER OVERVIEW

8: Electrochemistry

8.1: Oxidation-Reduction (Redox) Reactions

8.2: Redox Reactions in Organic Chemistry and Biochemistry

8.3: Electrolytic Cells

8.4: Electrochemical Corrosion

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8.1: Oxidation-Reduction (Redox) Reactions

Learning Objectives

- To identify a chemical reaction as an oxidation-reduction reaction.

When zinc metal is submerged into a quantity of aqueous $\mathbf{HCl}$, the following reaction occurs (Figure 8.1.1):

$$\mathrm{Zn\,(s) + 2\,HCl\,(aq) \longrightarrow H_2\,(g) + ZnCl_2\,(aq)} \tag{8.1.1}$$

This is one example of what is sometimes called a *single replacement reaction* because $\mathbf{Zn}$ replaces $\mathbf{H}$ in combination with $\mathbf{Cl}$.



Figure 8.1.1: Zinc Metal plus Hydrochloric Acid. It is fairly obvious that zinc metal reacts with aqueous hydrochloric acid! The bubbles are hydrogen gas (right side of Equation 8.1.1).

Because some of the substances in this reaction are aqueous, we can separate them into ions:

$$\mathrm{Zn\,(s) + 2\,H^+\,(aq) + 2\,Cl^-\,(aq) \longrightarrow H_2\,(g) + Zn^{2+}\,(aq) + 2\,Cl^-\,(aq)}$$

Viewed this way, the net reaction seems to be a charge transfer between zinc and hydrogen atoms. (There is no net change experienced by the chloride ion.) In fact, electrons are being transferred from the zinc atoms to the hydrogen atoms (which ultimately make a molecule of diatomic hydrogen), changing the charges on both elements.

To understand electron-transfer reactions like the one between zinc metal and hydrogen ions, chemists separate them into two parts: one part focuses on the loss of electrons, and one part focuses on the gain of electrons. The loss of electrons is called oxidation. The gain of electrons is called reduction. Because any loss of electrons by one substance must be accompanied by a gain in electrons by something else, oxidation and reduction always occur together. As such, electron-transfer reactions are also called oxidation-reduction reactions, or simply **redox reactions**. The atom that loses electrons is **oxidized**, and the atom that gains electrons is **reduced**. Also, because we can think of the species being oxidized as causing the reduction, the species being oxidized is called the **reducing agent**, and the species being reduced is called the **oxidizing agent**.

> *Because batteries are used as sources of electricity (that is, of electrons), all batteries are based on redox reactions.*

Although the two reactions occur together, it can be helpful to write the oxidation and reduction reactions separately as half reactions. In half reactions, we include only the reactant being oxidized or reduced, the corresponding product species, any other species needed to balance the half reaction, and the electrons being transferred. Electrons that are lost are written as products; electrons that are gained are written as reactants. For example, in our earlier equation, now written without the chloride ions,

$$\mathrm{Zn\,(s) + 2\,H^+\,(aq) \longrightarrow Zn^{2+}\,(aq) + H_2\,(g)}$$

zinc atoms are oxidized to Zn^{2+}. The **half reaction for the oxidation** reaction, omitting phase labels, is as follows:

$$\mathrm{Zn \longrightarrow Zn^{2+} + 2\,e^-}$$

This half reaction is balanced in terms of the number of zinc atoms, and it also shows the two electrons that are needed as products to account for the zinc atom losing two negative charges to become a 2+ ion. With half reactions, there is one more item to balance:

the overall charge on each side of the reaction. If you check each side of this reaction, you will note that both sides have a zero net charge.

Hydrogen is reduced in the reaction. The balanced **reduction half reaction** is as follows:

$$2\,H^+ + 2\,e^- \longrightarrow H_2$$

There are two hydrogen atoms on each side, and the two electrons written as reactants serve to neutralize the 2+ charge on the reactant hydrogen ions. Again, the overall charge on both sides is zero.

The overall reaction is simply the combination of the two half reactions and is shown by adding them together.

$$\begin{array}{r} Zn \rightarrow Zn^{2+} + \cancel{2e^-} \\ \underline{2H^+ + \cancel{2e^-} \rightarrow H_2} \\ Zn + 2H^+ \rightarrow Zn^{2+} + H_2 \end{array}$$

Because we have two electrons on each side of the equation, they can be canceled. This is the key criterion for a balanced redox reaction: the electrons have to cancel exactly. If we check the charge on both sides of the equation, we see they are the same—2+. (In reality, this positive charge is balanced by the negative charges of the chloride ions, which are not included in this reaction because chlorine does not participate in the charge transfer.)

Redox reactions are often balanced by balancing each individual half reaction and then combining the two balanced half reactions. **Sometimes a half reaction must have all of its coefficients multiplied by some integer for all the electrons to cancel**. The following example demonstrates this process.

Example 8.1.1: Reducing Silver Ions

Write and balance the redox reaction that has silver ions and aluminum metal as reactants and silver metal and aluminum ions as products. Identify the substance oxidized, substance reduced, reducing agent and reducing agent.

Solution

We start by using symbols of the elements and ions to represent the reaction:

$$Ag^+ + Al \longrightarrow Ag + Al^{3+}$$

The equation looks balanced as it is written. However, when we compare the overall charges on each side of the equation, we find a charge of +1 on the left but a charge of +3 on the right. This equation is not properly balanced. To balance it, let us write the two half reactions. Silver ions are reduced, and it takes one electron to change Ag^+ to Ag:

Reduction half-reaction:

$$Ag^+ + e^- \longrightarrow Ag$$

Aluminum is oxidized, losing three electrons to change from Al to Al^{3+}:

Oxidation half-reaction:

$$Al \longrightarrow Al^{3+} + 3\,e^-$$

To combine these two half reactions and cancel out all the electrons, we need to multiply the silver reduction reaction by 3:

$$\begin{array}{r} 3\left(Ag^+ + e^- \rightarrow Ag\right) \\ \underline{Al \rightarrow Al^{3+} + 3e^-} \\ 3Ag^+ + Al \rightarrow 3Ag + Al^{3+} \end{array}$$

Now the equation is balanced, not only in terms of elements but also in terms of charge.

- The **substance oxidized** is the reactant that had undergone oxidation: Al
- The **substance reduced** is the reactant that had undergone reduction: Ag^+
- The **reducing agent** is the same as the substance oxidized: Al

- The **oxidizing agent** is the same as the substance reduced: $\mathbf{Ag^+}$

Exercise 8.1.1

Write and balance the redox reaction that has calcium ions and potassium metal as reactants and calcium metal and potassium ions as products. Identify the substance oxidized, substance reduced, reducing agent and reducing agent.

Answer

Reduction: $\mathbf{Ca^{2+} + 2\,e^- \longrightarrow Ca}$

Oxidation: \(2 \times (\ce{K -> K^{+} + e^{-}})\)

Combined: $\mathbf{Ca^{2+} + 2\,K \longrightarrow Ca + 2\,K^+}$

- The **substance oxidized** is the reactant that had undergone oxidation: $\mathbf{K}$
- The **substance reduced** is the reactant that had undergone reduction: $\mathbf{Ca^{2+}}$
- The **reducing agent** is the same as the substance oxidized: $\mathbf{K}$
- The **oxidizing agent** is the same as the substance reduced: $\mathbf{Ca^{2+}}$

Potassium has been used as a reducing agent to obtain various metals in their elemental form.

To Your Health: Redox Reactions and Pacemaker Batteries

All batteries use redox reactions to supply electricity because electricity is basically a stream of electrons being transferred from one substance to another. Pacemakers—surgically implanted devices for regulating a person's heartbeat—are powered by tiny batteries, so the proper operation of a pacemaker depends on a redox reaction.

Pacemakers used to be powered by NiCad batteries, in which nickel and cadmium (hence the name of the battery) react with water according to this redox reaction:

$$\mathbf{Cd\,(s) + 2\,NiOOH\,(s) + 2\,H_2O(\ell) \longrightarrow Cd(OH)_2\,(s) + 2\,Ni(OH)_2\,(s)}$$

The cadmium is oxidized, while the nickel atoms in $\mathbf{NiOOH}$ are reduced. Except for the water, all the substances in this reaction are solids, allowing NiCad batteries to be recharged hundreds of times before they stop operating. Unfortunately, NiCad batteries are fairly heavy batteries to be carrying around in a pacemaker. Today, the lighter lithium/iodine battery is used instead. The iodine is dissolved in a solid polymer support, and the overall redox reaction is as follows:

$$\mathbf{2\,Li\,(s) + I_2\,(s) \longrightarrow 2\,LiI\,(s)}$$

Lithium is oxidized, and iodine is reduced. Although the lithium/iodine battery cannot be recharged, one of its advantages is that it lasts up to 10 years. Thus, a person with a pacemaker does not have to worry about periodic recharging; about once per decade a person requires minor surgery to replace the pacemaker/battery unit. Lithium/iodine batteries are also used to power calculators and watches.



Figure **8.1.1**: A small button battery like this is used to power a watch, pacemaker, or calculator. (CC BY-SA; Gerhard H Wrodnigg via Wikipedia)

Oxidation and reduction can also be defined in terms of changes in composition. The original meaning of **oxidation** was "**adding oxygen**," so when oxygen is added to a molecule, the molecule is being oxidized. The reverse is true for **reduction**: if a molecule

loses oxygen atoms, the molecule is being reduced. For example, the acetaldehyde (CH_3CHO) molecule takes on an oxygen atom to become acetic acid (CH_3COOH).

$$2\,CH_3CHO + O_2 \longrightarrow 2\,CH_3COOH$$

Thus, acetaldehyde is being oxidized.

Similarly, **reduction and oxidation can be defined in terms of the gain or loss of hydrogen atoms**. If a molecule adds hydrogen atoms, it is being reduced. If a molecule loses hydrogen atoms, the molecule is being oxidized. For example, in the conversion of acetaldehyde into ethanol (CH_3CH_2OH), hydrogen atoms are added to acetaldehyde, so the acetaldehyde is being reduced:

$$CH_3CHO + H_2 \longrightarrow CH_3CH_2OH$$

Table shows how each process affects the change in oxygen and change in hydrogen.

Process	Change in oxygen (some reactions)	Change in hydrogen (some reactions)
Oxidation	gain	lose
Reduction	lose	gain

Example 8.1.2

In each conversion, indicate whether oxidation or reduction is occurring.

a. $N_2 \longrightarrow NH_3$
b. $CH_3CH_2OHCH_3 \longrightarrow CH_3COCH_3$
c. $HCHO \longrightarrow HCOOH$

Solution

a. Hydrogen is being added to the original reactant molecule, so reduction is occurring.
b. Hydrogen is being removed from the original reactant molecule, so oxidation is occurring.
c. Oxygen is being added to the original reactant molecule, so oxidation is occurring.

Exercise 8.1.2

In each conversion, indicate whether oxidation or reduction is occurring.

a. $CH_4 \longrightarrow CO_2 + H_2O$
b. $NO_2 \longrightarrow N_2$
c. $CH_2{=}CH_2 \longrightarrow CH_3CH_3$

Answer a:

Oxygen is being added. Oxidation is occurring.

Answer b:

Oxygen is being removed. Reduction is occurring.

Answer a:

Hydrogen is being added. Reduction is occurring.

Key Takeaway

Chemical reactions in which electrons are transferred are called oxidation-reduction, or redox, reactions. Oxidation is the loss of electrons. Reduction is the gain of electrons. Oxidation and reduction always occur together, even though they can be written as separate chemical equations.

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8.2: Redox Reactions in Organic Chemistry and Biochemistry

Learning Objectives

- To identify oxidation-reduction reactions with organic compounds.

Oxidation-reduction reactions are of central importance in organic chemistry and biochemistry. The burning of fuels that provides the energy to maintain our civilization and the metabolism of foods that furnish the energy that keeps us alive both involve redox reactions.



Figure 8.2.1: The Burning of Natural Gas. The burning of natural gas is not only a combustion reaction but also a redox reaction. Similar reactions include the burning of gasoline and coal. These are also redox reactions. (CC BY-SA 2.0 Generic; Simon Law via Flickr).

All combustion reactions are also redox reactions. A typical combustion reaction is the burning of methane, the principal component of natural gas (Figure 8.2.1).

$$\mathrm{CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O} \tag{8.2.1}$$

In respiration, the biochemical process by which the oxygen we inhale in air oxidizes foodstuffs to carbon dioxide and water, redox reactions provide energy to living cells. A typical respiratory reaction is the oxidation of glucose ($\mathrm{C_6H_{12}O_6}$), the simple sugar we encountered in the chapter-opening essay that makes up the diet of yeast:

$$\mathrm{C_6H_{12}O_6 + 6\,O_2 \rightarrow 6\,CO_2 + 6\,H_2O} \tag{8.2.2}$$

Organic chemists use a variety of redox reactions. For example, potassium dichromate ($\mathrm{K_2Cr_2O_7}$) is a common oxidizing agent that can be used to oxidize alcohols (symbolized by the general formula ROH). The product of the reaction depends on the location of the OH functional group in the alcohol molecule, the relative proportions of alcohol and the dichromate ion, and reaction conditions such as temperature. If the OH group is attached to a terminal carbon atom and the product is distilled off as it forms, the product is an aldehyde, which has a terminal *carbonyl group* (C=O) and is often written as RCHO. One example is the reaction used by the Breathalyzer to detect ethyl alcohol ($\mathrm{CH_3CH_2OH}$) in a person's breath:

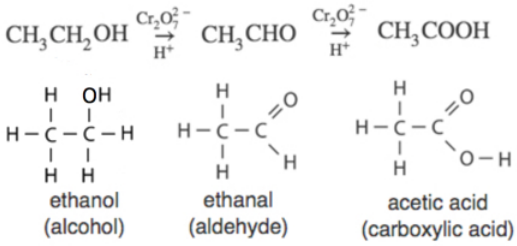
$$\mathrm{3\,CH_3CH_2OH + Cr_2O_7^{2-} + 8\,H^+ \rightarrow 3\,CH_3CHO + 2\,Cr^{3+} + 7\,H_2O} \tag{8.2.3}$$

If the product acetaldehyde ($\mathrm{CH_3CHO}$) is not removed as it forms, it is further oxidized to acetic acid ($\mathrm{CH_3COOH}$). In this case, the overall reaction is as follows:

$$\mathrm{3\,CH_3CH_2OH + 2\,Cr_2O_7^{2-} + 16\,H^+ \rightarrow 3\,CH_3COOH + 4\,Cr^{3+} + 11\,H_2O} \tag{8.2.4}$$

In this reaction, the chromium atom is reduced because it lost oxygen atoms from $Cr_2O_7^{2-}$ to Cr^{3+}. On the other hand, the carbon atom in ethanol is oxidized. In the **oxidation** of ethyl alcohol (CH_3CH_2OH, a.k.a. ethanol) to form acetaldehayde (CH_3CHO, a.k.a. ethanal), the **number of bonds to oxygen has increased and the number of hydrogen atoms has decreased** from six to four. Either or both of these indicate that an oxidation has occurred.

In the oxidation of acetaldehyde to acetic acid (a.k.a. ethanoic acid), the carbon atom that gained an additional oxygen is the element oxidized.



When the OH group of the alcohol is bonded to an interior carbon atom, the oxidation of an alcohol will produce a ketone (the formulas of ketones are often written as RCOR, and the carbon–oxygen bond is a double bond). The simplest ketone is derived from 2-propanol ($\mathbf{CH_3CHOHCH_3}$). It is the common solvent acetone [$\mathbf{(CH_3)_2CO}$], which is used in varnishes, lacquers, rubber cement, and nail polish remover. Acetone can be formed by the following redox reaction:

$$\mathbf{3\,CH_3CHOHCH_3 + Cr_2O_7^{2-} + 8\,H^+ \rightarrow 3\,(CH_3)_2CO + 2\,Cr^{3+} + 7\,H_2O} \tag{8.2.5}$$

As we have just seen, aldehydes and ketones can be formed by the oxidation of alcohols. Conversely, aldehydes and ketones can be reduced to alcohols. Reduction of the carbonyl group is important in living organisms. For example, in anaerobic metabolism, in which biochemical processes take place in the absence of oxygen, pyruvic acid ($\mathbf{CH_3COCOOH}$) is reduced to lactic acid ($\mathbf{CH_3CHOHCOOH}$) in the muscles.

$$\mathbf{CH_3COCOOH \rightarrow CH_3CHOHCOOH} \tag{8.2.6}$$

(Pyruvic acid is both a carboxylic acid and a ketone; only the ketone group is reduced.) The buildup of lactic acid during vigorous exercise is responsible in large part for the fatigue that we experience.

In food chemistry, the substances known as antioxidants are reducing agents. Ascorbic acid (vitamin C; $\mathbf{C_6H_8O_6}$) is thought to retard potentially damaging oxidation of living cells. In the process, it is oxidized to dehydroascorbic acid ($\mathbf{C_6H_6O_6}$). In the stomach, ascorbic acid reduces the nitrite ion ($\mathbf{NO_2^-}$) to nitric oxide ($\mathbf{NO}$):

$$\mathbf{C_6H_8O_6 + 2\,H^+ + 2\,NO_2^- \rightarrow C_6H_6O_6 + 2\,H_2O + 2\,NO} \tag{8.2.7}$$

> *If reaction in Equation 8.2.7 did not occur, nitrite ions from foods would oxidize the iron in hemoglobin, destroying its ability to carry oxygen.*

Tocopherol (vitamin E) is also an antioxidant. In the body, **vitamin E** is thought to act by scavenging harmful by-products of metabolism, such as the highly reactive molecular fragments called free radicals. In foods, vitamin E acts to prevent fats from being oxidized and thus becoming rancid. **Vitamin C** is also a good antioxidant (Figure **8.2.2**).



Figure **8.2.2**: Citrus Fruits. Citrus fruits, such as oranges, lemons, and limes, are good sources of vitamin C, which is an antioxidant. (Pexels License; Scott Webb via Pexels)

Finally, and of greatest importance, green plants carry out the redox reaction that makes possible almost all life on Earth. They do this through a process called photosynthesis, in which carbon dioxide and water are converted to glucose ($\mathbf{C_6H_{12}O_6}$). The synthesis

of glucose requires a variety of proteins called enzymes and a green pigment called chlorophyll that converts sunlight into chemical energy (Figure 8.2.3). The overall change that occurs is as follows:

$$6\,CO_2 + 6\,H_2O \rightarrow C_6H_{12}O_6 + 6\,O_2 \tag{8.2.8}$$

In this reaction, carbon dioxide is reduced to glucose, and water is oxidized to oxygen gas. Other reactions convert the glucose to more complex carbohydrates, plant proteins, and oils.



Figure 8.2.3: Life on Earth. Photosynthesis is the fundamental process by which plants use sunlight to convert carbon dioxide and water into glucose and oxygen. Then plants make more complex carbohydrates. It is the ultimate source of all food on Earth, and it is a redox reaction. (Public Domain; Wikipedia).

Summary

Redox reactions are common in organic and biological chemistry, including the combustion of organic chemicals, respiration, and photosynthesis.

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8.3: Electrolytic Cells

In 1989, two scientists announced that they had achieved "cold fusion", the process of fusing together elements at essentially room temperature to achieve energy production. The hypothesis was that the fusion would produce more energy than was required to cause the process to occur. Their process involved the electrolysis of heavy water (water molecules containing some deuterium instead of normal hydrogen) on a palladium electrode. The experiments could not be reproduced and their scientific reputations were pretty well shot. However, in more recent years, both industry and government researchers are taking another look at this process. The device illustrated above is part of a government project, and NASA is completing some studies on the topic as well. Cold fusion may not be so "cold" after all.

Electrolytic Cells

A voltaic cell uses a spontaneous redox reaction to generate an electric current. It is also possible to do the opposite. When an external source of direct current is applied to an electrochemical cell, a reaction that is normally nonspontaneous can be made to proceed. **Electrolysis** is the process in which electrical energy is used to cause a nonspontaneous chemical reaction to occur. Electrolysis is responsible for the appearance of many everyday objects, such as gold-plated or silver-plated jewelry, and chrome-plated car bumpers.

An **electrolytic cell** is the apparatus used for carrying out an electrolysis reaction. In an electrolytic cell, electric current is applied to provide a source of electrons for driving the reaction in a nonspontaneous direction. In a voltaic cell, the reaction goes in a direction that releases electrons spontaneously. In an electrolytic cell, the input of electrons from an external source forces the reaction to go in the opposite direction.

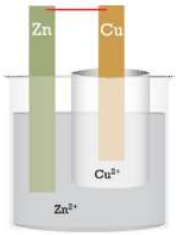


Figure 8.3.1: Zn/Cu cell.

The spontaneous direction for the reaction between Zn and Cu is for the Zn metal to be oxidized to Zn^{2+} ions, while the Cu^{2+} ions are reduced to Cu metal. This makes the zinc electrode the anode and the copper electrode the cathode. When the same half-cells are connected to a battery via the external wire, the reaction is forced to run in the opposite direction. The zinc electrode is now the cathode and the copper electrode is the anode.

oxidation (anode)	$Cu\,(s) \rightarrow Cu^{2+}\,(aq) + 2e^-$	$E^0 = -0.34\ V$
reduction (cathode)	$Zn^{2+}\,(aq) + 2e^- \rightarrow Zn\,(s)$	$E^0 = -0.76\ V$
overall reaction	$Cu\,(s) + Zn^{2+}\,(aq) \rightarrow Cu^{2+}\,(aq) + Zn\,(s)$	$E^0_{cell} = -1.10\ V$

The standard cell potential is negative, indicating a nonspontaneous reaction. The battery must be capable of delivering at least 1.10 V of direct current in order for the reaction to occur. Another difference between a voltaic cell and an electrolytic cell is the signs of the electrodes. In a voltaic cell, the anode is negative and the cathode is positive. In an electrolytic cell, the anode is negative and the cathode is positive. In an electrolytic cell, the anode is positive because it is connected to the positive terminal of the battery. The cathode is therefore negative. Electrons still flow through the cell from the anode to the cathode.

Summary

- The function of an electrolytic cell is described.
- Reactions illustrating electrolysis are given.

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8.4: Electrochemical Corrosion

Learning Objectives

Make sure you thoroughly understand the following essential ideas. It is especially important that you know the precise meanings of all the highlighted terms in the context of this topic.

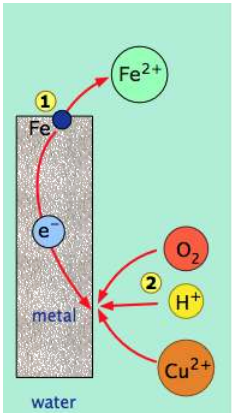
- Electrochemical corrosion of metals occurs when electrons from atoms at the surface of the metal are transferred to a suitable electron acceptor or *depolarizer*. Water must be present to serve as a medium for the transport of ions.
- The most common depolarizers are oxygen, acids, and the cations of less active metals.
- Because the electrons flow through the metallic object itself, the anodic and cathodic regions (the two halves of the electrochemical cell) can be at widely separated locations.
- Anodic regions tend to develop at locations where the metal is stressed or is protected from oxygen.
- Contact with a different kind of metal, either direct or indirect, can lead to corrosion of the more active one.
- Corrosion of steel can be inhibited by *galvanizing*, that is, by coating it with zinc, a more active metal whose dissolution leaves a negative charge on the metal which inhibits the further dissolution of Fe^{2+}.
- *Cathodic protection* using an external voltage source is widely used to protect underground structures such as tanks, pipelines and piers. The source can be a sacrificial anode of zinc or aluminum, or a line-operated or photovoltaic power supply.

Corrosion can be defined as the deterioration of materials by chemical processes. Of these, the most important by far is electrochemical corrosion of metals, in which the oxidation process $M \rightarrow M^{+} + e^{-}$ is facilitated by the presence of a suitable electron acceptor, sometimes referred to in corrosion science as a *depolarizer.*

In a sense, corrosion can be viewed as the spontaneous return of metals to their ores; the huge quantities of energy that were consumed in mining, refining, and manufacturing metals into useful objects is dissipated by a variety of different routes. The economic aspects of corrosion are far greater than most people realize; the estimated cost of corrosion in the U.S. alone was $276 billion per year. Of this, about $121 billion was spent to control corrosion, leaving the difference of $155 billion as the net loss to the economy. Utilities, especially drinking water and sewer systems, suffer the largest economic impact, with motor vehicles and transportation being a close second.

Corrosion Cells and Reactions

The special characteristic of most corrosion processes is that the oxidation and reduction steps occur at separate locations on the metal. This is possible because metals are conductive, so the electrons can flow through the metal from the anodic to the cathodic regions (Figure **8.4.1**). The presence of water is necessary in order to transport ions to and from the metal, but a thin film of adsorbed moisture can be sufficient.



① $Fe \rightarrow Fe^{2+} + 2e^-$
Fe atom at metal surface dissolves into moisture film, leaving negative charge in metal.

② Corrosion continues as a *depolarizer* removes electrons from metal. Common depolarizers are:

oxygen:
$O_2 + 4H_2O \rightarrow 4e^- + 4OH^-$

acid: $2H^+ + 2e^- \rightarrow H_2$

cation of more-noble metal:
$Cu^{2+} + 2e^- \rightarrow Cu$

Figure **8.4.1**: Corrosion is a two-step process. Figure **8.4.1**: Electrochemical corrosion of iron. Corrosion often begins at a location (1) where the metal is under stress (at a bend or weld) or is isolated from the air (where two pieces of metal are joined or under a loosely-adhering paint film.) The metal ions dissolve in the moisture film and the electrons migrate to another location (2) where they are taken up by a *depolarizer*. Oxygen is the most common depolarizer; the resulting hydroxide ions react with the Fe^{2+} to form the mixture of hydrous iron oxides known as *rust*. (CC BY 3.0 Unported; Stephen Lower)

A corrosion system can be regarded as a short-circuited electrochemical cell in which the anodic process is something like

$$\mathrm{Fe(s)} \rightarrow \mathrm{Fe^{2+}(aq) + 2e^-} \tag{8.4.1}$$

and the cathodic steps may invove the reduction of oxygen gas

$$\mathrm{O_2 + 2H_2O + 4e^- \rightarrow 4OH^-} \tag{8.4.2}$$

or the reduction of protons

$$\mathrm{H^+ + e^- \rightarrow \tfrac{1}{2} H_2(g)} \tag{8.4.3}$$

or the reduction of a metal ion

$$\mathrm{M^{2+} + 2e^- \rightarrow M(s)} \tag{8.4.4}$$

where M is a metal.

Which parts of the metal serve as anodes and cathodes can depend on many factors, as can be seen from the irregular corrosion patterns that are commonly observed. Atoms in regions that have undergone stress, as might be produced by forming or machining, often tend to have higher free energies, and thus tend to become anodic.

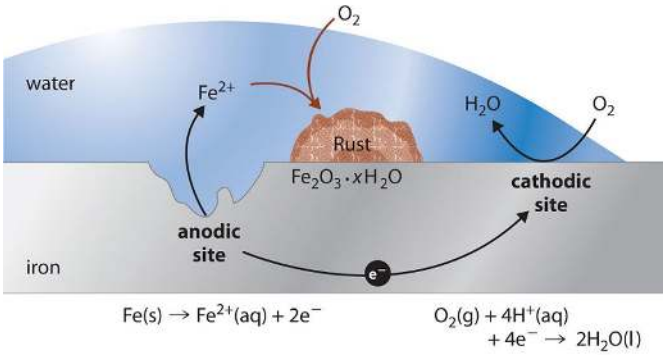


Figure **8.4.2**: Schematic diagram of corrosion cells on iron. (CC BY-NSA-NC; Anonymous by request)

If one part of a metallic object is protected from the atmosphere so that there is insufficient $\mathrm{O_2}$ to build or maintain the oxide film, this "protected" region will often be the site at which corrosion is most active. The fact that such sites are usually hidden from view accounts for much of the difficulty in detecting and controlling corrosion.

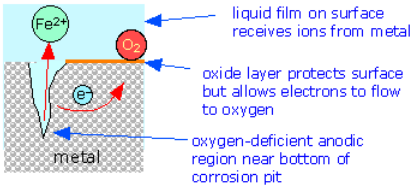


Figure **8.4.3**: Pitting corrosion Most metals are covered with a thin oxide film which inhibits anodic dissolution. When corrosion does occur, it sometimes hollows out a narrow hole or pit in the metal. The bottoms of these pits tend to be deprived of oxygen, thus promoting further growth of the pit into the metal. (CC BY 3.0 Unported; Stephen Lower)

In contrast to anodic sites, which tend to be localized to specific regions of the surface, the cathodic part of the process can occur almost anywhere. Because metallic oxides are usually semiconductors, most oxide coatings do not inhibit the flow of electrons to the surface, so almost any region that is exposed to $\mathbf{O_2}$ or to some other electron acceptor can act as a cathode. The tendency of oxygen-deprived locations to become anodic is the cause of many commonly-observed patterns of corrosion.

Anyone who has owned an older car has seen corrosion occur at joints between body parts and under paint films. You will also have noticed that once corrosion starts, it tends to feed on itself. One reason for this is that one of the products of the O_2 reduction reaction is hydroxide ion. The high pH produced in these cathodic regions tends to destroy the protective oxide film, and may even soften or weaken paint films, so that these sites can become anodic. The greater supply of electrons promotes more intense cathodic action, which spawns even more anodic sites, and so on.



Figure **8.4.4**: Rusted out car. Severely rusted floorboards of 1990 Chrysler New Yorker. Car was damaged to the point where it became unsafe to drive. Under the rusting section between the two holes were the two brake lines (Public Domain; Bige1977 via Wikipedia).

A very common cause of corrosion is having two dissimilar metals in contact, as might occur near a fastener or at a weld joint. Moisture collects at the junction point, acting as an electrolyte and forming a cell in which the two metals serve as electrodes. Moisture and conductive salts on the outside surfaces provide an external conductive path, effectively short-circuiting the cell and producing very rapid corrosion; this is why cars rust out so quickly in places where salt is placed on roads to melt ice.

Dissimilar-metal corrosion can occur even if the two metals are not initially in direct contact. For example, in homes where copper tubing is used for plumbing, there is always a small amount of dissolved $\mathbf{Cu^{2+}}$ in the water. When this water encounters steel piping or a chrome-plated bathroom sink drain, the more-noble copper will plate out on the other metal, producing a new metals-in-contact corrosion cell. In the case of chrome bathroom sink fittings, this leads to the formation of $\mathbf{Cr^{3+}}$ salts which precipitate as greenish stains.

Control of Corrosion

Since both the cathodic and anodic steps must take place for corrosion to occur, prevention of either one will stop corrosion. The most obvious strategy is to stop both processes by coating the object with a paint or other protective coating. Even if this is done, there are likely to be places where the coating is broken or does not penetrate, particularly if there are holes or screw threads. A more sophisticated approach is to apply a slight negative charge to the metal, thus making it more difficult for the reaction to take place:

$$M \longrightarrow M^{2+} + 2e^{-}. \tag{8.4.5}$$

Protection Method 1: Sacrificial Coatings

One way of supplying this negative charge is to apply a coating of a more active metal. Thus a very common way of protecting steel from corrosion is to coat it with a thin layer of zinc; this process is known as galvanizing.The zinc coating, being less noble than iron, tends to corrode selectively. Dissolution of this sacrificial coating leaves behind electrons which concentrate in the iron, making it cathodic and thus inhibiting its dissolution.

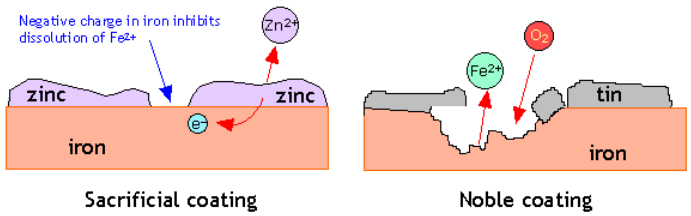


Figure 8.4.5: Sacrificial Coatings (CC BY 3.0 Unported; Stephen Lower)

The effect of plating iron with a less active metal provides an interesting contrast. The common tin-plated can (on the right) is a good example. As long as the tin coating remains intact, all is well, but exposure of even a tiny part of the underlying iron to the moist atmosphere initiates corrosion. The electrons released from the iron flow into the tin, making the iron more anodic so now the tin is actively promoting corrosion of the iron! You have probably observed how tin cans disintegrate very rapidly when left outdoors.

Protection Method 2: Cathodic Protection

A more sophisticated strategy is to maintain a continual negative electrical charge on a metal, so that its dissolution as positive ions is inhibited. Since the entire surface is forced into the cathodic condition, this method is known as *cathodic protection*. The source of electrons can be an external direct current power supply (commonly used to protect oil pipelines and other buried structures), or it can be the corrosion of another, more active metal such as a piece of zinc or aluminum buried in the ground nearby, as is shown in the illustration of the buried propane storage tank below.

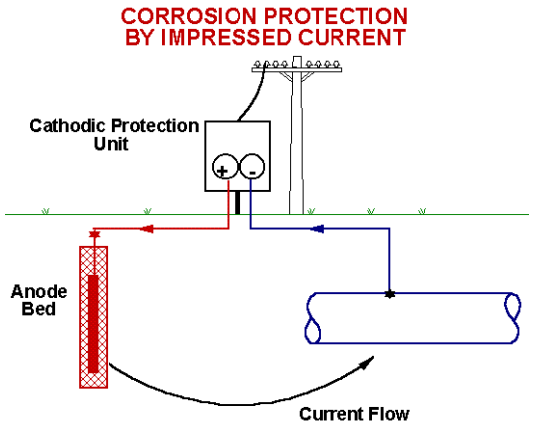


Figure 8.4.6: Cathodic Protection (CC BY 3.0 Unported; Stephen Lower)

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Index

A

Abegg's rule
2.7: Lewis Dot and Bonding

acid strength
7.10: The Strengths of Acids and Bases

B

base strength
7.10: The Strengths of Acids and Bases

C

cathodic protection
8.4: Electrochemical Corrosion

combination reaction
4.4: Some Types of Chemical Reactions

combustion reaction
4.4: Some Types of Chemical Reactions

common system
3.2: Ionic Nomenclature

compound
1.10: Classifying Matter According to Its Composition

corrosion
8.4: Electrochemical Corrosion

corrosion resistance
8.4: Electrochemical Corrosion

covalent bond
2.8: Covalent Bonds

D

decomposition reaction
4.4: Some Types of Chemical Reactions

dynamic equilibrium
7.10: The Strengths of Acids and Bases

E

element
1.10: Classifying Matter According to Its Composition

I

Ionic Nomenclature
3.2: Ionic Nomenclature

L

law of conservation of mass
4.2: The Law of Conservation of Matter

law of definite proportions
1.8: Law of Definite Proportions

Lewis diagram
2.7: Lewis Dot and Bonding

M

mixture
1.10: Classifying Matter According to Its Composition

monatomic anions
3.2: Ionic Nomenclature

O

octet rule
2.7: Lewis Dot and Bonding

P

pOH
7.11: The pOH Concept

R

redox reaction
8.1: Oxidation-Reduction (Redox) Reactions

Redox Reactions (Organic Chemistry)
8.2: Redox Reactions in Organic Chemistry and Biochemistry

rust
8.4: Electrochemical Corrosion

S

Sacrificial Coatings
8.4: Electrochemical Corrosion

Stock system
3.2: Ionic Nomenclature

stoichiometry
5.3: Quantitative Relationships Based on Chemical Equations

V

VSEPR
2.10: Characteristics of Molecules

Glossary

Sample Word 1 | Sample Definition 1

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By Page

- Chemistry - Academic and Career Preparation - *Undeclared*
  - Front Matter - *Undeclared*
    - TitlePage - *Undeclared*
    - InfoPage - *Undeclared*
    - Table of Contents - *Undeclared*
    - Licensing - *Undeclared*
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    - 1.6: Dalton's Atomic Theory - *CC BY-NC 4.0*
    - 1.7: Conservation of Mass - *CC BY-NC 4.0*
    - 1.8: Law of Definite Proportions - *CC BY-NC 4.0*
    - 1.9: Law of Multiple Proportions - *CC BY-NC 4.0*
    - 1.10: Classifying Matter According to Its Composition - *Undeclared*
    - 1.11: The Structure of Atoms - *CC BY-NC-SA 4.0*
    - 1.12: Protons - *CC BY-NC 4.0*
    - 1.13: Electrons - *CC BY-NC 4.0*
    - 1.14: Neutrons - *CC BY-NC 4.0*
    - 1.15: Nuclei of Atoms - *CC BY-NC-SA 4.0*
    - 1.16: Atomic Masses - *CC BY-NC-SA 4.0*
  - 2: Trends and Bonding - *Undeclared*
    - 2.1: The Periodic Table - *CC BY-NC-SA 4.0*
    - 2.2: Periodic Trends- Atomic Radius - *CC BY-NC 4.0*
    - 2.3: Periodic Trends- Ionization Energy - *CC BY-NC 4.0*
    - 2.4: Periodic Trends- Electronegativity - *CC BY-NC 4.0*
    - 2.5: Prelude to Ionic Bonding and Simple Ionic Compounds - *CC BY-NC-SA 4.0*
    - 2.6: Prelude to Covalent Bonding and Simple Molecular Compounds - *CC BY-NC-SA 4.0*
    - 2.7: Lewis Dot and Bonding - *CC BY-NC-SA 4.0*
    - 2.8: Covalent Bonds - *CC BY-NC-SA 4.0*
    - 2.9: Drawing Lewis Structures - *CC BY-NC-SA 4.0*
    - 2.10: Characteristics of Molecules - *CC BY-NC-SA 4.0*
    - 2.11: Exceptions to the Octet Rule - *CC BY-NC 4.0*
  - 3: Nomenclature - *Undeclared*
    - 3.1: Formulas for Ionic Compounds - *CC BY-NC-SA 4.0*
    - 3.2: Ionic Nomenclature - *CC BY-NC-SA 4.0*
    - 3.3: Covalent Compounds - Formulas and Names - *CC BY-NC-SA 4.0*
    - 3.4: Naming Acids - *CC BY-NC 4.0*
    - 3.5: Names and Formulas of Bases - *CC BY-NC 4.0*
  - 4: Chemical Calculations 1 - *Undeclared*
    - 4.1: Prelude to Introduction to Chemical Reactions - *CC BY-NC-SA 4.0*
    - 4.2: The Law of Conservation of Matter - *CC BY-NC-SA 4.0*
    - 4.3: Chemical Equations - *CC BY-NC-SA 4.0*
    - 4.4: Some Types of Chemical Reactions - *CC BY-NC-SA 4.0*
    - 4.5: Single Replacement Reactions - *CC BY-NC 4.0*
    - 4.6: Activity Series - *CC BY-NC 4.0*
    - 4.7: Double Replacement Reactions - *CC BY-NC 4.0*
    - 4.8: Avogadro's Number - *CC BY-NC 4.0*

- 4.9: The Mole - *CC BY-NC-SA 4.0*
- 4.10: Molar Mass - *CC BY-NC 4.0*
- 4.11: Atomic and Molar Masses - *CC BY-NC-SA 4.0*
- 4.12: Mole-Mass Conversions - *CC BY-NC-SA 4.0*
- 4.13: Percent Composition - *CC BY-NC 4.0*
- 4.14: Percent of Water in a Hydrate - *CC BY-NC 4.0*

5: Chemical Calculations 2 - *Undeclared*

- 5.1: Everyday Stoichiometry - *CC BY-NC 4.0*
- 5.2: Mole Ratios - *CC BY-NC 4.0*
- 5.3: Quantitative Relationships Based on Chemical Equations - *CC BY-NC-SA 4.0*
- 5.4: Mole-Mole Relationships in Chemical Reactions - *CC BY-NC-SA 4.0*
- 5.5: Mole-Mass and Mass-Mass Problems - *CC BY-NC-SA 4.0*
- 5.6: Mass-Volume and Volume-Mass Stoichiometry - *CC BY-NC 4.0*
- 5.7: Concentration - *CC BY-NC-SA 4.0*
- 5.8: Limiting Reactant - *CC BY-NC 4.0*
- 5.9: Determining the Limiting Reactant - *CC BY-NC 4.0*
- 5.10: Theoretical Yield and Percent Yield - *CC BY-NC 4.0*
- 5.11: Percent Error - *CC BY-NC 4.0*

6: Organic Chemistry - *Undeclared*

- 6.1: Organic Chemistry - *CC BY-NC-SA 4.0*
- 6.2: Structures and Names of Alkanes - *CC BY-NC-SA 4.0*
- 6.3: Branched-Chain Alkanes - *CC BY-NC-SA 4.0*
- 6.4: Condensed Structural and Line-Angle Formulas - *CC BY-NC-SA 4.0*
- 6.5: IUPAC Nomenclature - *CC BY-NC-SA 4.0*
- 6.6: Constitutional Isomers - *CC BY 4.0*
- 6.7: Physical Properties of Alkanes - *CC BY-NC-SA 4.0*
- 6.8: Chemical Properties of Alkanes - *CC BY-NC-SA 4.0*
- 6.9: Cycloalkanes - *CC BY-NC-SA 4.0*
- 6.10: Alkenes- Structures and Names - *CC BY-NC-SA 4.0*
- 6.11: Physical Properties of Alkenes - *CC BY-NC-SA 4.0*
- 6.12: Chemical Properties of Alkenes - *CC BY-NC-SA 4.0*
- 6.13: Polymers - *CC BY-NC-SA 4.0*
- 6.14: Alkynes - *CC BY-NC-SA 4.0*
- 6.15: Aromatic Compounds- Benzene - *CC BY-NC-SA 4.0*
- 6.16: Structure and Nomenclature of Aromatic Compounds - *CC BY-NC-SA 4.0*

7: Chemistry in the Environment - *Undeclared*

- 7.1: Prelude to Solids, Liquids, and Gases - *CC BY-NC-SA 4.0*
- 7.2: Solids and Liquids - *CC BY-NC-SA 4.0*
- 7.3: Gases and Pressure - *CC BY-NC-SA 4.0*
- 7.4: Gas Laws - *CC BY-NC-SA 4.0*
- 7.5: Gay-Lussac's Law - *CC BY-NC 4.0*
- 7.6: Prelude to Acids and Bases - *CC BY-NC-SA 4.0*
- 7.7: Arrhenius Definition of Acids and Bases - *CC BY-NC-SA 4.0*
- 7.8: Brønsted-Lowry Definition of Acids and Bases - *CC BY-NC-SA 4.0*
- 7.9: Water - Both an Acid and a Base - *CC BY-NC-SA 4.0*
- 7.10: The Strengths of Acids and Bases - *CC BY-NC-SA 4.0*
- 7.11: The pOH Concept - *CC BY-NC 4.0*
- 7.12: Titration Experiment - *CC BY-NC 4.0*
- 7.13: Titration Calculations - *CC BY-NC 4.0*
- 7.14: Buffers - *CC BY-NC-SA 4.0*

8: Electrochemistry - *Undeclared*

- 8.1: Oxidation-Reduction (Redox) Reactions - *CC BY-NC-SA 4.0*
- 8.2: Redox Reactions in Organic Chemistry and Biochemistry - *CC BY-NC-SA 4.0*
- 8.3: Electrolytic Cells - *CC BY-NC 4.0*
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- Index - *Undeclared*
- Glossary - *Undeclared*
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