CHEM1500: CHEMICAL BONDING AND ORGANIC CHEMISTRY



Department of Chemistry
Thompson Rivers University

LibreTexts™

Chemical Bonding and Organic Chemistry (CHEM1500)

This text is disseminated via the Open Education Resource (OER) LibreTexts Project (https://LibreTexts.org) and like the thousands of other texts available within this powerful platform, it is freely available for reading, printing, and "consuming."

The LibreTexts mission is to bring together students, faculty, and scholars in a collaborative effort to provide and accessible, and comprehensive platform that empowers our community to develop, curate, adapt, and adopt openly licensed resources and technologies; through these efforts we can reduce the financial burden born from traditional educational resource costs, ensuring education is more accessible for students and communities worldwide.

Most, but not all, pages in the library have licenses that may allow individuals to make changes, save, and print this book. Carefully consult the applicable license(s) before pursuing such effects. Instructors can adopt existing LibreTexts texts or Remix them to quickly build course-specific resources to meet the needs of their students. Unlike traditional textbooks, LibreTexts' web based origins allow powerful integration of advanced features and new technologies to support learning.



LibreTexts is the adaptable, user-friendly non-profit open education resource platform that educators trust for creating, customizing, and sharing accessible, interactive textbooks, adaptive homework, and ancillary materials. We collaborate with individuals and organizations to champion open education initiatives, support institutional publishing programs, drive curriculum development projects, and more.

The LibreTexts libraries are Powered by NICE CXone Expert and was supported by the Department of Education Open Textbook Pilot Project, the California Education Learning Lab, the UC Davis Office of the Provost, the UC Davis Library, the California State University Affordable Learning Solutions Program, and Merlot. This material is based upon work supported by the National Science Foundation under Grant No. 1246120, 1525057, and 1413739.

Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation nor the US Department of Education.

Have questions or comments? For information about adoptions or adaptions contact info@LibreTexts.org or visit our main website at https://LibreTexts.org.

This text was compiled on 06/08/2025

TABLE OF CONTENTS

Licensing

1: Background Material

- 1.1: Essential Ideas of Chemistry
  - 1.1.1: Chemistry in Context
  - 1.1.2: Phases and Classification of Matter
  - 1.1.3: Physical and Chemical Properties
  - 1.1.4: Measurements
  - 1.1.5: Measurement Uncertainty, Accuracy, and Precision
  - 1.1.6: Mathematical Treatment of Measurement Results
  - 1.1.E: Essential Ideas of Chemistry (Exercises)
- 1.2: Atoms, Molecules, and Ions
  - 1.2.1: Prelude to Atoms
  - 1.2.2: Early Ideas in Atomic Theory
  - 1.2.3: Evolution of Atomic Theory
  - 1.2.4: Atomic Structure and Symbolism
  - 1.2.5: Chemical Formulas
  - 1.2.6: The Periodic Table
  - 1.2.7: Molecular and Ionic Compounds
  - 1.2.8: Chemical Nomenclature
  - 1.2.E: Atoms, Molecules, and Ions (Exercises)

2: Quantum Theory and Electronic Structure of Atoms

- 2.1: Electromagnetic Energy
- 2.2: Atomic Spectroscopy and The Bohr Model
- 2.3: The Wavelength Nature of Matter
- 2.4: Quantum Mechanics and The Atom
- 2.5: The Shape of Atomic Orbitals
- 2.6: Electronic Structure of Atoms (Electron Configurations)
- 2.E: Quantum Theory and Electronic Structure (Exercises)
- 2.S: Study Guide

3: Periodic Relationships Among the Elements

- 3.1: The Periodic Table
- 3.2: Periodic Variations in Element Properties
- 3.E: Periodic Properties (Exercises)
- 3.S: Study Guide

4: Chemical Bonding I- Basic Concepts

- 4.1: Ionic Bonding
- 4.2: Lattice Enthalpies and Born Haber Cycles
- 4.3: Covalent Bonding
- 4.4: Lewis Symbols and Structures
- 4.5: Formal Charges and Resonance
- 4.6: Strengths of Ionic and Covalent Bonds

- 4.E: Chemical Bonding and Molecular Geometry (Exercises)
- 4.S: Study Guide

5: Chemical Bonding II- Molecular Geometry and Hybridization of Atomic Orbitals

- 5.1: Molecular Structure and Polarity
- 5.2: Valence Bond Theory
- 5.3: Hybrid Atomic Orbitals
- 5.4: Multiple Bonds
- 5.5: Molecular Orbital Theory
- 5.E: Advanced Theories of Covalent Bonding (Exercises)
- 5.S: Study Guide

6: Intermolecular Forces and Liquids and Solids

- 6.1: Intermolecular Forces
- 6.E: Intermolecular Forces and Liquids and Solids (Exercises)
- 6.S: Study Guide

7: Organic Chemistry I - Bonding and Structure

- 7.1: Bonding and Structure I- Review of Bonding
  - 7.1.1: Introduction to Organic Chemistry
  - 7.1.2: Development of Chemical Bonding Theory
  - 7.1.3: Describing Chemical Bonds - Valence Bond Theory
  - 7.1.4: sp^3 Hybrid Orbitals and the Structure of Methane
  - 7.1.5: sp^3 Hybrid Orbitals and the Structure of Ethane
  - 7.1.6: sp^2 Hybrid Orbitals and the Structure of Ethylene
  - 7.1.7: sp Hybrid Orbitals and the Structure of Acetylene
  - 7.1.8: Hybridization of Nitrogen, Oxygen, Phosphorus and Sulfur
  - 7.1.9: Describing Chemical Bonds- Molecular Orbital Theory
- 7.2: Drawing Chemical Structures
- 7.3: Functional Groups
- 7.4: Alkanes and Alkane Isomers
- 7.5: Naming of Alkanes and Cycloalkanes
  - 7.5.1: Naming Alkanes
  - 7.5.2: Naming Cycloalkanes
- 7.6: Study Guide

8: Organic Chemistry II - Stereochemistry

- 8.1: Types of Isomers
- 8.2: Chiral Molecules
- 8.3: Optical Activity
- 8.4: Absolute Configuration- R-S Sequence Rules
- 8.5: Stereochemistry of the Alkenes
  - 8.5.1: Cis-Trans Isomerism in Alkenes
  - 8.5.2: Sequence Rules - The E,Z Designation
- 8.6: Study Guide

9: Organic Chemistry III - Conformational Analysis

- 9.1: Rotation about Single Bonds- Conformations
- 9.2: Rotation in Substituted Ethanes
- 9.3: Ring Strain and the Structure of Cycloalkanes
- 9.4: Cyclohexane- A Strain-Free Cycloalkane
- 9.5: Substituted Cyclohexanes
- 9.S: Study Guide

Index

Glossary

Detailed Licensing

Licensing

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

CHAPTER OVERVIEW

1: Background Material

1.1: Essential Ideas of Chemistry

1.1.1: Chemistry in Context

1.1.2: Phases and Classification of Matter

1.1.3: Physical and Chemical Properties

1.1.4: Measurements

1.1.5: Measurement Uncertainty, Accuracy, and Precision

1.1.6: Mathematical Treatment of Measurement Results

1.1.E: Essential Ideas of Chemistry (Exercises)

1.2: Atoms, Molecules, and Ions

1.2.1: Prelude to Atoms

1.2.2: Early Ideas in Atomic Theory

1.2.3: Evolution of Atomic Theory

1.2.4: Atomic Structure and Symbolism

1.2.5: Chemical Formulas

1.2.6: The Periodic Table

1.2.7: Molecular and Ionic Compounds

1.2.8: Chemical Nomenclature

1.2.E: Atoms, Molecules, and Ions (Exercises)

1: Background Material is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

SECTION OVERVIEW

1.1: Essential Ideas of Chemistry

A general chemistry Libretexts Textbook remixed and remastered from OpenStax's textbook:

General Chemistry

Most everything you do and encounter during your day involves chemistry. Making coffee, cooking eggs, and toasting bread involve chemistry. The products you use—like soap and shampoo, the fabrics you wear, the electronics that keep you connected to your world, the gasoline that propels your car—all of these and more involve chemical substances and processes. Whether you are aware or not, chemistry is part of your everyday world. In this course, you will learn many of the essential principles underlying the chemistry of modern-day life.

1.1.1: Chemistry in Context

1.1.2: Phases and Classification of Matter

1.1.3: Physical and Chemical Properties

1.1.4: Measurements

1.1.5: Measurement Uncertainty, Accuracy, and Precision

1.1.6: Mathematical Treatment of Measurement Results

1.1.E: Essential Ideas of Chemistry (Exercises)

This page titled 1.1: Essential Ideas of Chemistry is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

1.1.1: Chemistry in Context

Learning Objectives

- Outline the historical development of chemistry
- Provide examples of the importance of chemistry in everyday life
- Describe the scientific method and informs the scientific process
- Differentiate among hypotheses, theories, and laws
- Provide examples illustrating macroscopic, microscopic, and symbolic domains

Throughout human history, people have tried to convert matter into more useful forms. Our Stone Age ancestors chipped pieces of flint into useful tools and carved wood into statues and toys. These endeavors involved changing the shape of a substance without changing the substance itself. But as our knowledge increased, humans began to change the composition of the substances as well—clay was converted into pottery, hides were cured to make garments, copper ores were transformed into copper tools and weapons, and grain was made into bread.

Humans began to practice chemistry when they learned to control fire and use it to cook, make pottery, and smelt metals. Subsequently, they began to separate and use specific components of matter. A variety of drugs such as aloe, myrrh, and opium were isolated from plants. Dyes, such as indigo and Tyrian purple, were extracted from plant and animal matter. Metals were combined to form alloys—for example, copper and tin were mixed together to make bronze—and more elaborate smelting techniques produced iron. Alkalis were extracted from ashes, and soaps were prepared by combining these alkalis with fats. Alcohol was produced by fermentation and purified by distillation.

Attempts to understand the behavior of matter extend back for more than 2500 years. As early as the sixth century BC, Greek philosophers discussed a system in which water was the basis of all things. You may have heard of the Greek postulate that matter consists of four elements: earth, air, fire, and water. Subsequently, an amalgamation of chemical technologies and philosophical speculations were spread from Egypt, China, and the eastern Mediterranean by alchemists, who endeavored to transform “base metals” such as lead into “noble metals” like gold, and to create elixirs to cure disease and extend life (Figure 1.1.1.1).



Figure 1.1.1.1: This portrayal shows an alchemist’s workshop circa 1580. Although alchemy made some useful contributions to how to manipulate matter, it was not scientific by modern standards. (credit: Chemical Heritage Foundation).

A sketch depicts 4 people stirring and handling chemicals. The chemicals are held in a variety of barrels and large cylinders. Several of the containers are being heated over burning embers. A large stove in the laboratory is filled with burning embers. There is also a large chest in the corner that is producing steam.

From alchemy came the historical progressions that led to modern chemistry: the isolation of drugs from natural sources, metallurgy, and the dye industry. Today, chemistry continues to deepen our understanding and improve our ability to harness and control the behavior of matter. This effort has been so successful that many people do not realize either the central position of chemistry among the sciences or the importance and universality of chemistry in daily life.

1.1.1.1: Chemistry: The Central Science

Chemistry is sometimes referred to as “the central science” due to its interconnectedness with a vast array of other STEM disciplines (STEM stands for areas of study in the science, technology, engineering, and math fields). Chemistry and the language of chemists play vital roles in biology, medicine, materials science, forensics, environmental science, and many other fields (Figure 1.1.1.2). The basic principles of physics are essential for understanding many aspects of chemistry, and there is extensive overlap between many subdisciplines within the two fields, such as chemical physics and nuclear chemistry. Mathematics, computer science, and information theory provide important tools that help us calculate, interpret, describe, and generally make sense of the chemical world. Biology and chemistry converge in biochemistry, which is crucial to understanding the many complex factors and processes that keep living organisms (such as us) alive. Chemical engineering, materials science, and nanotechnology combine chemical principles and empirical findings to produce useful substances, ranging from gasoline to fabrics to electronics. Agriculture, food science, veterinary science, and brewing and wine making help provide sustenance in the form of food and drink to the world’s population. Medicine, pharmacology, biotechnology, and botany identify and produce substances that help keep us healthy. Environmental science, geology, oceanography, and atmospheric science incorporate many chemical ideas to help us better understand and protect our physical world. Chemical ideas are used to help understand the universe in astronomy and cosmology.

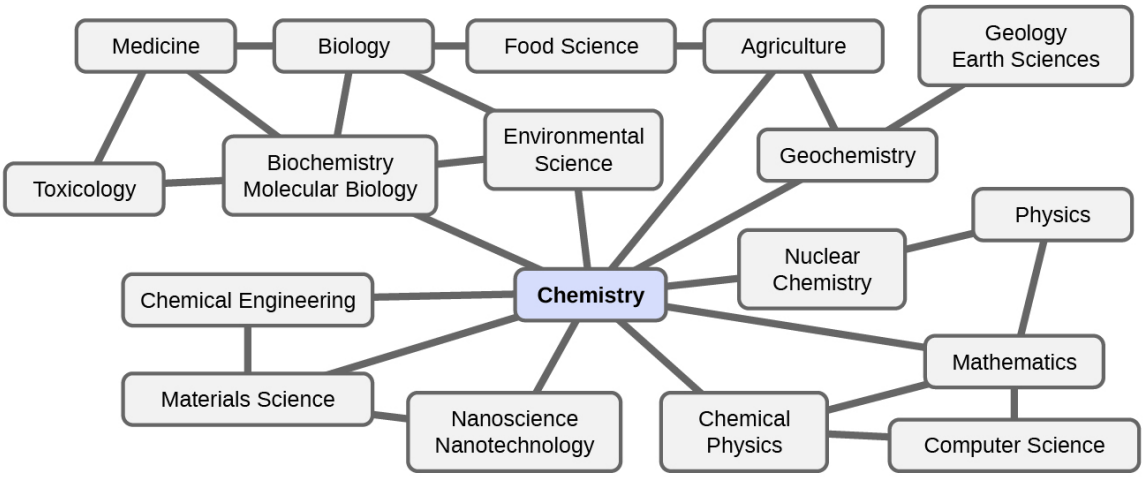


Figure 1.1.1.2: Knowledge of chemistry is central to understanding a wide range of scientific disciplines. This diagram shows just some of the interrelationships between chemistry and other fields.

A flowchart shows a box containing chemistry at its center. Chemistry is connected to geochemistry, nuclear chemistry, chemical physics, nanoscience and nanotechnology, materials science, chemical engineering, biochemistry and molecular biology, environmental science, agriculture, and mathematics. Each of these disciplines is further connected to other related fields including medicine, biology, food science, geology earth sciences, toxicology, physics, and computer science.

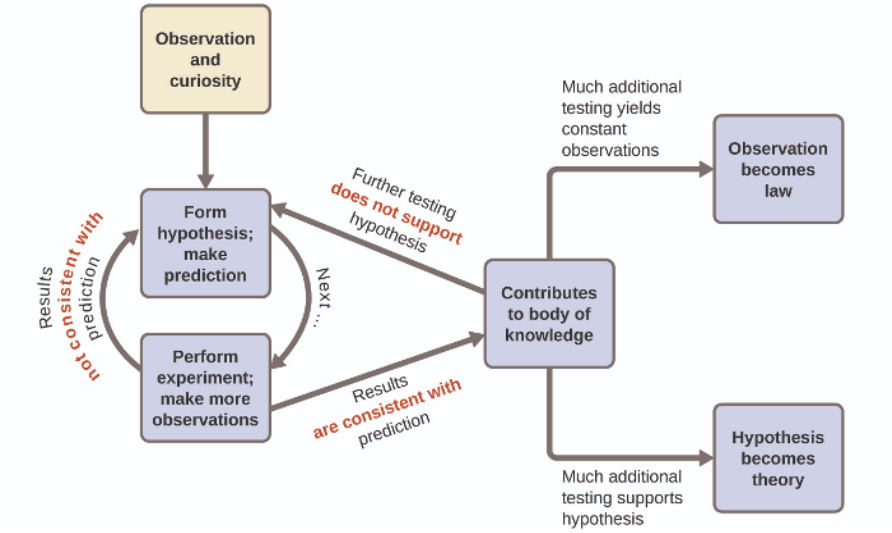
What are some changes in matter that are essential to daily life? Digesting and assimilating food, synthesizing polymers that are used to make clothing, containers, cookware, and credit cards, and refining crude oil into gasoline and other products are just a few examples. As you proceed through this course, you will discover many different examples of changes in the composition and structure of matter, how to classify these changes and how they occurred, their causes, the changes in energy that accompany them, and the principles and laws involved. As you learn about these things, you will be learning chemistry, the study of the composition, properties, and interactions of matter. The practice of chemistry is not limited to chemistry books or laboratories: It happens whenever someone is involved in changes in matter or in conditions that may lead to such changes.

1.1.1.2: The Scientific Method

Chemistry is a science based on observation and experimentation. Doing chemistry involves attempting to answer questions and explain observations in terms of the laws and theories of chemistry, using procedures that are accepted by the scientific community. There is no single route to answering a question or explaining an observation, but there is an aspect common to every approach: Each uses knowledge based on experiments that can be reproduced to verify the results. Some routes involve a hypothesis, a tentative explanation of observations that acts as a guide for gathering and checking information. We test a hypothesis by experimentation, calculation, and/or comparison with the experiments of others and then refine it as needed.

Some hypotheses are attempts to explain the behavior that is summarized in laws. The laws of science summarize a vast number of experimental observations, and describe or predict some facet of the natural world. If such a hypothesis turns out to be capable of

explaining a large body of experimental data, it can reach the status of a theory. Scientific theories are well-substantiated, comprehensive, testable explanations of particular aspects of nature. Theories are accepted because they provide satisfactory explanations, but they can be modified if new data become available. The path of discovery that leads from question and observation to law or hypothesis to theory, combined with experimental verification of the hypothesis and any necessary modification of the theory, is called the scientific method (Figure 1.1.1.3).



In this flowchart, the observation and curiosity box has an arrow pointing to a box labeled form hypothesis; make prediction. A curved arrow labeled next connects this box to a box labeled perform experiment; make more observations. Another arrow points back to the box that says form hypothesis; make prediction. This arrow is labeled results not consistent with prediction. Another arrow, labeled results are consistent with prediction points from the perform experiment box to a box labeled contributes to body of knowledge. However, an arrow also points from contributes to body of knowledge back to the form hypothesis; make prediction box. This arrow is labeled further testing does not support hypothesis. There are also two other arrows leading out from contributes to body of knowledge. One arrow is labeled much additional testing yields constant observations. This leads to the observation becomes law box. The other arrow is labeled much additional testing supports hypothesis. This arrow leads to the hypothesis becomes theory box.

Figure 1.1.1.3: The scientific method follows a process similar to the one shown in this diagram. All the key components are shown, in roughly the right order. Scientific progress is seldom neat and clean: It requires open inquiry and the reworking of questions and ideas in response to findings.

1.1.1.3: The Domains of Chemistry

Chemists study and describe the behavior of matter and energy in three different domains: macroscopic, microscopic, and symbolic. These domains provide different ways of considering and describing chemical behavior.

Macro is a Greek word that means “large.” The macroscopic domain is familiar to us: It is the realm of everyday things that are large enough to be sensed directly by human sight or touch. In daily life, this includes the food you eat and the breeze you feel on your face. The macroscopic domain includes everyday and laboratory chemistry, where we observe and measure physical and chemical properties, or changes such as density, solubility, and flammability.

The microscopic domain of chemistry is almost always visited in the imagination. *Micro* also comes from Greek and means “small.” Some aspects of the microscopic domains are visible through a microscope, such as a magnified image of graphite or bacteria. Viruses, for instance, are too small to be seen with the naked eye, but when we’re suffering from a cold, we’re reminded of how real they are.

However, most of the subjects in the microscopic domain of chemistry—such as atoms and molecules—are too small to be seen even with standard microscopes and often must be pictured in the mind. Other components of the microscopic domain include ions and electrons, protons and neutrons, and chemical bonds, each of which is far too small to see. This domain includes the individual metal atoms in a wire, the ions that compose a salt crystal, the changes in individual molecules that result in a color change, the conversion of nutrient molecules into tissue and energy, and the evolution of heat as bonds that hold atoms together are created.

The symbolic domain contains the specialized language used to represent components of the macroscopic and microscopic domains. Chemical symbols (such as those used in the periodic table), chemical formulas, and chemical equations are part of the symbolic domain, as are graphs and drawings. We can also consider calculations as part of the symbolic domain. These symbols

play an important role in chemistry because they help interpret the behavior of the macroscopic domain in terms of the components of the microscopic domain. One of the challenges for students learning chemistry is recognizing that the same symbols can represent different things in the macroscopic and microscopic domains, and one of the features that makes chemistry fascinating is the use of a domain that must be imagined to explain behavior in a domain that can be observed.

A helpful way to understand the three domains is via the essential and ubiquitous substance of water. That water is a liquid at moderate temperatures, will freeze to form a solid at lower temperatures, and boil to form a gas at higher temperatures (Figure 1.1.4) are macroscopic observations. But some properties of water fall into the microscopic domain—what we cannot observe with the naked eye. The description of water as comprised of two hydrogen atoms and one oxygen atom, and the explanation of freezing and boiling in terms of attractions between these molecules, is within the microscopic arena. The formula H_2O, which can describe water at either the macroscopic or microscopic levels, is an example of the symbolic domain. The abbreviations (*g*) for gas, (*s*) for solid, and (*l*) for liquid are also symbolic.

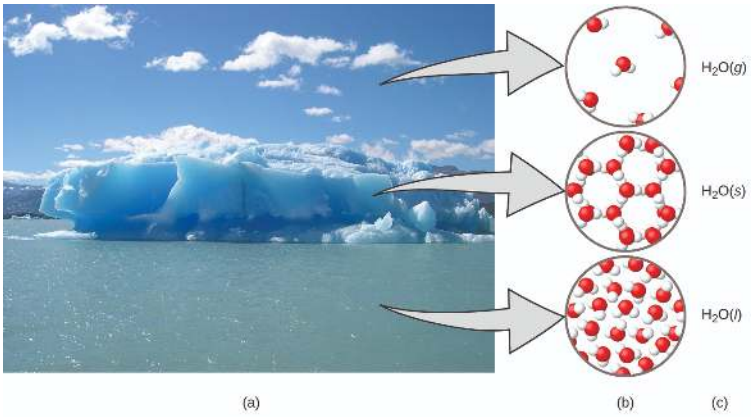


Figure 1.1.1.4: (a) Moisture in the air, icebergs, and the ocean represent water in the macroscopic domain. (b) At the molecular level (microscopic domain), gas molecules are far apart and disorganized, solid water molecules are close together and organized, and liquid molecules are close together and disorganized. (c) The formula H_2O symbolizes water, and (g), (s), and (l) symbolize its phases. Note that clouds are actually comprised of either very small liquid water droplets or solid water crystals; gaseous water in our atmosphere is not visible to the naked eye, although it may be sensed as humidity. (credit a: modification of work by "Gorkaazk"/Wikimedia Commons).

Figure A shows a photo of an iceberg floating in a sea has three arrows. Each arrow points to figure B, which contains three diagrams showing how the water molecules are organized in the air, ice, and sea. In the air, which contains the gaseous form of water, H subscript 2 O gas, the water molecules are disconnected and widely spaced. In the ice, which is the solid form of water, H subscript 2 O solid, the water molecules are bonded together into rings, with each ring containing six water molecules. Three of these rings are connected to each other. In the sea, which is the liquid form of water, H subscript 2 O liquid, the water molecules are very densely packed. The molecules are not bonded together.

1.1.1.4: Key Concepts and Summary

Chemistry deals with the composition, structure, and properties of matter, and the ways by which various forms of matter may be interconverted. Thus, it occupies a central place in the study and practice of science and technology. Chemists use the scientific method to perform experiments, pose hypotheses, and formulate laws and develop theories, so that they can better understand the behavior of the natural world. To do so, they operate in the macroscopic, microscopic, and symbolic domains. Chemists measure, analyze, purify, and synthesize a wide variety of substances that are important to our lives.

Glossary

chemistry

study of the composition, properties, and interactions of matter

hypothesis

tentative explanation of observations that acts as a guide for gathering and checking information

law

statement that summarizes a vast number of experimental observations, and describes or predicts some aspect of the natural world

macroscopic domain

realm of everyday things that are large enough to sense directly by human sight and touch

microscopic domain

realm of things that are much too small to be sensed directly

scientific method

path of discovery that leads from question and observation to law or hypothesis to theory, combined with experimental verification of the hypothesis and any necessary modification of the theory

symbolic domain

specialized language used to represent components of the macroscopic and microscopic domains, such as chemical symbols, chemical formulas, chemical equations, graphs, drawings, and calculations

theory

well-substantiated, comprehensive, testable explanation of a particular aspect of nature

---

This page titled 1.1.1: Chemistry in Context is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **1.1: Chemistry in Context** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

1.1.2: Phases and Classification of Matter

Learning Objectives

- Describe the basic properties of each physical state of matter: solid, liquid, and gas.
- Define and give examples of atoms and molecules.
- Classify matter as an element, compound, homogeneous mixture, or heterogeneous mixture with regard to its physical state and composition.
- Use symbolic, particulate, or macroscopic representations to describe or classify the different types of matter.
- Distinguish between mass and weight.
- Apply the law of conservation of matter.

Matter is defined as anything that occupies space and has mass, and it is all around us. Solids and liquids are more obviously matter: We can see that they take up space, and their weight tells us that they have mass. Gases are also matter; if gases did not take up space, a balloon would stay collapsed rather than inflate when filled with gas.

Solids, liquids, and gases are the three states of matter commonly found on earth (Figure 1.1.2.1). A solid is rigid and possesses a definite shape. A liquid flows and takes the shape of a container, except that it forms a flat or slightly curved upper surface when acted upon by gravity. (In zero gravity, liquids assume a spherical shape.) Both liquid and solid samples have volumes that are very nearly independent of pressure. A gas takes both the shape and volume of its container.

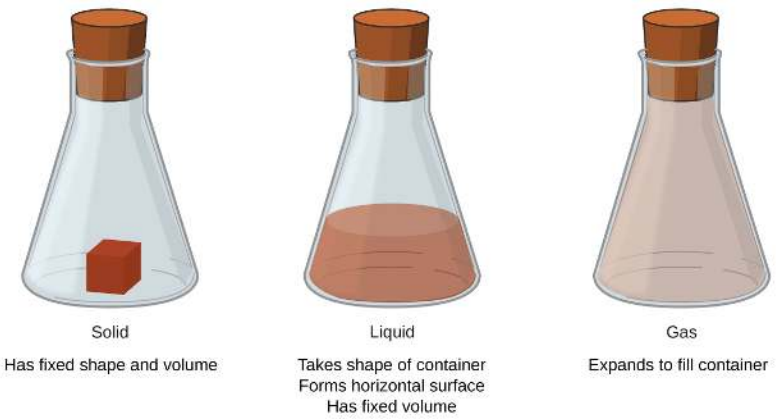


Figure 1.1.2.1: The three most common states or phases of matter are solid, liquid, and gas.

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.

A fourth state of matter, plasma, occurs naturally in the interiors of stars. A plasma is a gaseous state of matter that contains appreciable numbers of electrically charged particles (Figure 1.1.2.2). The presence of these charged particles imparts unique properties to plasmas that justify their classification as a state of matter distinct from gases. In addition to stars, plasmas are found in some other high-temperature environments (both natural and man-made), such as lightning strikes, certain television screens, and specialized analytical instruments used to detect trace amounts of metals.



Figure 1.1.2.2: A plasma torch can be used to cut metal. (credit: “Hypertherm”/Wikimedia Commons)

A cutting torch is being used to cut a piece of metal. Bright, white colored plasma can be seen near the tip of the torch, where it is contacting the metal.



***Video* 1.1.2.1** *: In a tiny cell in a plasma television, the plasma emits ultraviolet light, which in turn causes the display at that location to appear a specific color. The composite of these tiny dots of color makes up the image that you see. Watch this video to learn more about plasma and the places you encounter it.*

Some samples of matter appear to have properties of solids, liquids, and/or gases at the same time. This can occur when the sample is composed of many small pieces. For example, we can pour sand as if it were a liquid because it is composed of many small grains of solid sand. Matter can also have properties of more than one state when it is a mixture, such as with clouds. Clouds appear to behave somewhat like gases, but they are actually mixtures of air (gas) and tiny particles of water (liquid or solid).

The mass of an object is a measure of the amount of matter in it. One way to measure an object’s mass is to measure the force it takes to accelerate the object. It takes much more force to accelerate a car than a bicycle because the car has much more mass. A more common way to determine the mass of an object is to use a balance to compare its mass with a standard mass.

Although weight is related to mass, it is not the same thing. Weight refers to the force that gravity exerts on an object. This force is directly proportional to the mass of the object. The weight of an object changes as the force of gravity changes, but its mass does not. An astronaut’s mass does not change just because she goes to the moon. But her weight on the moon is only one-sixth her earth-bound weight because the moon’s gravity is only one-sixth that of the earth’s. She may feel “weightless” during her trip when she experiences negligible external forces (gravitational or any other), although she is, of course, never “massless.”

The law of conservation of matter summarizes many scientific observations about matter: It states that *there is no detectable change in the total quantity of matter present when matter converts from one type to another (a chemical change) or changes among solid, liquid, or gaseous states (a physical change)*. Brewing beer and the operation of batteries provide examples of the conservation of matter (Figure 1.1.2.4). During the brewing of beer, the ingredients (water, yeast, grains, malt, hops, and sugar) are converted into beer (water, alcohol, carbonation, and flavoring substances) with no actual loss of substance. This is most clearly seen during the bottling process, when glucose turns into ethanol and carbon dioxide, and the total mass of the substances does not change. This can also be seen in a lead-acid car battery: The original substances (lead, lead oxide, and sulfuric acid), which are

capable of producing electricity, are changed into other substances (lead sulfate and water) that do not produce electricity, with no change in the actual amount of matter.

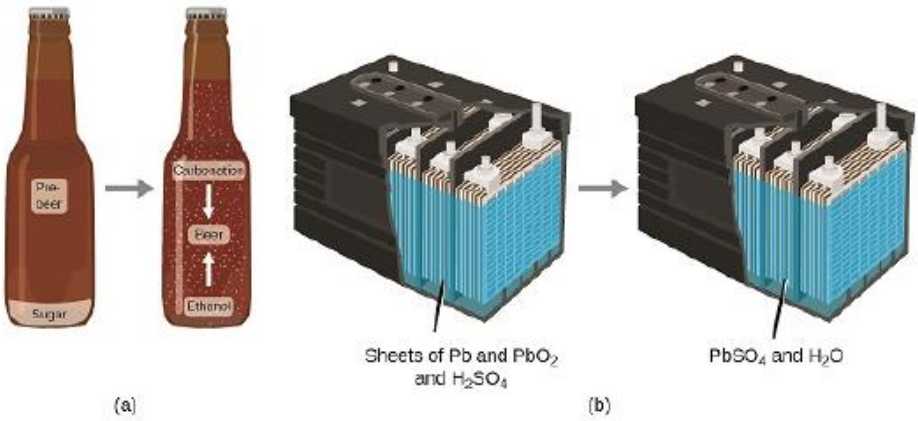


Figure 1.1.2.3: (a) The mass of beer precursor materials is the same as the mass of beer produced: Sugar has become alcohol and carbonation. (b) The mass of the lead, lead oxide plates, and sulfuric acid that goes into the production of electricity is exactly equal to the mass of lead sulfate and water that is formed.

Diagram A shows a beer bottle containing pre-beer and sugar. An arrow points from this bottle to a second bottle. This second bottle contains the same volume of liquid, however, the sugar has been converted into ethanol and carbonation as beer was made. Diagram B shows a car battery that contains sheets of P B and P B O subscript 2 along with H subscript 2 S O subscript 4. After the battery is used, it contains an equal mass of P B S O subscript 4 and H subscript 2 O.

Although this conservation law holds true for all conversions of matter, convincing examples are few and far between because, outside of the controlled conditions in a laboratory, we seldom collect all of the material that is produced during a particular conversion. For example, when you eat, digest, and assimilate food, all of the matter in the original food is preserved. But because some of the matter is incorporated into your body, and much is excreted as various types of waste, it is challenging to verify by measurement.

1.1.2.1: Atoms and Molecules

An atom is the smallest particle of an element that has the properties of that element and can enter into a chemical combination. Consider the element gold, for example. Imagine cutting a gold nugget in half, then cutting one of the halves in half, and repeating this process until a piece of gold remained that was so small that it could not be cut in half (regardless of how tiny your knife may be). This minimally sized piece of gold is an atom (from the Greek *atomos*, meaning “indivisible”) (Figure 1.2.4). This atom would no longer be gold if it were divided any further.

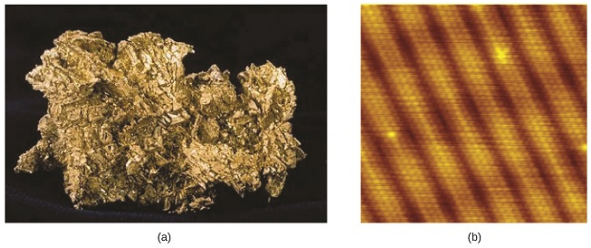


Figure 1.1.2.4: (a) This photograph shows a gold nugget. (b) A scanning-tunneling microscope (STM) can generate views of the surfaces of solids, such as this image of a gold crystal. Each sphere represents one gold atom. (credit a: modification of work by United States Geological Survey; credit b: modification of work by “Erwinrossen”/Wikimedia Commons)

Figure A shows a gold nugget as it would appear to the naked eye. The gold nugget is very irregular, with many sharp edges. It appears gold in color. The microscope image of a gold crystal shows many similarly sized gold stripes that are separated by dark areas. Looking closely, one can see that the gold stripes are made of many, tiny, circular atoms.

The first suggestion that matter is composed of atoms is attributed to the Greek philosophers Leucippus and Democritus, who developed their ideas in the 5th century BCE. However, it was not until the early nineteenth century that John Dalton (1766–1844), a British schoolteacher with a keen interest in science, supported this hypothesis with quantitative measurements. Since that time, repeated experiments have confirmed many aspects of this hypothesis, and it has become one of the central theories of chemistry.

Other aspects of Dalton's atomic theory are still used but with minor revisions (details of Dalton's theory are provided in the chapter on atoms and molecules).

An atom is so small that its size is difficult to imagine. One of the smallest things we can see with our unaided eye is a single thread of a spider web: These strands are about 1/10,000 of a centimeter (0.0001 cm) in diameter. Although the cross-section of one strand is almost impossible to see without a microscope, it is huge on an atomic scale. A single carbon atom in the web has a diameter of about 0.000000015 centimeter, and it would take about 7000 carbon atoms to span the diameter of the strand. To put this in perspective, if a carbon atom were the size of a dime, the cross-section of one strand would be larger than a football field, which would require about 150 million carbon atom "dimes" to cover it. (Figure 1.1.2.5) shows increasingly close microscopic and atomic-level views of ordinary cotton.

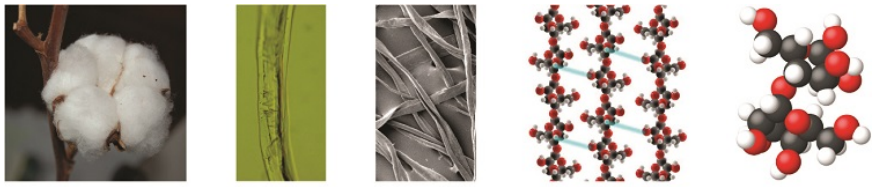


Figure 1.1.2.5: These images provide an increasingly closer view: (a) a cotton boll, (b) a single cotton fiber viewed under an optical microscope (magnified 40 times), (c) an image of a cotton fiber obtained with an electron microscope (much higher magnification than with the optical microscope); and (d and e) atomic-level models of the fiber (spheres of different colors represent atoms of different elements). (credit c: modification of work by "Featheredtar"/Wikimedia Commons)

Figure A shows a puffy white cotton boll growing on a brown twig. Figure B shows a magnified cotton strand. The strand appears transparent but contains dark areas within its interior. Figure C shows the surface of several crisscrossing and overlapping cotton fibers. Its surface is rough along the edges but smooth near the center of each strand. Figure D shows three strands of molecules connected into three vertical chains. Each strand contains about five molecules. Figure E shows that the cotton molecule contains about a dozen atoms. The black carbon atoms form rings that are connected by red oxygen atoms. Many of the carbon atoms are also bonded to hydrogen atoms, shown as white balls, or other oxygen atoms.

An atom is so light that its mass is also difficult to imagine. A billion lead atoms (1,000,000,000 atoms) weigh about 3×10^{-13} grams, a mass that is far too light to be weighed on even the world's most sensitive balances. It would require over 300,000,000,000,000 lead atoms (300 trillion, or 3×10^{14}) to be weighed, and they would weigh only 0.0000001 gram.

It is rare to find collections of individual atoms. Only a few elements, such as the gases helium, neon, and argon, consist of a collection of individual atoms that move about independently of one another. Other elements, such as the gases hydrogen, nitrogen, oxygen, and chlorine, are composed of units that consist of pairs of atoms (Figure 1.1.2.6). One form of the element phosphorus consists of units composed of four phosphorus atoms. The element sulfur exists in various forms, one of which consists of units composed of eight sulfur atoms. These units are called molecules. A molecule consists of two or more atoms joined by strong forces called chemical bonds. The atoms in a molecule move around as a unit, much like the cans of soda in a six-pack or a bunch of keys joined together on a single key ring. A molecule may consist of two or more identical atoms, as in the molecules found in the elements hydrogen, oxygen, and sulfur, or it may consist of two or more different atoms, as in the molecules found in water. Each water molecule is a unit that contains two hydrogen atoms and one oxygen atom. Each glucose molecule is a unit that contains 6 carbon atoms, 12 hydrogen atoms, and 6 oxygen atoms. Like atoms, molecules are incredibly small and light. If an ordinary glass of water were enlarged to the size of the earth, the water molecules inside it would be about the size of golf balls.

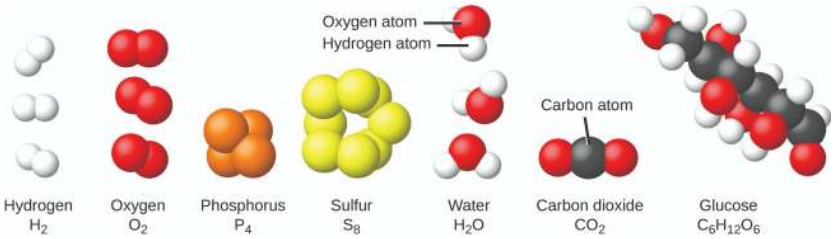


Figure 1.1.2.6: The elements hydrogen, oxygen, phosphorus, and sulfur form molecules consisting of two or more atoms of the same element. The compounds water, carbon dioxide, and glucose consist of combinations of atoms of different elements.

The hydrogen molecule, H subscript 2, is shown as two small, white balls bonded together. The oxygen molecule O subscript 2, is shown as two red balls bonded together. The phosphorous molecule, P subscript 4, is shown as four orange balls bonded tightly together. The sulfur molecule, S subscript 8, is shown as 8 yellow balls linked together. Water molecules, H subscript 2 O, consist of one red oxygen atom bonded to two smaller white hydrogen atoms. The hydrogen atoms are at an angle on the oxygen molecule. Carbon dioxide, C O subscript 2, consists of one carbon atom and two oxygen atoms. One oxygen atom is bonded to the carbon's right side and the other oxygen is bonded to the carbon's left side. Glucose, C subscript 6 H subscript 12 O subscript 6, contains a chain of carbon atoms that have attached oxygen or hydrogen atoms.

1.1.2.2: Classifying Matter

We can classify matter into several categories. Two broad categories are mixtures and pure substances. A pure substance has a constant composition. All specimens of a pure substance have exactly the same makeup and properties. Any sample of sucrose (table sugar) consists of 42.1% carbon, 6.5% hydrogen, and 51.4% oxygen by mass. Any sample of sucrose also has the same physical properties, such as melting point, color, and sweetness, regardless of the source from which it is isolated.

We can divide pure substances into two classes: elements and compounds. Pure substances that cannot be broken down into simpler substances by chemical changes are called elements. Iron, silver, gold, aluminum, sulfur, oxygen, and copper are familiar examples of the more than 100 known elements, of which about 90 occur naturally on the earth, and two dozen or so have been created in laboratories.

Pure substances that can be broken down by chemical changes are called compounds. This breakdown may produce either elements or other compounds, or both. Mercury(II) oxide, an orange, crystalline solid, can be broken down by heat into the elements mercury and oxygen (Figure 1.1.2.7). When heated in the absence of air, the compound sucrose is broken down into the element carbon and the compound water. (The initial stage of this process, when the sugar is turning brown, is known as caramelization—this is what imparts the characteristic sweet and nutty flavor to caramel apples, caramelized onions, and caramel). Silver(I) chloride is a white solid that can be broken down into its elements, silver and chlorine, by absorption of light. This property is the basis for the use of this compound in photographic films and photochromic eyeglasses (those with lenses that darken when exposed to light).

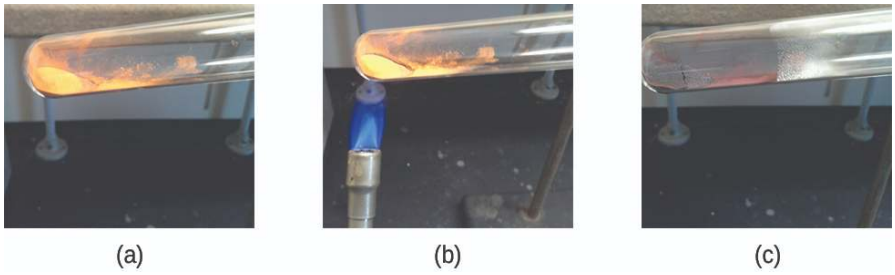


Figure 1.1.2.7: (a)The compound mercury(II) oxide, (b)when heated, (c) decomposes into silvery droplets of liquid mercury and invisible oxygen gas. (credit: modification of work by Paul Flowers)

This figure shows a series of three photos labeled a, b, and c. Photo a shows the bottom of a test tube that is filled with an orange-red substance. A slight amount of a silver substance is also visible. Photo b shows the substance in the test tube being heated over a flame. Photo c shows a test tube that is not longer being heated. The orange-red substance is almost completely gone, and small, silver droplets of a substance are left.

The properties of combined elements are different from those in the free, or uncombined, state. For example, white crystalline sugar (sucrose) is a compound resulting from the chemical combination of the element carbon, which is a black solid in one of its uncombined forms, and the two elements hydrogen and oxygen, which are colorless gases when uncombined. Free sodium, an element that is a soft, shiny, metallic solid, and free chlorine, an element that is a yellow-green gas, combine to form sodium chloride (table salt), a compound that is a white, crystalline solid.

A mixture is composed of two or more types of matter that can be present in varying amounts and can be separated by physical changes, such as evaporation (you will learn more about this later). A mixture with a composition that varies from point to point is called a heterogeneous mixture. Italian dressing is an example of a heterogeneous mixture (Figure 1.1.2.1*a*). Its composition can vary because we can make it from varying amounts of oil, vinegar, and herbs. It is not the same from point to point throughout the mixture—one drop may be mostly vinegar, whereas a different drop may be mostly oil or herbs because the oil and vinegar separate and the herbs settle. Other examples of heterogeneous mixtures are chocolate chip cookies (we can see the separate bits of chocolate, nuts, and cookie dough) and granite (we can see the quartz, mica, feldspar, and more).

A homogeneous mixture, also called a solution, exhibits a uniform composition and appears visually the same throughout. An example of a solution is a sports drink, consisting of water, sugar, coloring, flavoring, and electrolytes mixed together uniformly (Figure 1.1.2.1*b*). Each drop of a sports drink tastes the same because each drop contains the same amounts of water, sugar, and other components. Note that the composition of a sports drink can vary—it could be made with somewhat more or less sugar, flavoring, or other components, and still be a sports drink. Other examples of homogeneous mixtures include air, maple syrup, gasoline, and a solution of salt in water.



Figure 1.1.2.7: (a) Oil and vinegar salad dressing is a heterogeneous mixture because its composition is not uniform throughout. (b) A commercial sports drink is a homogeneous mixture because its composition is uniform throughout. (credit a “left”: modification of work by John Mayer; credit a “right”: modification of work by Umberto Salvagnin; credit b “left: modification of work by Jeff Bedford)

Diagram A shows a glass containing a red liquid with a layer of yellow oil floating on the surface of the red liquid. A zoom in box is magnifying a portion of the red liquid that contains some of the yellow oil. The zoomed in image shows that oil is forming round droplets within the red liquid. Diagram B shows a photo of Gatorade G 2. A zoom in box is magnifying a portion of the Gatorade, which is uniformly red.

Although there are just over 100 elements, tens of millions of chemical compounds result from different combinations of these elements. Each compound has a specific composition and possesses definite chemical and physical properties by which we can distinguish it from all other compounds. And, of course, there are innumerable ways to combine elements and compounds to form different mixtures. A summary of how to distinguish between the various major classifications of matter is shown in (Figure 1.2.8).

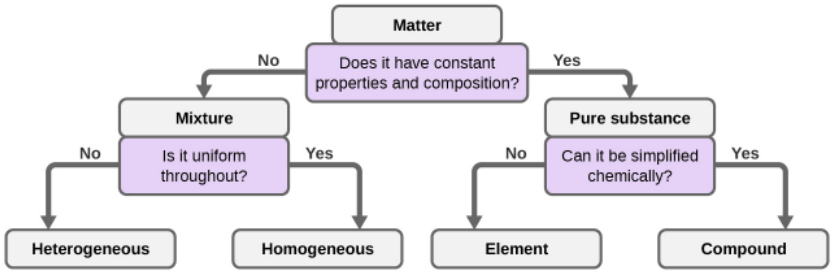


Figure 1.1.2.8: Depending on its properties, a given substance can be classified as a homogeneous mixture, a heterogeneous mixture, a compound, or an element.

This flow chart begins with matter at the top and the question: does the matter have constant properties and composition? If no, then it is a mixture. This leads to the next question: is it uniform throughout? If no, it is heterogeneous. If yes, it is homogenous. If the matter does have constant properties and composition, it is a pure substance. This leads to the next question: can it be simplified chemically? If no, it is an element. If yes, then it is a compound.

Eleven elements make up about 99% of the earth’s crust and atmosphere (Table 1.1.2.1). Oxygen constitutes nearly one-half and silicon about one-quarter of the total quantity of these elements. A majority of elements on earth are found in chemical combinations with other elements; about one-quarter of the elements are also found in the free state.

Table 1.1.2.1: Elemental Composition of Earth

Element	Symbol	Percent Mass	Element	Symbol	Percent Mass

Element	Symbol	Percent Mass		Element	Symbol	Percent Mass
oxygen	O	49.20		chlorine	Cl	0.19
silicon	Si	25.67		phosphorus	P	0.11
aluminum	Al	7.50		manganese	Mn	0.09
iron	Fe	4.71		carbon	C	0.08
calcium	Ca	3.39		sulfur	S	0.06
sodium	Na	2.63		barium	Ba	0.04
potassium	K	2.40		nitrogen	N	0.03
magnesium	Mg	1.93		fluorine	F	0.03
hydrogen	H	0.87		strontium	Sr	0.02
titanium	Ti	0.58		all others	-	0.47

1.1.2.3: Decomposition of Water / Production of Hydrogen

Water consists of the elements hydrogen and oxygen combined in a 2 to 1 ratio. Water can be broken down into hydrogen and oxygen gases by the addition of energy. One way to do this is with a battery or power supply, as shown in (Figure 1.1.2.9).

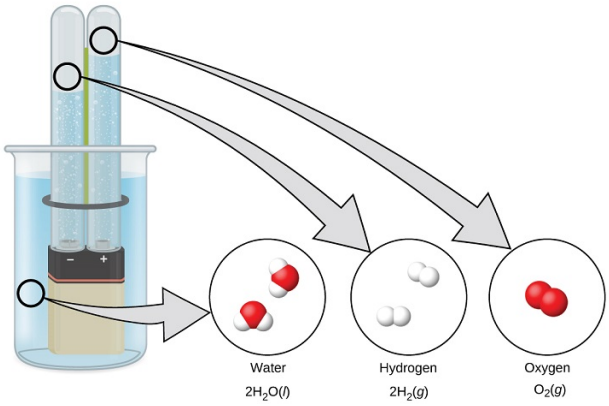


Figure 1.1.2.9: The decomposition of water is shown at the macroscopic, microscopic, and symbolic levels. The battery provides an electric current (microscopic) that decomposes water. At the macroscopic level, the liquid separates into the gases hydrogen (on the left) and oxygen (on the right). Symbolically, this change is presented by showing how liquid H_2O separates into H_2 and O_2 gases.

A rectangular battery is immersed in a beaker filled with liquid. Each of the battery terminals are covered by an overturned test tube. The test tubes each contain a bubbling liquid. Zoom in areas indicate that the liquid in the beaker is water, 2 H subscript 2 O liquid. The bubbles in the test tube over the negative terminal are hydrogen gas, 2 H subscript 2 gas. The bubbles in the test tube over the positive terminal are oxygen gas, O subscript 2 gas.

The breakdown of water involves a rearrangement of the atoms in water molecules into different molecules, each composed of two hydrogen atoms and two oxygen atoms, respectively. Two water molecules form one oxygen molecule and two hydrogen molecules. The representation for what occurs, $2\,\mathrm{H_2O}(l) \rightarrow 2\,\mathrm{H_2}(g) + \mathrm{O_2}(g)$, will be explored in more depth in later chapters.

The two gases produced have distinctly different properties. Oxygen is not flammable but is required for combustion of a fuel, and hydrogen is highly flammable and a potent energy source. How might this knowledge be applied in our world? One application involves research into more fuel-efficient transportation. Fuel-cell vehicles (FCV) run on hydrogen instead of gasoline (Figure 1.1.2.10). They are more efficient than vehicles with internal combustion engines, are nonpolluting, and reduce greenhouse gas emissions, making us less dependent on fossil fuels. FCVs are not yet economically viable, however, and current hydrogen production depends on natural gas. If we can develop a process to economically decompose water, or produce hydrogen in another environmentally sound way, FCVs may be the way of the future.

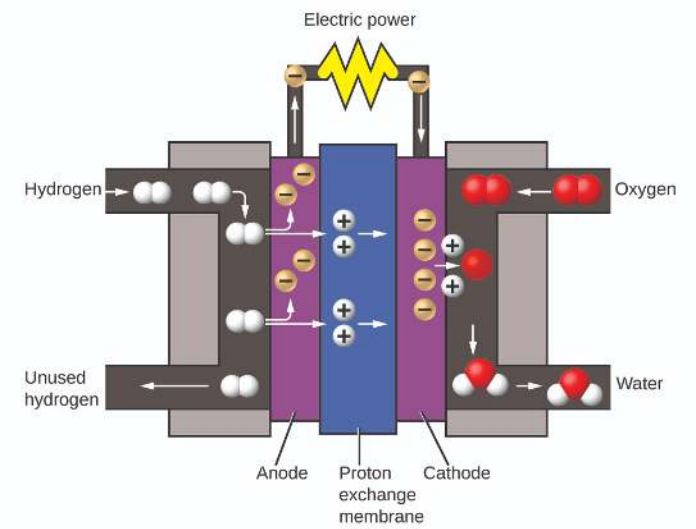


Figure 1.1.2.10: A fuel cell generates electrical energy from hydrogen and oxygen via an electrochemical process and produces only water as the waste product.

The fuel cell consists of a proton exchange membrane sandwiched between an anode and a cathode. Hydrogen gas enters the battery near the anode. Oxygen gas enters the battery near the cathode. The entering hydrogen gas is broken up into single white spheres that each have a positive charge. These are protons. The protons repel negatively-charged electrons within the anode. These electrons travel through a circuit, providing electricity to anything attached to the battery. The protons continue through the proton exchange membrane and through the cathode to reach the oxygen gas molecules at the opposite end of the battery. There, the oxygen atoms split up into single red spheres. Each oxygen atom takes on two of the incoming protons to form a water molecule.

1.1.2.4: Chemistry of Cell Phones

Imagine how different your life would be without cell phones (Figure 1.1.2.11) and other smart devices. Cell phones are made from numerous chemical substances, which are extracted, refined, purified, and assembled using an extensive and in-depth understanding of chemical principles. About 30% of the elements that are found in nature are found within a typical smart phone. The case/body/frame consists of a combination of sturdy, durable polymers comprised primarily of carbon, hydrogen, oxygen, and nitrogen [acrylonitrile butadiene styrene (ABS) and polycarbonate thermoplastics], and light, strong, structural metals, such as aluminum, magnesium, and iron. The display screen is made from a specially toughened glass (silica glass strengthened by the addition of aluminum, sodium, and potassium) and coated with a material to make it conductive (such as indium tin oxide). The circuit board uses a semiconductor material (usually silicon); commonly used metals like copper, tin, silver, and gold; and more unfamiliar elements such as yttrium, praseodymium, and gadolinium. The battery relies upon lithium ions and a variety of other materials, including iron, cobalt, copper, polyethylene oxide, and polyacrylonitrile.



Figure 1.1.2.11: Almost one-third of naturally occurring elements are used to make a modern cell phone. (credit: modification of work by John Taylor)

A cell phone is labeled to show what its components are made of. The case components are made of polymers such as A B S and or metals such as aluminum, iron, and magnesium. The processor components are made of silicon, common metals such as copper, tin and gold, and uncommon elements such as yttrium and gadolinium. The screen components are made of silicon oxide, also known as glass. The glass is strengthened by the addition of aluminum, sodium, and potassium. The battery components contain lithium combined with other metals such as cobalt, iron, and copper.

Summary

Matter is anything that occupies space and has mass. The basic building block of matter is the atom, the smallest unit of an element that can enter into combinations with atoms of the same or other elements. In many substances, atoms are combined into molecules. On earth, matter commonly exists in three states: solids, of fixed shape and volume; liquids, of variable shape but fixed volume; and gases, of variable shape and volume. Under high-temperature conditions, matter also can exist as a plasma. Most matter is a mixture: It is composed of two or more types of matter that can be present in varying amounts and can be separated by physical means. Heterogeneous mixtures vary in composition from point to point; homogeneous mixtures have the same composition from point to point. Pure substances consist of only one type of matter. A pure substance can be an element, which consists of only one type of atom and cannot be broken down by a chemical change, or a compound, which consists of two or more types of atoms.

Glossary

atom
: smallest particle of an element that can enter into a chemical combination

compound
: pure substance that can be decomposed into two or more elements

element
: substance that is composed of a single type of atom; a substance that cannot be decomposed by a chemical change

gas
: state in which matter has neither definite volume nor shape

heterogeneous mixture
: combination of substances with a composition that varies from point to point

homogeneous mixture
: (also, solution) combination of substances with a composition that is uniform throughout

liquid
: state of matter that has a definite volume but indefinite shape

law of conservation of matter
: when matter converts from one type to another or changes form, there is no detectable change in the total amount of matter present

mass
: fundamental property indicating amount of matter

matter
: anything that occupies space and has mass

mixture
: matter that can be separated into its components by physical means

molecule
: bonded collection of two or more atoms of the same or different elements

plasma
: gaseous state of matter containing a large number of electrically charged atoms and/or molecules

pure substance
: homogeneous substance that has a constant composition

solid

state of matter that is rigid, has a definite shape, and has a fairly constant volume

weight

force that gravity exerts on an object

This page titled 1.1.2: Phases and Classification of Matter is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **1.2: Phases and Classification of Matter** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

1.1.3: Physical and Chemical Properties

Learning Objectives

- Describe the difference between physical and chemical properties or changed.
- Identify a property or transformation as either physical or chemical using symbolic, particulate, or macroscopic representations.
- Identify the properties of matter as extensive or intensive.
- Recognize and describe the parts of the NFPA hazard diamond.

The characteristics that enable us to distinguish one substance from another are called properties. A physical property is a characteristic of matter that is not associated with a change in its chemical composition. Familiar examples of physical properties include density, color, hardness, melting and boiling points, and electrical conductivity. We can observe some physical properties, such as density and color, without changing the physical state of the matter observed. Other physical properties, such as the melting temperature of iron or the freezing temperature of water, can only be observed as matter undergoes a physical change. A physical change is a change in the state or properties of matter without any accompanying change in its chemical composition (the identities of the substances contained in the matter). We observe a physical change when wax melts, when sugar dissolves in coffee, and when steam condenses into liquid water (Figure 1.1.3.1). Other examples of physical changes include magnetizing and demagnetizing metals (as is done with common antitheft security tags) and grinding solids into powders (which can sometimes yield noticeable changes in color). In each of these examples, there is a change in the physical state, form, or properties of the substance, but no change in its chemical composition.



Figure 1.1.3.1: (a) Wax undergoes a physical change when solid wax is heated and forms liquid wax. (b) Steam condensing inside a cooking pot is a physical change, as water vapor is changed into liquid water. (credit a: modification of work by "95jb14"/Wikimedia Commons; credit b: modification of work by "mjneuby"/Flickr).

The change of one type of matter into another type (or the inability to change) is a chemical property. Examples of chemical properties include flammability, toxicity, acidity, reactivity (many types), and heat of combustion. Iron, for example, combines with oxygen in the presence of water to form rust; chromium does not oxidize (Figure 1.1.3.2). Nitroglycerin is very dangerous because it explodes easily; neon poses almost no hazard because it is very unreactive.



Figure 1.1.3.2: (a) One of the chemical properties of iron is that it rusts; (b) one of the chemical properties of chromium is that it does not. (credit a: modification of work by Tony Hisgett; credit b: modification of work by "Atoma"/Wikimedia Commons)

Comparison of two metal equipments. The first image shows a rusted brown appearance and the following image shows a shiny metallic appearance.

To identify a chemical property, we look for a chemical change. A chemical change always produces one or more types of matter that differ from the matter present before the change. The formation of rust is a chemical change because rust is a different kind of matter than the iron, oxygen, and water present before the rust formed. The explosion of nitroglycerin is a chemical change because the gases produced are very different kinds of matter from the original substance. Other examples of chemical changes include reactions that are performed in a lab (such as copper reacting with nitric acid), all forms of combustion (burning), and food being cooked, digested, or rotting (Figure 1.1.3.3).

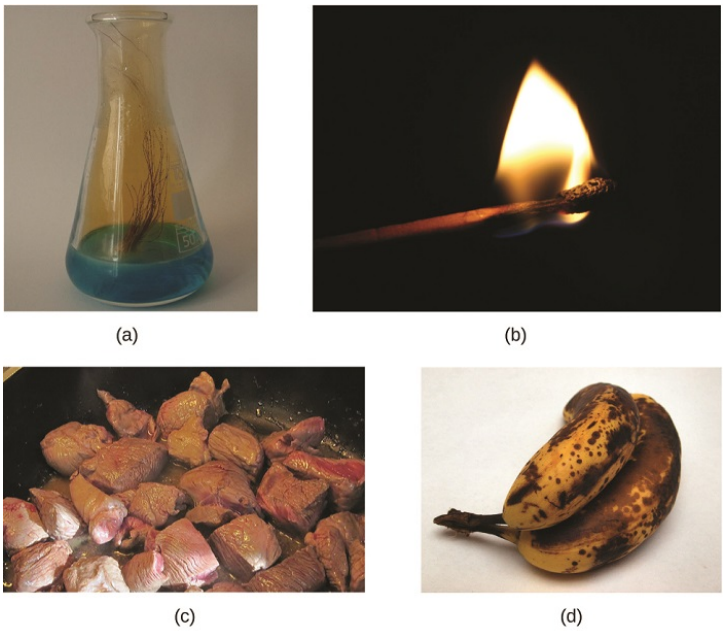


Figure 1.1.3.3: (a) Copper and nitric acid undergo a chemical change to form copper nitrate and brown, gaseous nitrogen dioxide. (b) During the combustion of a match, cellulose in the match and oxygen from the air undergo a chemical change to form carbon dioxide and water vapor. (c) Cooking red meat causes a number of chemical changes, including the oxidation of iron in myoglobin that results in the familiar red-to-brown color change. (d) A banana turning brown is a chemical change as new, darker (and less tasty) substances form. (credit b: modification of work by Jeff Turner; credit c: modification of work by Gloria Cabada-Leman; credit d: modification of work by Roberto Verzo)

Four pictures. A. a flask with copper wires placed in a blue solution and also the presence of a gas. B. A lighted match. C. meat cubes being cooked on a pan. D. Bananas forming black spots on its peel.

Properties of matter fall into one of two categories. If the property depends on the amount of matter present, it is an extensive property. The mass and volume of a substance are examples of extensive properties; for instance, a gallon of milk has a larger mass and volume than a cup of milk. The value of an extensive property is directly proportional to the amount of matter in question. If the property of a sample of matter does not depend on the amount of matter present, it is an intensive property. Temperature is an example of an intensive property. If the gallon and cup of milk are each at 20 °C (room temperature), when they are combined, the temperature remains at 20 °C. As another example, consider the distinct but related properties of heat and temperature. A drop of hot cooking oil spattered on your arm causes brief, minor discomfort, whereas a pot of hot oil yields severe burns. Both the drop and the pot of oil are at the same temperature (an intensive property), but the pot clearly contains much more heat (extensive property).

1.1.3.1: Hazard Diamond

You may have seen the symbol shown in Figure 1.1.3.4on containers of chemicals in a laboratory or workplace. Sometimes called a “fire diamond” or “hazard diamond,” this chemical hazard diamond provides valuable information that briefly summarizes the various dangers of which to be aware when working with a particular substance.

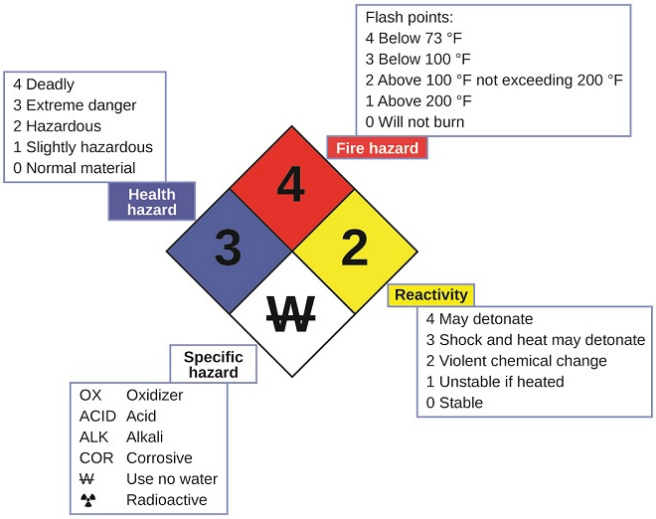


Figure 1.1.3.4: The National Fire Protection Agency (NFPA) hazard diamond summarizes the major hazards of a chemical substance.

The National Fire Protection Agency (NFPA) 704 Hazard Identification System was developed by NFPA to provide safety information about certain substances. The system details flammability, reactivity, health, and other hazards. Within the overall diamond symbol, the top (red) diamond specifies the level of fire hazard (temperature range for flash point). The blue (left) diamond indicates the level of health hazard. The yellow (right) diamond describes reactivity hazards, such as how readily the substance will undergo detonation or a violent chemical change. The white (bottom) diamond points out special hazards, such as if it is an oxidizer (which allows the substance to burn in the absence of air/oxygen), undergoes an unusual or dangerous reaction with water, is corrosive, acidic, alkaline, a biological hazard, radioactive, and so on. Each hazard is rated on a scale from 0 to 4, with 0 being no hazard and 4 being extremely hazardous.

While many elements differ dramatically in their chemical and physical properties, some elements have similar properties. We can identify sets of elements that exhibit common behaviors. For example, many elements conduct heat and electricity well, whereas others are poor conductors. These properties can be used to sort the elements into three classes: metals (elements that conduct well), nonmetals (elements that conduct poorly), and metalloids (elements that have properties of both metals and nonmetals).

The periodic table is a table of elements that places elements with similar properties close together (Figure 1.1.3.5). You will learn more about the periodic table as you continue your study of chemistry.

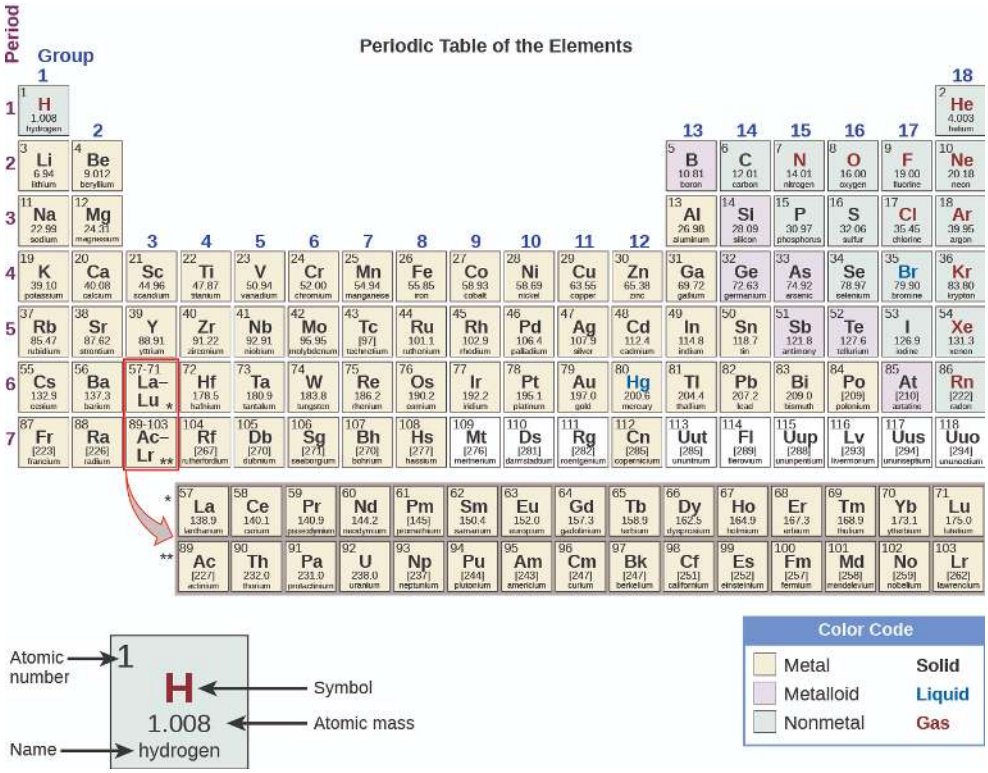


Figure 1.1.3.5: The periodic table shows how elements may be grouped according to certain similar properties. Note the background color denotes whether an element is a metal, metalloid, or nonmetal, whereas the element symbol color indicates whether it is a solid, liquid, or gas.

Summary

All substances have distinct physical and chemical properties, and may undergo physical or chemical changes. Physical properties, such as hardness and boiling point, and physical changes, such as melting or freezing, do not involve a change in the composition of matter. Chemical properties, such flammability and acidity, and chemical changes, such as rusting, involve production of matter that differs from that present beforehand.

Measurable properties fall into one of two categories. Extensive properties depend on the amount of matter present, for example, the mass of gold. Intensive properties do not depend on the amount of matter present, for example, the density of gold. Heat is an example of an extensive property, and temperature is an example of an intensive property.

Glossary

chemical change

change producing a different kind of matter from the original kind of matter

chemical property

behavior that is related to the change of one kind of matter into another kind of matter

extensive property

property of a substance that depends on the amount of the substance

intensive property

property of a substance that is independent of the amount of the substance

physical change

change in the state or properties of matter that does not involve a change in its chemical composition

physical property

characteristic of matter that is not associated with any change in its chemical composition

---

This page titled 1.1.3: Physical and Chemical Properties is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **1.3: Physical and Chemical Properties** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

1.1.4: Measurements

Learning Objectives

- Explain the process of measurement and describe the three basic parts of a quantity.
- Describe the properties and units of length, mass, volume, density, temperature, and time.
- Recognize the common unit prefixes and use them to describe the magnitude of a measurement.
- Describe and calculate the density of a substance.
- Perform basic unit calculations and conversions in the metric and other unit systems.

Measurements provide the macroscopic information that is the basis of most of the hypotheses, theories, and laws that describe the behavior of matter and energy in both the macroscopic and microscopic domains of chemistry. Every measurement provides three kinds of information: the size or magnitude of the measurement (a number); a standard of comparison for the measurement (a unit); and an indication of the uncertainty of the measurement. While the number and unit are explicitly represented when a quantity is written, the uncertainty is an aspect of the measurement result that is more implicitly represented and will be discussed later.

The number in the measurement can be represented in different ways, including decimal form and scientific notation. For example, the maximum takeoff weight of a Boeing 777-200ER airliner is 298,000 kilograms, which can also be written as 2.98×10^5 kg. The mass of the average mosquito is about 0.0000025 kilograms, which can be written as 2.5×10^{-6} kg.

Units, such as liters, pounds, and centimeters, are standards of comparison for measurements. When we buy a 2-liter bottle of a soft drink, we expect that the volume of the drink was measured, so it is two times larger than the volume that everyone agrees to be 1 liter. The meat used to prepare a 0.25-pound hamburger is measured so it weighs one-fourth as much as 1 pound. Without units, a number can be meaningless, confusing, or possibly life threatening. Suppose a doctor prescribes phenobarbital to control a patient's seizures and states a dosage of "100" without specifying units. Not only will this be confusing to the medical professional giving the dose, but the consequences can be dire: 100 mg given three times per day can be effective as an anticonvulsant, but a single dose of 100 g is more than 10 times the lethal amount.

We usually report the results of scientific measurements in SI units, an updated version of the metric system, using the units listed in Table 1.1.4.1. Other units can be derived from these base units. The standards for these units are fixed by international agreement, and they are called the International System of Units or SI Units (from the French, *Le Système International d'Unités*). SI units have been used by the United States National Institute of Standards and Technology (NIST) since 1964.

Table 1.1.4.1: Base Units of the SI System

Property Measured	Name of Unit	Symbol of Unit
length	meter	m
mass	kilogram	kg
time	second	s
temperature	kelvin	K
electric current	ampere	A
amount of substance	mole	mol
luminous intensity	candela	cd

Sometimes we use units that are fractions or multiples of a base unit. Ice cream is sold in quarts (a familiar, non-SI base unit), pints (0.5 quart), or gallons (4 quarts). We also use fractions or multiples of units in the SI system, but these fractions or multiples are always powers of 10. Fractional or multiple SI units are named using a prefix and the name of the base unit. For example, a length of 1000 meters is also called a kilometer because the prefix *kilo* means "one thousand," which in scientific notation is 10^3 (1 kilometer = 1000 m = 10^3 m). The prefixes used and the powers to which 10 are raised are listed in Table 1.1.4.2

NG, equals 4 times ten to the negative 9, or 0.000000004 g. The prefix micro has the greek letter mu as its symbol and a factor of 10 to the negative sixth power. Therefore, 1 microliter, or mu L, is equal to one times ten to the negative 6 or 0.000001 L. The

prefix milli has a lowercase M as its symbol and a factor of 10 to the negative third power. Therefore, 2 millimoles, or M mol, are equal to two times ten to the negative 3 or 0.002 mol. The prefix centi has a lowercase C as its symbol and a factor of 10 to the negative second power. Therefore, 7 centimeters, or C M, are equal to seven times ten to the negative 2 meters or 0.07 M O L. The prefix deci has a lowercase D as its symbol and a factor of 10 to the negative first power. Therefore, 1 deciliter, or lowercase D uppercase L, are equal to one times ten to the negative 1 meters or 0.1 L. The prefix kilo has a lowercase K as its symbol and a factor of 10 to the third power. Therefore, 1 kilometer, or K M, is equal to one times ten to the third meters or 1000 M. The prefix mega has an uppercase M as its symbol and a factor of 10 to the sixth power. Therefore, 3 megahertz, or M H Z, are equal to three times 10 to the sixth hertz, or 3000000 H Z. The prefix giga has an uppercase G as its symbol and a factor of 10 to the ninth power. Therefore, 8 gigayears, or G Y R, are equal to eight times 10 to the ninth years, or 800000000 G Y R. The prefix tera has an uppercase T as its symbol and a factor of 10 to the twelfth power. Therefore, 5 terawatts, or T W, are equal to five times 10 to the twelfth watts, or 5000000000000 W." data-quail-id="64" data-mt-width="1076">

Table 1.1.4.2: Common Unit Prefixes

Prefix	Symbol	Factor	Example
femto	f	10^{-15}	1 femtosecond (fs) = 1×10^{-15} s (0.000000000000001 s)
pico	p	10^{-12}	1 picometer (pm) = 1×10^{-12} m (0.000000000001 m)
nano	n	10^{-9}	4 nanograms (ng) = 4×10^{-9} g (0.000000004 g)
micro	µ	10^{-6}	1 microliter (µL) = 1×10^{-6} L (0.000001 L)
milli	m	10^{-3}	2 millimoles (mmol) = 2×10^{-3} mol (0.002 mol)
centi	c	10^{-2}	7 centimeters (cm) = 7×10^{-2} m (0.07 m)
deci	d	10^{-1}	1 deciliter (dL) = 1×10^{-1} L (0.1 L)
kilo	k	10^{3}	1 kilometer (km) = 1×10^{3} m (1000 m)
mega	M	10^{6}	3 megahertz (MHz) = 3×10^{6} Hz (3,000,000 Hz)
giga	G	10^{9}	8 gigayears (Gyr) = 8×10^{9} yr (8,000,000,000 Gyr)
tera	T	10^{12}	5 terawatts (TW) = 5×10^{12} W (5,000,000,000,000 W)

1.1.4.1: SI Base Units

The initial units of the metric system, which eventually evolved into the SI system, were established in France during the French Revolution. The original standards for the meter and the kilogram were adopted there in 1799 and eventually by other countries. This section introduces four of the SI base units commonly used in chemistry. Other SI units will be introduced in subsequent chapters.

1.1.4.1.1: Length

The standard unit of length in both the SI and original metric systems is the meter (m). A meter was originally specified as 1/10,000,000 of the distance from the North Pole to the equator. It is now defined as the distance light in a vacuum travels in 1/299,792,458 of a second. A meter is about 3 inches longer than a yard (Figure 1.1.4.1); one meter is about 39.37 inches or 1.094

yards. Longer distances are often reported in kilometers (1 km = 1000 m = 10^3 m), whereas shorter distances can be reported in centimeters (1 cm = 0.01 m = 10^{-2} m) or millimeters (1 mm = 0.001 m = 10^{-3} m).

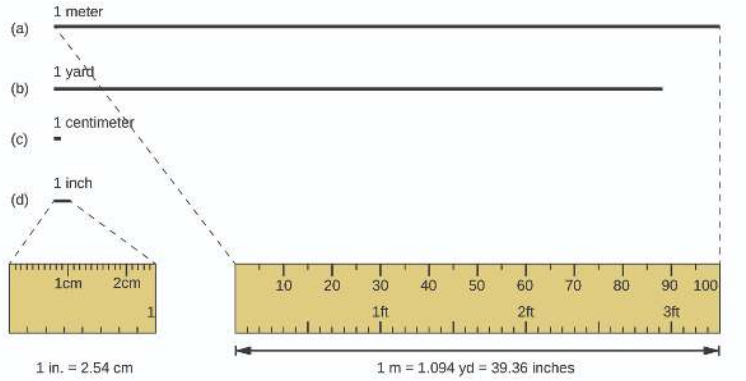


Figure 1.1.4.1: The relative lengths of 1 m, 1 yd, 1 cm, and 1 in. are shown (not actual size), as well as comparisons of 2.54 cm and 1 in., and of 1 m and 1.094 yd.

A ruler is shown with various lengths of black line shown above it to compare the relative lengths of 1 inch, meter, centimeter, and yard.

1.1.4.1.2: Mass

The standard unit of mass in the SI system is the kilogram (kg). A kilogram was originally defined as the mass of a liter of water (a cube of water with an edge length of exactly 0.1 meter). It is now defined by a certain cylinder of platinum-iridium alloy, which is kept in France (Figure 1.4.2). Any object with the same mass as this cylinder is said to have a mass of 1 kilogram. One kilogram is about 2.2 pounds. The gram (g) is exactly equal to 1/1000 of the mass of the kilogram (10^{-3} kg).



Figure 1.1.4.2: This replica prototype kilogram is housed at the National Institute of Standards and Technology (NIST) in Maryland. (credit: National Institutes of Standards and Technology).

1.1.4.1.3: Temperature

Temperature is an intensive property. The SI unit of temperature is the kelvin (K). The IUPAC convention is to use kelvin (all lowercase) for the word, K (uppercase) for the unit symbol, and neither the word “degree” nor the degree symbol (°). The degree Celsius (°C) is also allowed in the SI system, with both the word “degree” and the degree symbol used for Celsius measurements. Celsius degrees are the same magnitude as those of kelvin, but the two scales place their zeros in different places. Water freezes at 273.15 K (0 °C) and boils at 373.15 K (100 °C) by definition, and normal human body temperature is approximately 310 K (37 °C). The conversion between these two units and the Fahrenheit scale will be discussed later in this chapter.

1.1.4.1.4: Time

The SI base unit of time is the second (s). Small and large time intervals can be expressed with the appropriate prefixes; for example, 3 microseconds = 0.000003 s = 3×10^{-6} and 5 megaseconds = 5,000,000 s = 5×10^6 s. Alternatively, hours, days, and years can be used.

1.1.4.2: Derived SI Units

We can derive many units from the seven SI base units. For example, we can use the base unit of length to define a unit of volume, and the base units of mass and length to define a unit of density.

1.1.4.2.1: Volume

Volume is the measure of the amount of space occupied by an object. The standard SI unit of volume is defined by the base unit of length (Figure 1.1.4.3). The standard volume is a cubic meter (m^3), a cube with an edge length of exactly one meter. To dispense a cubic meter of water, we could build a cubic box with edge lengths of exactly one meter. This box would hold a cubic meter of water or any other substance.

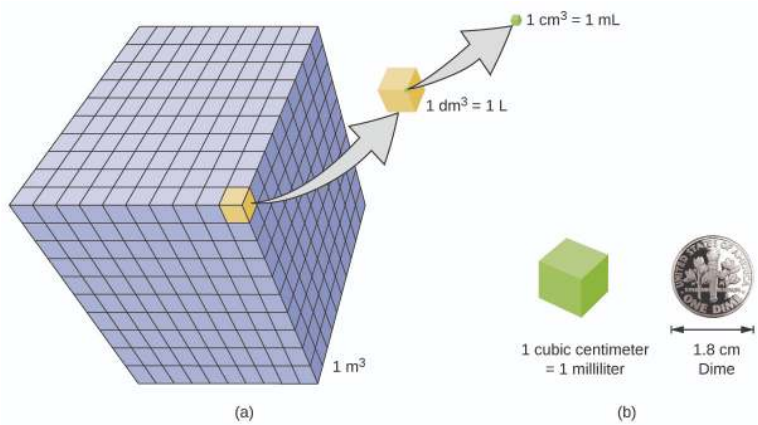


Figure 1.1.4.3: (a) The relative volumes are shown for cubes of 1 m^3, 1 dm^3 (1 L), and 1 cm^3 (1 mL) (not to scale). (b) The diameter of a dime is compared relative to the edge length of a 1-cm^3 (1-mL) cube.

A more commonly used unit of volume is derived from the decimeter (0.1 m, or 10 cm). A cube with edge lengths of exactly one decimeter contains a volume of one cubic decimeter (dm^3). A liter (L) is the more common name for the cubic decimeter. One liter is about 1.06 quarts. A cubic centimeter (cm^3) is the volume of a cube with an edge length of exactly one centimeter. The abbreviation **cc** (for **c**ubic **c**entimeter) is often used by health professionals. A cubic centimeter is also called a milliliter (mL) and is 1/1000 of a liter.

1.1.4.2.2: Density

We use the mass and volume of a substance to determine its density. Thus, the units of density are defined by the base units of mass and length.

The density of a substance is the ratio of the mass of a sample of the substance to its volume. The SI unit for density is the kilogram per cubic meter (kg/m^3). For many situations, however, this as an inconvenient unit, and we often use grams per cubic centimeter (g/cm^3) for the densities of solids and liquids, and grams per liter (g/L) for gases. Although there are exceptions, most liquids and solids have densities that range from about 0.7 g/cm^3 (the density of gasoline) to 19 g/cm^3 (the density of gold). The density of air is about 1.2 g/L. Table 1.1.4.3shows the densities of some common substances.

Table 1.1.4.3: Densities of Common Substances

Solids	Liquids	Gases (at 25 °C and 1 atm)
ice (at 0 °C) 0.92 g/cm^3	water 1.0 g/cm^3	dry air 1.20 g/L
oak (wood) 0.60–0.90 g/cm^3	ethanol 0.79 g/cm^3	oxygen 1.31 g/L
iron 7.9 g/cm^3	acetone 0.79 g/cm^3	nitrogen 1.14 g/L
copper 9.0 g/cm^3	glycerin 1.26 g/cm^3	carbon dioxide 1.80 g/L
lead 11.3 g/cm^3	olive oil 0.92 g/cm^3	helium 0.16 g/L
silver 10.5 g/cm^3	gasoline 0.70–0.77 g/cm^3	neon 0.83 g/L
gold 19.3 g/cm^3	mercury 13.6 g/cm^3	radon 9.1 g/L

While there are many ways to determine the density of an object, perhaps the most straightforward method involves separately finding the mass and volume of the object, and then dividing the mass of the sample by its volume. In the following example, the mass is found directly by weighing, but the volume is found indirectly through length measurements.

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

Example 1.1.4.1

Calculation of Density Gold—in bricks, bars, and coins—has been a form of currency for centuries. In order to swindle people into paying for a brick of gold without actually investing in a brick of gold, people have considered filling the centers of hollow gold bricks with lead to fool buyers into thinking that the entire brick is gold. It does not work: Lead is a dense substance, but its density is not as great as that of gold, 19.3 g/cm^3. What is the density of lead if a cube of lead has an edge length of 2.00 cm and a mass of 90.7 g?

Solution

The density of a substance can be calculated by dividing its mass by its volume. The volume of a cube is calculated by cubing the edge length.

$$\text{volume of lead cube} = 2.00\ \text{cm} \times 2.00\ \text{cm} \times 2.00\ \text{cm} = 8.00\ \text{cm}^3$$

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{90.7\ \text{g}}{8.00\ \text{cm}^3} = \frac{11.3\ \text{g}}{1.00\ \text{cm}^3} = 11.3\ \text{g/cm}^3$$

(We will discuss the reason for rounding to the first decimal place in the next section.)

Exercise 1.1.4.1

a. To three decimal places, what is the volume of a cube (cm^3) with an edge length of 0.843 cm?
b. If the cube in part (a) is copper and has a mass of 5.34 g, what is the density of copper to two decimal places?

Answer a

0.599 cm^3;

Answer b

8.91 g/cm^3

Example 1.1.4.2: Using Displacement of Water to Determine Density

This PhET simulation illustrates another way to determine density, using displacement of water. Determine the density of the red and yellow blocks.

Solution

When you open the density simulation and select Same Mass, you can choose from several 5.00-kg colored blocks that you can drop into a tank containing 100.00 L water. The yellow block floats (it is less dense than water), and the water level rises to 105.00 L. While floating, the yellow block displaces 5.00 L water, an amount equal to the weight of the block. The red block sinks (it is more dense than water, which has density = 1.00 kg/L), and the water level rises to 101.25 L.

The red block therefore displaces 1.25 L water, an amount equal to the volume of the block. The density of the red block is:

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{5.00\ \text{kg}}{1.25\ \text{L}} = 4.00\ \text{kg/L}$$

Note that since the yellow block is not completely submerged, you cannot determine its density from this information. But if you hold the yellow block on the bottom of the tank, the water level rises to 110.00 L, which means that it now displaces 10.00 L water, and its density can be found:

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{5.00\ \text{kg}}{10.00\ \text{L}} = 0.500\ \text{kg/L}$$

? Exercise 1.1.4.1

Remove all of the blocks from the water and add the green block to the tank of water, placing it approximately in the middle of the tank. Determine the density of the green block.

Answer

2.00 kg/L

Summary

Measurements provide quantitative information that is critical in studying and practicing chemistry. Each measurement has an amount, a unit for comparison, and an uncertainty. Measurements can be represented in either decimal or scientific notation. Scientists primarily use the SI (International System) or metric systems. We use base SI units such as meters, seconds, and kilograms, as well as derived units, such as liters (for volume) and g/cm^3 (for density). In many cases, we find it convenient to use unit prefixes that yield fractional and multiple units, such as microseconds (10^{-6} seconds) and megahertz (10^6 hertz), respectively.

1.1.4.3: Key Equations

- $\text{density} = \dfrac{\text{mass}}{\text{volume}}$

Glossary

Celsius (°C)
unit of temperature; water freezes at 0 °C and boils at 100 °C on this scale

cubic centimeter (cm^3 or cc)
volume of a cube with an edge length of exactly 1 cm

cubic meter (m^3)
SI unit of volume

density
ratio of mass to volume for a substance or object

kelvin (K)
SI unit of temperature; 273.15 K = 0 ºC

kilogram (kg)
standard SI unit of mass; 1 kg = approximately 2.2 pounds

length
measure of one dimension of an object

liter (L)
(also, cubic decimeter) unit of volume; 1 L = 1,000 cm^3

meter (m)
standard metric and SI unit of length; 1 m = approximately 1.094 yards

milliliter (mL)
1/1,000 of a liter; equal to 1 cm^3

second (s)
SI unit of time

SI units (International System of Units)

standards fixed by international agreement in the International System of Units (*Le Système International d'Unités*)

unit

standard of comparison for measurements

volume

amount of space occupied by an object

This page titled 1.1.4: Measurements is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **1.4: Measurements** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.



https://chem.libretexts.org/@go/page/393196

1.1.5: Measurement Uncertainty, Accuracy, and Precision

Learning Objectives

- Compare and contrast exact and uncertain numbers.
- Correctly represent uncertainty in quantities using significant figures.
- Identify the number of significant figures in value.
- Solve problems that involve various calculations and report the results with the appropriate number of significant figures.
- Apply proper rounding rules to computed quantities
- Define accuracy and precision, and use accuracy and precision to describe data sets.

Counting is the only type of measurement that is free from uncertainty, provided the number of objects being counted does not change while the counting process is underway. The result of such a counting measurement is an example of an exact number. If we count eggs in a carton, we know *exactly* how many eggs the carton contains. The numbers of defined quantities are also exact. By definition, 1 foot is exactly 12 inches, 1 inch is exactly 2.54 centimeters, and 1 gram is exactly 0.001 kilogram. Quantities derived from measurements other than counting, however, are uncertain to varying extents due to practical limitations of the measurement process used.

1.1.5.1: Significant Figures in Measurement

The numbers of measured quantities, unlike defined or directly counted quantities, are not exact. To measure the volume of liquid in a graduated cylinder, you should make a reading at the bottom of the meniscus, the lowest point on the curved surface of the liquid.

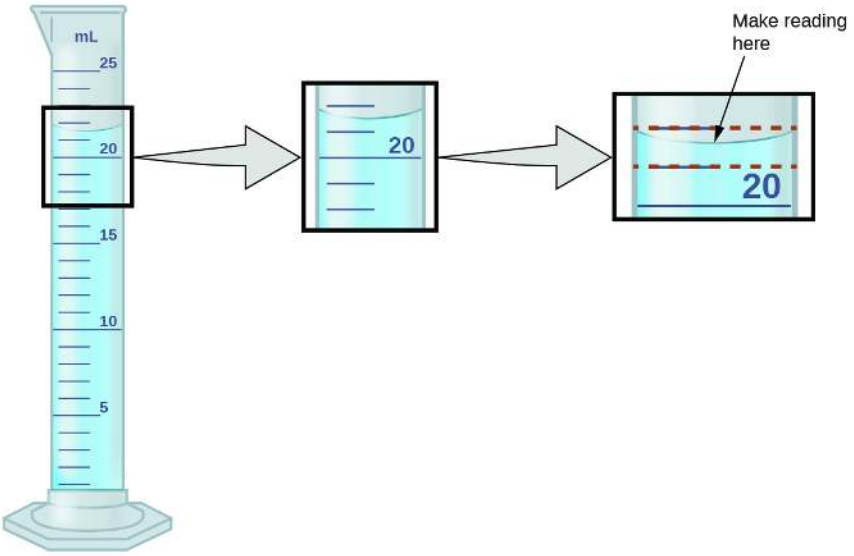


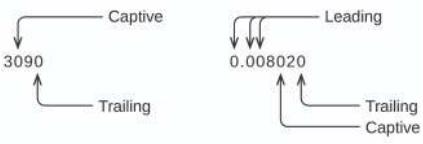
Figure 1.1.5.1: To measure the volume of liquid in this graduated cylinder, you must mentally subdivide the distance between the 21 and 22 mL marks into tenths of a milliliter, and then make a reading (estimate) at the bottom of the meniscus.

A 25 millilter graduated cylinder filled with liquid. The markings on the cylinders is zoomed in to show the bottom of the meniscus between 21 and 22 milliliters.

Refer to the illustration in Figure 1.1.5.1 The bottom of the meniscus in this case clearly lies between the 21 and 22 markings, meaning the liquid volume is *certainly* greater than 21 mL but less than 22 mL. The meniscus appears to be a bit closer to the 22-mL mark than to the 21-mL mark, and so a reasonable estimate of the liquid's volume would be 21.6 mL. In the number 21.6, then, the digits 2 and 1 are certain, but the 6 is an estimate. Some people might estimate the meniscus position to be equally distant from each of the markings and estimate the tenth-place digit as 5, while others may think it to be even closer to the 22-mL mark and estimate this digit to be 7. Note that it would be pointless to attempt to estimate a digit for the hundredths place, given that the tenths-place digit is uncertain. In general, numerical scales such as the one on this graduated cylinder will permit measurements to one-tenth of the smallest scale division. The scale in this case has 1-mL divisions, and so volumes may be measured to the nearest 0.1 mL.

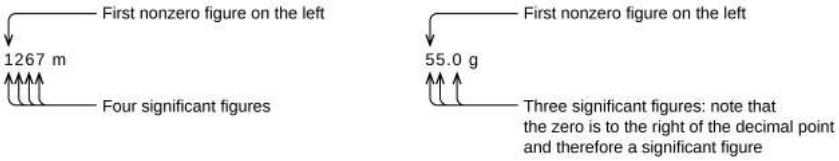
This concept holds true for all measurements, even if you do not actively make an estimate. If you place a quarter on a standard electronic balance, you may obtain a reading of 6.72 g. The digits 6 and 7 are certain, and the 2 indicates that the mass of the quarter is likely between 6.71 and 6.73 grams. The quarter weighs *about* 6.72 grams, with a nominal uncertainty in the measurement of ± 0.01 gram. If we weigh the quarter on a more sensitive balance, we may find that its mass is 6.723 g. This means its mass lies between 6.722 and 6.724 grams, an uncertainty of 0.001 gram. Every measurement has some uncertainty, which depends on the device used (and the user's ability). All of the digits in a measurement, including the uncertain last digit, are called significant figures or significant digits. Note that zero may be a measured value; for example, if you stand on a scale that shows weight to the nearest pound and it shows "120," then the 1 (hundreds), 2 (tens) and 0 (ones) are all significant (measured) values.

Whenever you make a measurement properly, all the digits in the result are significant. But what if you were analyzing a reported value and trying to determine what is significant and what is not? Well, for starters, all nonzero digits are significant, and it is only zeros that require some thought. We will use the terms "leading," "trailing," and "captive" for the zeros and will consider how to deal with them.



The left diagram uses the example of 3090. The zero in the hundreds place is labeled "captive" and the zero in the ones place is labeled trailing. The right diagram uses the example 0.008020. The three zeros in the ones, tenths, and hundredths places are labeled "leading." The zero in the ten-thousandths place is labeled "captive" and the zero in the millionths place is labeled "trailing."

Starting with the first nonzero digit on the left, count this digit and all remaining digits to the right. This is the number of significant figures in the measurement unless the last digit is a trailing zero lying to the left of the decimal point.



The left diagram uses the example of 1267 meters. The number 1 is the first nonzero figure on the left. 1267 has 4 significant figures in total. The right diagram uses the example of 55.0 grams. The number 5 in the tens place is the first nonzero figure on the left. 55.0 has 3 significant figures. Note that the 0 is to the right of the decimal point and therefore is a significant figure.

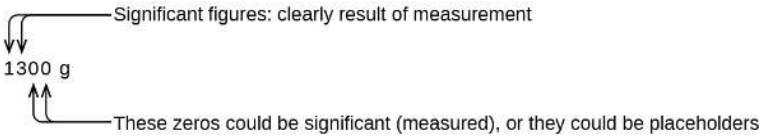
Captive zeros result from measurement and are therefore always significant. Leading zeros, however, are never significant—they merely tell us where the decimal point is located.



The left diagram uses the example of 70.607 milliliters. The number 7 is the first nonzero figure on the left. 70.607 has 5 significant figures in total, as all figures are measured including the 2 zeros. The right diagram uses the example of 0.00832407 M L. The number 8 is the first nonzero figure on the left. 0.00832407 has 6 significant figures.

The leading zeros in this example are not significant. We could use exponential notation (as described in Appendix B) and express the number as 8.32407×10^{-3}; then the number 8.32407 contains all of the significant figures, and 10^{-3} locates the decimal point.

The number of significant figures is uncertain in a number that ends with a zero to the left of the decimal point location. The zeros in the measurement 1,300 grams could be significant or they could simply indicate where the decimal point is located. The ambiguity can be resolved with the use of exponential notation: 1.3×10^3 (two significant figures), 1.30×10^3 (three significant figures, if the tens place was measured), or 1.300×10^3 (four significant figures, if the ones place was also measured). In cases where only the decimal-formatted number is available, it is prudent to assume that all trailing zeros are not significant.



This figure uses the example of 1300 grams. The one and the 3 are significant figures as they are clearly the result of measurement. The 2 zeros could be significant if they were measured or they could be placeholders.

When determining significant figures, be sure to pay attention to reported values and think about the measurement and significant figures in terms of what is reasonable or likely—that is, whether the value makes sense. For example, the official January 2014 census reported the resident population of the US as 317,297,725. Do you think the US population was correctly determined to the reported nine significant figures, that is, to the exact number of people? People are constantly being born, dying, or moving into or out of the country, and assumptions are made to account for the large number of people who are not actually counted. Because of these uncertainties, it might be more reasonable to expect that we know the population to within perhaps a million or so, in which case the population should be reported as 317 million, or 3.17×10^8 people.

1.1.5.2: Significant Figures in Calculations

A second important principle of uncertainty is that results calculated from a measurement are at least as uncertain as the measurement itself. We must take the uncertainty in our measurements into account to avoid misrepresenting the uncertainty in calculated results. One way to do this is to report the result of a calculation with the correct number of significant figures, which is determined by the following three rules for rounding numbers:

1. When we add or subtract numbers, we should round the result to the same number of decimal places as the number with the least number of decimal places (the least precise value in terms of addition and subtraction).
2. When we multiply or divide numbers, we should round the result to the same number of digits as the number with the least number of significant figures (the least precise value in terms of multiplication and division).
3. If the digit to be dropped (the one immediately to the right of the digit to be retained) is less than 5, we "round down" and leave the retained digit unchanged; if it is more than 5, we "round up" and increase the retained digit by 1; if the dropped digit *is* 5, we round up or down, whichever yields an even value for the retained digit. (The last part of this rule may strike you as a bit odd, but it's based on reliable statistics and is aimed at avoiding any bias when dropping the digit "5," since it is equally close to both possible values of the retained digit.)

The following examples illustrate the application of this rule in rounding a few different numbers to three significant figures:

- 0.028675 rounds "up" to 0.0287 (the dropped digit, 7, is greater than 5)
- 18.3384 rounds "down" to 18.3 (the dropped digit, 3, is less than 5)
- 6.8752 rounds "up" to 6.88 (the dropped digit is 5, and the retained digit is even)
- 92.85 rounds "down" to 92.8 (the dropped digit is 5, and the retained digit is even)

Let's work through these rules with a few examples.

Example 1.1.5.1: Rounding Numbers

Round the following to the indicated number of significant figures:

a. 31.57 (to two significant figures)
b. 8.1649 (to three significant figures)
c. 0.051065 (to four significant figures)
d. 0.90275 (to four significant figures)

Solution

a. 31.57 rounds "up" to 32 (the dropped digit is 5, and the retained digit is even)
b. 8.1649 rounds "down" to 8.16 (the dropped digit, 4, is less than 5)
c. 0.051065 rounds "down" to 0.05106 (the dropped digit is 5, and the retained digit is even)
d. 0.90275 rounds "up" to 0.9028 (the dropped digit is 5, and the retained digit is even)

Exercise 1.1.5.1

Round the following to the indicated number of significant figures:

a. 0.424 (to two significant figures)
b. 0.0038661 (to three significant figures)
c. 421.25 (to four significant figures)
d. 28,683.5 (to five significant figures)

Answer a

0.42

Answer b

0.00387

Answer c

421.2

Answer d

28,684

Example 1.1.5.2: Addition and Subtraction with Significant Figures Rule:

When we add or subtract numbers, we should round the result to the same number of decimal places as the number with the least number of decimal places (i.e., the least precise value in terms of addition and subtraction).

a. Add 1.0023 g and 4.383 g.
b. Subtract 421.23 g from 486 g.

Solution

(a)

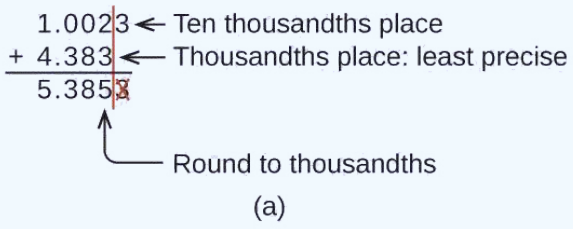
$$\begin{array}{r} 1.0023\ \text{g} \\ +\ 4.383\ \text{g} \\ \hline 5.3853\ \text{g} \end{array}$$

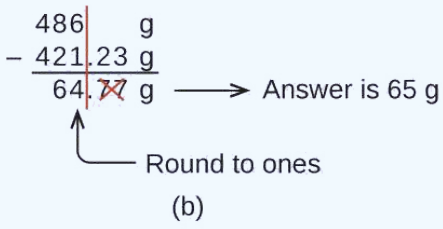
Answer is 5.385 g (round to the thousandths place; three decimal places)

(b)

$$\begin{array}{r} 486\ \text{g} \\ -\ 421.23\ \text{g} \\ \hline 64.77\ \text{g} \end{array}$$

Answer is 65 g (round to the ones place; no decimal places)





https://chem.libretexts.org/@go/page/393197

Exercise 1.1.5.2

a. Add 2.334 mL and 0.31 mL.
b. Subtract 55.8752 m from 56.533 m.

Answer a

2.64 mL

Answer b

0.658 m

Example 1.1.5.3: Multiplication and Division with Significant Figures

Rule: When we multiply or divide numbers, we should round the result to the same number of digits as the number with the least number of significant figures (the least precise value in terms of multiplication and division).

a. Multiply 0.6238 cm by 6.6 cm.
b. Divide 421.23 g by 486 mL.

Solution

(a)

$$0.6238\ \text{cm} \times 6.6\ \text{cm} = 4.11708\ \text{cm}^2 \rightarrow \text{result is } 4.1\ \text{cm}^2\ (\text{round to two significant figures})$$

$$\text{four significant figures} \times \text{two significant figures} \rightarrow \text{two significant figures answer}$$

(b)

$$\frac{421.23\ \text{g}}{486\ \text{mL}} = 0.86728\ldots\ \text{g/mL} \rightarrow \text{result is } 0.867\ \text{g/mL}\ (\text{round to three significant figures})$$

$$\frac{\text{five significant figures}}{\text{three significant figures}} \rightarrow \text{three significant figures answer}$$

Exercise 1.1.5.3

a. Multiply 2.334 cm and 0.320 cm.
b. Divide 55.8752 m by 56.53 s.

Answer a

0.747 cm^2

Answer b

0.9884 m/s

In the midst of all these technicalities, it is important to keep in mind the reason why we use significant figures and rounding rules—to correctly represent the certainty of the values we report and to ensure that a calculated result is not represented as being more certain than the least certain value used in the calculation.

Example 1.1.5.4: Calculation with Significant Figures

One common bathtub is 13.44 dm long, 5.920 dm wide, and 2.54 dm deep. Assume that the tub is rectangular and calculate its approximate volume in liters.

Solution

$$\begin{aligned} V &= l \times w \times d \\ &= 13.44\ \text{dm} \times 5.920\ \text{dm} \times 2.54\ \text{dm} \\ &= 202.09459\ldots \text{dm}^3\ \text{(value from calculator)} \\ &= 202\ \text{dm}^3\text{, or } 202\ \text{L (answer rounded to three significant figures)} \end{aligned}$$

Exercise 1.1.5.4: Determination of Density Using Water Displacement

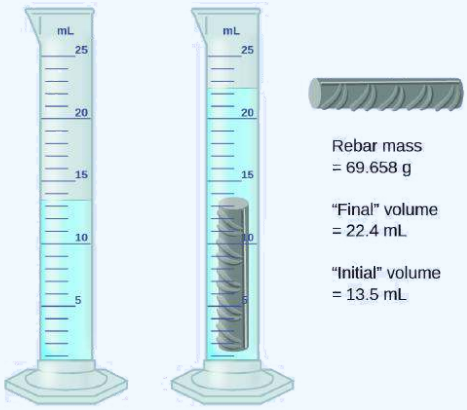
What is the density of a liquid with a mass of 31.1415 g and a volume of 30.13 cm^3?

Answer

1.034 g/mL

Example 1.1.5.4

A piece of rebar is weighed and then submerged in a graduated cylinder partially filled with water, with results as shown.



A graduated cylinder filled with liquid is shown. One shows the level before the rebar is added and the other shows the level with the rebar submerged in the liquid. Rebar mass is 69.658 grams, final volume is 22.4 milliliters, and initial volume is 13.5 milliliters.

a. Use these values to determine the density of this piece of rebar.
b. Rebar is mostly iron. Does your result in (a) support this statement? How?

Solution

The volume of the piece of rebar is equal to the volume of the water displaced:

$$\text{volume} = 22.4\ \text{mL} - 13.5\ \text{mL} = 8.9\ \text{mL} = 8.9\ \text{cm}^3$$

(rounded to the nearest 0.1 mL, per the rule for addition and subtraction)

The density is the mass-to-volume ratio:

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{69.658\ \text{g}}{8.9\ \text{cm}^3} = 7.8\ \text{g/cm}^3$$

(rounded to two significant figures, per the rule for multiplication and division)

The density of iron is 7.9 g/cm^3, very close to that of rebar, which lends some support to the fact that rebar is mostly iron.

Exercise 1.1.5.4

An irregularly shaped piece of a shiny yellowish material is weighed and then submerged in a graduated cylinder, with results as shown.



A graduated cylinder filled with liquid is shown. One shows the level before the material is added and the other shows the level with the material submerged in the liquid. Mass is 51.842 grams, final volume is 19.8 milliliters, and initial volume is 17.1 milliliters.

a. Use these values to determine the density of this material.
b. Do you have any reasonable guesses as to the identity of this material? Explain your reasoning.

Answer a

19 g/cm^3

Answer b

It is likely gold; it has the right appearance for gold and very close to the density given for gold.

1.1.5.3: Accuracy and Precision

Scientists typically make repeated measurements of a quantity to ensure the quality of their findings and to know both the precision and the accuracy of their results. Measurements are said to be precise if they yield very similar results when repeated in the same manner. A measurement is considered accurate if it yields a result that is very close to the true or accepted value. Precise values agree with each other; accurate values agree with a true value. These characterizations can be extended to other contexts, such as the results of an archery competition (Figure 1.1.5.2).

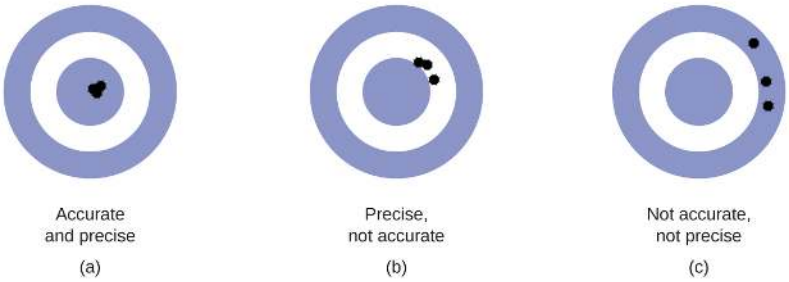


Figure 1.1.5.2: (a) These arrows are close to both the bull's eye and one another, so they are both accurate and precise. (b) These arrows are close to one another but not on target, so they are precise but not accurate. (c) These arrows are neither on target nor close to one another, so they are neither accurate nor precise.

Suppose a quality control chemist at a pharmaceutical company is tasked with checking the accuracy and precision of three different machines that are meant to dispense 10 ounces (296 mL) of cough syrup into storage bottles. She proceeds to use each machine to fill five bottles and then carefully determines the actual volume dispensed, obtaining the results tabulated in Table 1.1.5.2

Table 1.1.5.2: Volume (mL) of Cough Medicine Delivered by 10-oz (296 mL) Dispensers

Dispenser #1	Dispenser #2	Dispenser #3
283.3	298.3	296.1

Dispenser #1	Dispenser #2	Dispenser #3
284.1	294.2	295.9
283.9	296.0	296.1
284.0	297.8	296.0
284.1	293.9	296.1

Considering these results, she will report that dispenser #1 is precise (values all close to one another, within a few tenths of a milliliter) but not accurate (none of the values are close to the target value of 296 mL, each being more than 10 mL too low). Results for dispenser #2 represent improved accuracy (each volume is less than 3 mL away from 296 mL) but worse precision (volumes vary by more than 4 mL). Finally, she can report that dispenser #3 is working well, dispensing cough syrup both accurately (all volumes within 0.1 mL of the target volume) and precisely (volumes differing from each other by no more than 0.2 mL).

Summary

Quantities can be exact or measured. Measured quantities have an associated uncertainty that is represented by the number of significant figures in the measurement. The uncertainty of a calculated value depends on the uncertainties in the values used in the calculation and is reflected in how the value is rounded. Measured values can be accurate (close to the true value) and/or precise (showing little variation when measured repeatedly).

Glossary

uncertainty
: estimate of amount by which measurement differs from true value

significant figures
: (also, significant digits) all of the measured digits in a determination, including the uncertain last digit

rounding
: procedure used to ensure that calculated results properly reflect the uncertainty in the measurements used in the calculation

precision
: how closely a measurement matches the same measurement when repeated

exact number
: number derived by counting or by definition

accuracy
: how closely a measurement aligns with a correct value

This page titled 1.1.5: Measurement Uncertainty, Accuracy, and Precision is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **1.5: Measurement Uncertainty, Accuracy, and Precision** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

1.1.6: Mathematical Treatment of Measurement Results

Learning Objectives

- Explain the dimensional analysis (factor label) approach to mathematical calculations involving quantities.
- Describe how to use dimensional analysis to carry out unit conversions for a given property and computations involving two or more properties.
- Convert between the three main temperature units: Fahrenheit, Celsius, and Kelvin.

It is often the case that a quantity of interest may not be easy (or even possible) to measure directly but instead must be calculated from other directly measured properties and appropriate mathematical relationships. For example, consider measuring the average speed of an athlete running sprints. This is typically accomplished by measuring the *time* required for the athlete to run from the starting line to the finish line, and the *distance* between these two lines, and then computing *speed* from the equation that relates these three properties:

$$\text{speed} = \frac{\text{distance}}{\text{time}}$$

An Olympic-quality sprinter can run 100 m in approximately 10 s, corresponding to an average speed of

$$\frac{100\ \text{m}}{10\ \text{s}} = 10\ \text{m/s}$$

Note that this simple arithmetic involves dividing the numbers of each measured quantity to yield the number of the computed quantity (100/10 = 10) *and likewise* dividing the units of each measured quantity to yield the unit of the computed quantity (m/s = m/s). Now, consider using this same relation to predict the time required for a person running at this speed to travel a distance of 25 m. The same relation between the three properties is used, but in this case, the two quantities provided are a speed (10 m/s) and a distance (25 m). To yield the sought property, time, the equation must be rearranged appropriately:

$$\text{time} = \frac{\text{distance}}{\text{speed}}$$

The time can then be computed as:

$$\frac{25\ \text{m}}{10\ \text{m/s}} = 2.5\ \text{s}$$

Again, arithmetic on the numbers (25/10 = 2.5) was accompanied by the same arithmetic on the units (m/m/s = s) to yield the number and unit of the result, 2.5 s. Note that, just as for numbers, when a unit is divided by an identical unit (in this case, m/m), the result is "1"—or, as commonly phrased, the units "cancel."

These calculations are examples of a versatile mathematical approach known as dimensional analysis (or the factor-label method). Dimensional analysis is based on this premise: *the units of quantities must be subjected to the same mathematical operations as their associated numbers*. This method can be applied to computations ranging from simple unit conversions to more complex, multi-step calculations involving several different quantities.

1.1.6.1: Conversion Factors and Dimensional Analysis

A ratio of two equivalent quantities expressed with different measurement units can be used as a unit conversion factor. For example, the lengths of 2.54 cm and 1 in. are equivalent (by definition), and so a unit conversion factor may be derived from the ratio,

$$\frac{2.54\ \text{cm}}{1\ \text{in.}}\ (2.54\ \text{cm} = 1\ \text{in.}) \text{ or } 2.54\ \frac{\text{cm}}{\text{in.}}$$

Several other commonly used conversion factors are given in Table 1.1.6.1.

Table 1.1.6.1: Common Conversion Factors

Length	Volume	Mass
1 m = 1.0936 yd	1 L = 1.0567 qt	1 kg = 2.2046 lb
1 in. = 2.54 cm (exact)	1 qt = 0.94635 L	1 lb = 453.59 g
1 km = 0.62137 mi	1 ft^3 = 28.317 L	1 (avoirdupois) oz = 28.349 g
1 mi = 1609.3 m	1 tbsp = 14.787 mL	1 (troy) oz = 31.103 g

When we multiply a quantity (such as distance given in inches) by an appropriate unit conversion factor, we convert the quantity to an equivalent value with different units (such as distance in centimeters). For example, a basketball player's vertical jump of 34 inches can be converted to centimeters by:

$$34\ \cancel{\text{in.}} \times \frac{2.54\ \text{cm}}{1\ \cancel{\text{in.}}} = 86\ \text{cm}$$

Since this simple arithmetic involves *quantities*, the premise of dimensional analysis requires that we multiply both *numbers and units*. The numbers of these two quantities are multiplied to yield the number of the product quantity, 86, whereas the units are multiplied to yield

$$\frac{\text{in.} \times \text{cm}}{\text{in.}}.$$

Just as for numbers, a ratio of identical units is also numerically equal to one,

$$\frac{\text{in.}}{\text{in.}} = 1$$

and the unit product thus simplifies to *cm*. (When identical units divide to yield a factor of 1, they are said to "cancel.") Using dimensional analysis, we can determine that a unit conversion factor has been set up correctly by checking to confirm that the original unit will cancel, and the result will contain the sought (converted) unit.

Example 1.1.6.1: Using a Unit Conversion Factor

The mass of a competition Frisbee is 125 g. Convert its mass to ounces using the unit conversion factor derived from the relationship 1 oz = 28.349 g (Table 1.1.6.1).

Solution

If we have the conversion factor, we can determine the mass in kilograms using an equation similar the one used for converting length from inches to centimeters.

$$x\ \text{oz} = 125\ \text{g} \times \text{unit conversion factor}$$

We write the unit conversion factor in its two forms:

$$\frac{1\ \text{oz}}{28.349\ \text{g}} \text{ and } \frac{28.349\ \text{g}}{1\ \text{oz}}$$

The correct unit conversion factor is the ratio that cancels the units of grams and leaves ounces.

$$\begin{aligned} x \text{ oz} &= 125 \text{ g} \times \frac{1 \text{ oz}}{28.349 \text{ g}} \\ &= \left(\frac{125}{28.349}\right) \text{ oz} \\ &= 4.41 \text{ oz (three significant figures)} \end{aligned}$$

? Exercise 1.1.6.1

Convert a volume of 9.345 qt to liters.

Answer

8.844 L

Beyond simple unit conversions, the factor-label method can be used to solve more complex problems involving computations. Regardless of the details, the basic approach is the same—all the *factors* involved in the calculation must be appropriately oriented to insure that their *labels* (units) will appropriately cancel and/or combine to yield the desired unit in the result. This is why it is referred to as the factor-label method. As your study of chemistry continues, you will encounter many opportunities to apply this approach.

✓ Example 1.1.6.2: Computing Quantities from Measurement Results

What is the density of common antifreeze in units of g/mL? A 4.00-qt sample of the antifreeze weighs 9.26 lb.

Solution

Since density $= \frac{\text{mass}}{\text{volume}}$, we need to divide the mass in grams by the volume in milliliters. In general: the number of units of B = the number of units of A $\times$ unit conversion factor. The necessary conversion factors are given in Table 1.7.1: 1 lb = 453.59 g; 1 L = 1.0567 qt; 1 L = 1,000 mL. We can convert mass from pounds to grams in one step:

$$9.26 \text{ lb} \times \frac{453.59 \text{ g}}{1 \text{ lb}} = 4.20 \times 10^3 \text{ g}$$

We need to use two steps to convert volume from quarts to milliliters.

1. *Convert quarts to liters.*

$$4.00 \text{ qt} \times \frac{1 \text{ L}}{1.0567 \text{ qt}} = 3.78 \text{ L}$$

2. *Convert liters to milliliters.*

$$3.78 \text{ L} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 3.78 \times 10^3 \text{ mL}$$

Then,

$$\text{density} = \frac{4.20 \times 10^3 \text{ g}}{3.78 \times 10^3 \text{ mL}} = 1.11 \text{ g/mL}$$

Alternatively, the calculation could be set up in a way that uses three unit conversion factors sequentially as follows:

$$\frac{9.26 \text{ lb}}{4.00 \text{ qt}} \times \frac{453.59 \text{ g}}{1 \text{ lb}} \times \frac{1.0567 \text{ qt}}{1 \text{ L}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 1.11 \text{ g/mL}$$

? Exercise 1.1.6.2

What is the volume in liters of 1.000 oz, given that 1 L = 1.0567 qt and 1 qt = 32 oz (exactly)?

Answer

2.956×10^{-2} L

✓ Example 1.1.6.3: Computing Quantities from Measurement Results

While being driven from Philadelphia to Atlanta, a distance of about 1250 km, a 2014 Lamborghini Aventador Roadster uses 213 L gasoline.

a. What (average) fuel economy, in miles per gallon, did the Roadster get during this trip?
b. If gasoline costs $3.80 per gallon, what was the fuel cost for this trip?

Solution

(a) We first convert distance from kilometers to miles:

$$1250 \text{ km} \times \frac{0.62137 \text{ mi}}{1 \text{ km}} = 777 \text{ mi}$$

and then convert volume from liters to gallons:

$$213 \text{ L} \times \frac{1.0567 \text{ qt}}{1 \text{ L}} \times \frac{1 \text{ gal}}{4 \text{ qt}} = 56.3 \text{ gal}$$

Then,

$$\text{(average) mileage} = \frac{777 \text{ mi}}{56.3 \text{ gal}} = 13.8 \text{ miles/gallon} = 13.8 \text{ mpg}$$

Alternatively, the calculation could be set up in a way that uses all the conversion factors sequentially, as follows:

$$\frac{1250 \text{ km}}{213 \text{ L}} \times \frac{0.62137 \text{ mi}}{1 \text{ km}} \times \frac{1 \text{ L}}{1.0567 \text{ qt}} \times \frac{4 \text{ qt}}{1 \text{ gal}} = 13.8 \text{ mpg}$$

(b) Using the previously calculated volume in gallons, we find:

$$56.3 \text{ gal} \times \frac{\$3.80}{1 \text{ gal}} = \$214$$

? Exercise 1.1.6.3

A Toyota Prius Hybrid uses 59.7 L gasoline to drive from San Francisco to Seattle, a distance of 1300 km (two significant digits).

a. What (average) fuel economy, in miles per gallon, did the Prius get during this trip?
b. If gasoline costs $3.90 per gallon, what was the fuel cost for this trip?

Answer a

51 mpg

Answer b

$62

1.1.6.2: Conversion of Temperature Units

We use the word temperature to refer to the hotness or coldness of a substance. One way we measure a change in temperature is to use the fact that most substances expand when their temperature increases and contract when their temperature decreases. The mercury or alcohol in a common glass thermometer changes its volume as the temperature changes. Because the volume of the liquid changes more than the volume of the glass, we can see the liquid expand when it gets warmer and contract when it gets cooler.

To mark a scale on a thermometer, we need a set of reference values: Two of the most commonly used are the freezing and boiling temperatures of water at a specified atmospheric pressure. On the Celsius scale, 0 °C is defined as the freezing temperature of water and 100 °C as the boiling temperature of water. The space between the two temperatures is divided into 100 equal intervals, which we call degrees. On the Fahrenheit scale, the freezing point of water is defined as 32 °F and the boiling temperature as 212 °F. The space between these two points on a Fahrenheit thermometer is divided into 180 equal parts (degrees).

Defining the Celsius and Fahrenheit temperature scales as described in the previous paragraph results in a slightly more complex relationship between temperature values on these two scales than for different units of measure for other properties. Most measurement units for a given property are directly proportional to one another (y = mx). Using familiar length units as one example:

$$\text{length in feet} = \left(\frac{1 \text{ ft}}{12 \text{ in.}}\right) \times \text{length in inches}$$

where

- y = length in feet,
- x = length in inches, and
- the proportionality constant, m, is the conversion factor.

The Celsius and Fahrenheit temperature scales, however, do not share a common zero point, and so the relationship between these two scales is a linear one rather than a proportional one ($y = mx + b$). Consequently, converting a temperature from one of these scales into the other requires more than simple multiplication by a conversion factor, m, it also must take into account differences in the scales' zero points (b).

The linear equation relating Celsius and Fahrenheit temperatures is easily derived from the two temperatures used to define each scale. Representing the Celsius temperature as x and the Fahrenheit temperature as y, the slope, m, is computed to be:

$$\begin{aligned} m &= \frac{\Delta y}{\Delta x} \\ &= \frac{212 \text{ °F} - 32 \text{ °F}}{100 \text{ °C} - 0 \text{ °C}} \\ &= \frac{180 \text{ °F}}{100 \text{ °C}} \\ &= \frac{9 \text{ °F}}{5 \text{ °C}} \end{aligned}$$

The y-intercept of the equation, b, is then calculated using either of the equivalent temperature pairs, (100 °C, 212 °F) or (0 °C, 32 °F), as:

$$\begin{aligned} b &= y - mx \\ &= 32 \text{ °F} - \frac{9 \text{ °F}}{5 \text{ °C}} \times 0 \text{ °C} \\ &= 32 \text{ °F} \end{aligned}$$

The equation relating the temperature scales is then:

$$T_{\text{°F}} = \left(\frac{9 \text{ °F}}{5 \text{ °C}} \times T_{\text{°C}}\right) + 32 \text{ °C}$$

An abbreviated form of this equation that omits the measurement units is:

$$T_{\text{°F}} = \frac{9}{5} \times T_{\text{°C}} + 32$$

Rearrangement of this equation yields the form useful for converting from Fahrenheit to Celsius:

$$T_{\text{°C}} = \frac{5}{9}(T_{\text{°F}} + 32)$$

As mentioned earlier in this chapter, the SI unit of temperature is the kelvin (K). Unlike the Celsius and Fahrenheit scales, the kelvin scale is an absolute temperature scale in which 0 (zero) K corresponds to the lowest temperature that can theoretically be achieved. The early 19th-century discovery of the relationship between a gas's volume and temperature suggested that the volume of a gas would be zero at −273.15 °C. In 1848, British physicist William Thompson, who later adopted the title of Lord Kelvin, proposed an absolute temperature scale based on this concept (further treatment of this topic is provided in this text's chapter on gases).

The freezing temperature of water on this scale is 273.15 K and its boiling temperature 373.15 K. Notice the numerical difference in these two reference temperatures is 100, the same as for the Celsius scale, and so the linear relation between these two temperature scales will exhibit a slope of 1 $\frac{\text{K}}{\text{°C}}$. Following the same approach, the equations for converting between the kelvin and Celsius temperature scales are derived to be:

$$T_{\text{K}} = T_{^\circ\text{C}} + 273.15$$

$$T_{^\circ\text{C}} = T_{\text{K}} - 273.15$$

The 273.15 in these equations has been determined experimentally, so it is not exact. Figure 1.1.6.1 shows the relationship among the three temperature scales. Recall that we do not use the degree sign with temperatures on the kelvin scale.

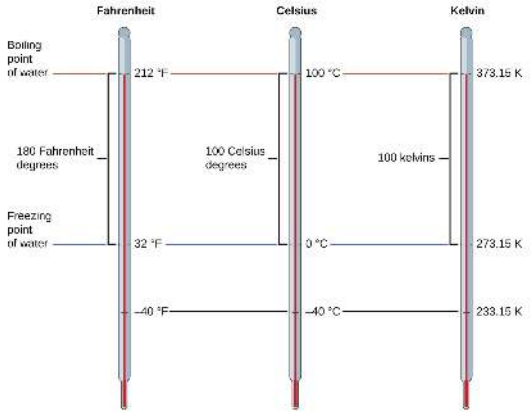


Figure 1.1.6.1: The Fahrenheit, Celsius, and kelvin temperature scales are compared.

Although the kelvin (absolute) temperature scale is the official SI temperature scale, Celsius is commonly used in many scientific contexts and is the scale of choice for nonscience contexts in almost all areas of the world. Very few countries (the U.S. and its territories, the Bahamas, Belize, Cayman Islands, and Palau) still use Fahrenheit for weather, medicine, and cooking.

Example 1.1.6.4: Conversion from Celsius

Normal body temperature has been commonly accepted as 37.0 °C (although it varies depending on time of day and method of measurement, as well as among individuals). What is this temperature on the kelvin scale and on the Fahrenheit scale?

Solution

$$\text{K} = {}^\circ\text{C} + 273.15 = 37.0 + 273.2 = 310.2\ \text{K}$$

$${}^\circ\text{F} = \frac{9}{5}\,{}^\circ\text{C} + 32.0 = \left(\frac{9}{5} \times 37.0\right) + 32.0 = 66.6 + 32.0 = 98.6\ {}^\circ\text{F}$$

Exercise 1.1.6.4

Convert 80.92 °C to K and °F.

Answer

354.07 K, 177.7 °F

Example 1.1.6.5: Conversion from Fahrenheit

Baking a ready-made pizza calls for an oven temperature of 450 °F. If you are in Europe, and your oven thermometer uses the Celsius scale, what is the setting? What is the kelvin temperature?

Solution

$${}^\circ\text{C} = \frac{5}{9}({}^\circ\text{F} - 32) = \frac{5}{9}(450 - 32) = \frac{5}{9} \times 418 = 232{}^\circ\text{C} \rightarrow \text{set oven to } 230{}^\circ\text{C} \quad \text{(two significant figures)}$$

$$\text{K} = {}^\circ\text{C} + 273.15 = 230 + 273 = 503\ \text{K} \rightarrow 5.0 \times 10^2\ \text{K} \quad \text{(two significant figures)}$$

Exercise 1.1.6.5

Convert 50 °F to °C and K.

Answer

10 °C, 280 K

Summary

Measurements are made using a variety of units. It is often useful or necessary to convert a measured quantity from one unit into another. These conversions are accomplished using unit conversion factors, which are derived by simple applications of a mathematical approach called the factor-label method or dimensional analysis. This strategy is also employed to calculate sought quantities using measured quantities and appropriate mathematical relations.

1.1.6.3: Key Equations

- $T_{^\circ\text{C}} = \frac{5}{9} \times T_{^\circ\text{F}} - 32$
- $T_{^\circ\text{F}} = \frac{9}{5} \times T_{^\circ\text{C}} + 32$
- $T_{\text{K}} = {}^\circ\text{C} + 273.15$
- $T_{^\circ\text{C}} = \text{K} - 273.15$

Glossary

dimensional analysis
(also, factor-label method) versatile mathematical approach that can be applied to computations ranging from simple unit conversions to more complex, multi-step calculations involving several different quantities

Fahrenheit
unit of temperature; water freezes at 32 °F and boils at 212 °F on this scale

unit conversion factor
ratio of equivalent quantities expressed with different units; used to convert from one unit to a different unit

---

This page titled 1.1.6: Mathematical Treatment of Measurement Results is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **1.6: Mathematical Treatment of Measurement Results** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

https://chem.libretexts.org/@go/page/393198

1.1.E: Essential Ideas of Chemistry (Exercises)

1.1.E.1: 1.1: Chemistry in Context

1.1.E.1.1: Q1.1.1

Explain how you could experimentally determine whether the outside temperature is higher or lower than 0 °C (32 °F) without using a thermometer.

1.1.E.1.2: S1.1.1

Place a glass of water outside. It will freeze if the temperature is below 0 °C.

1.1.E.1.3: Q1.1.2

Identify each of the following statements as being most similar to a hypothesis, a law, or a theory. Explain your reasoning.

a. Falling barometric pressure precedes the onset of bad weather.
b. All life on earth has evolved from a common, primitive organism through the process of natural selection.
c. My truck's gas mileage has dropped significantly, probably because it's due for a tune-up.

1.1.E.1.4: Q1.1.3

Identify each of the following statements as being most similar to a hypothesis, a law, or a theory. Explain your reasoning.

a. The pressure of a sample of gas is directly proportional to the temperature of the gas.
b. Matter consists of tiny particles that can combine in specific ratios to form substances with specific properties.
c. At a higher temperature, solids (such as salt or sugar) will dissolve better in water.

1.1.E.1.5: S1.1.3

(a) law (states a consistently observed phenomenon, can be used for prediction); (b) theory (a widely accepted explanation of the behavior of matter); (c) hypothesis (a tentative explanation, can be investigated by experimentation)

Identify each of the underlined items as a part of either the macroscopic domain, the microscopic domain, or the symbolic domain of chemistry. For any in the symbolic domain, indicate whether they are symbols for a macroscopic or a microscopic feature.

a. (a) The mass of a lead pipe is 14 lb.
b. (b) The mass of a certain chlorine atom is 35 amu.
c. (c) A bottle with a label that reads Al contains aluminum metal.
d. (d) Al is the symbol for an aluminum atom.

Identify each of the underlined items as a part of either the macroscopic domain, the microscopic domain, or the symbolic domain of chemistry. For those in the symbolic domain, indicate whether they are symbols for a macroscopic or a microscopic feature.

a. (a) A certain molecule contains one H atom and one Cl atom.
b. (b) Copper wire has a density of about 8 g/cm^3.
c. (c) The bottle contains 15 grams of Ni powder.
d. (d) A sulfur molecule is composed of eight sulfur atoms.

(a) symbolic, microscopic; (b) macroscopic; (c) symbolic, macroscopic; (d) microscopic

According to one theory, the pressure of a gas increases as its volume decreases because the molecules in the gas have to move a shorter distance to hit the walls of the container. Does this theory follow a macroscopic or microscopic description of chemical behavior? Explain your answer.

The amount of heat required to melt 2 lbs of ice is twice the amount of heat required to melt 1 lb of ice. Is this observation a macroscopic or microscopic description of chemical behavior? Explain your answer.

Macroscopic. The heat required is determined from macroscopic properties.

1.1.E.2: 1.2: Phases and Classification of Matter

1.1.E.2.1: Questions

1. Why do we use an object's mass, rather than its weight, to indicate the amount of matter it contains?
2. What properties distinguish solids from liquids? Liquids from gases? Solids from gases?
3. How does a heterogeneous mixture differ from a homogeneous mixture? How are they similar?
4. How does a homogeneous mixture differ from a pure substance? How are they similar?
5. How does an element differ from a compound? How are they similar?
6. How do molecules of elements and molecules of compounds differ? In what ways are they similar?
7. How does an atom differ from a molecule? In what ways are they similar?
8. Many of the items you purchase are mixtures of pure compounds. Select three of these commercial products and prepare a list of the ingredients that are pure compounds.
9. Classify each of the following as an element, a compound, or a mixture:
    a. copper
    b. water
    c. nitrogen
    d. sulfur
    e. air
    f. sucrose
    g. a substance composed of molecules each of which contains two iodine atoms
    h. gasoline
10. Classify each of the following as an element, a compound, or a mixture:
    a. iron
    b. oxygen
    c. mercury oxide
    d. pancake syrup
    e. carbon dioxide
    f. a substance composed of molecules each of which contains one hydrogen atom and one chlorine atom
    g. baking soda
    h. baking powder
11. A sulfur atom and a sulfur molecule are not identical. What is the difference?
12. How are the molecules in oxygen gas, the molecules in hydrogen gas, and water molecules similar? How do they differ?
13. We refer to astronauts in space as weightless, but not without mass. Why?
14. As we drive an automobile, we don't think about the chemicals consumed and produced. Prepare a list of the principal chemicals consumed and produced during the operation of an automobile.
15. Matter is everywhere around us. Make a list by name of fifteen different kinds of matter that you encounter every day. Your list should include (and label at least one example of each) the following: a solid, a liquid, a gas, an element, a compound, a homogenous mixture, a heterogeneous mixture, and a pure substance.
16. When elemental iron corrodes it combines with oxygen in the air to ultimately form red brown iron(III) oxide which we call rust. (a) If a shiny iron nail with an initial mass of 23.2 g is weighed after being coated in a layer of rust, would you expect the mass to have increased, decreased, or remained the same? Explain. (b) If the mass of the iron nail increases to 24.1 g, what mass of oxygen combined with the iron?
17. As stated in the text, convincing examples that demonstrate the law of conservation of matter outside of the laboratory are few and far between. Indicate whether the mass would increase, decrease, or stay the same for the following scenarios where chemical reactions take place:
    a. Exactly one pound of bread dough is placed in a baking tin. The dough is cooked in an oven at 350 °F releasing a wonderful aroma of freshly baked bread during the cooking process. Is the mass of the baked loaf less than, greater than, or the same as the one pound of original dough? Explain.
    b. When magnesium burns in air a white flaky ash of magnesium oxide is produced. Is the mass of magnesium oxide less than, greater than, or the same as the original piece of magnesium? Explain.
    c. Antoine Lavoisier, the French scientist credited with first stating the law of conservation of matter, heated a mixture of tin and air in a sealed flask to produce tin oxide. Did the mass of the sealed flask and contents decrease, increase, or remain the same after the heating?

18. Yeast converts glucose to ethanol and carbon dioxide during anaerobic fermentation as depicted in the simple chemical equation here:

$$\text{glucose} \rightarrow \text{ethanol} + \text{carbon dioxide} \tag{1.1.E.1}$$

a. If 200.0 g of glucose is fully converted, what will be the total mass of ethanol and carbon dioxide produced?
b. If the fermentation is carried out in an open container, would you expect the mass of the container and contents after fermentation to be less than, greater than, or the same as the mass of the container and contents before fermentation? Explain.
c. If 97.7 g of carbon dioxide is produced, what mass of ethanol is produced?

1.1.E.2.2: Solutions

2 Liquids can change their shape (flow); solids can't. Gases can undergo large volume changes as pressure changes; liquids do not. Gases flow and change volume; solids do not.

4.The mixture can have a variety of compositions; a pure substance has a definite composition. Both have the same composition from point to point.

6 Molecules of elements contain only one type of atom; molecules of compounds contain two or more types of atoms. They are similar in that both are comprised of two or more atoms chemically bonded together.

8. Answers will vary. Sample answer: Gatorade contains water, sugar, dextrose, citric acid, salt, sodium chloride, monopotassium phosphate, and sucrose acetate isobutyrate.

11. (a) element; (b) element; (c) compound; (d) mixture, (e) compound; (f) compound; (g) compound; (h) mixture

12. In each case, a molecule consists of two or more combined atoms. They differ in that the types of atoms change from one substance to the next.

14. Gasoline (a mixture of compounds), oxygen, and to a lesser extent, nitrogen are consumed. Carbon dioxide and water are the principal products. Carbon monoxide and nitrogen oxides are produced in lesser amounts.

16. (a) Increased as it would have combined with oxygen in the air thus increasing the amount of matter and therefore the mass. (b) 0.9 g

18. (a) 200.0 g; (b) The mass of the container and contents would decrease as carbon dioxide is a gaseous product and would leave the container. (c) 102.3 g

1.1.E.3: 1.3: Physical and Chemical Properties

Classify the six underlined properties in the following paragraph as chemical or physical:

Fluorine is a pale yellow gas that reacts with most substances. The free element melts at −220 °C and boils at −188 °C. Finely divided metals burn in fluorine with a bright flame. Nineteen grams of fluorine will react with 1.0 gram of hydrogen.

Classify each of the following changes as physical or chemical:

a. condensation of steam
b. burning of gasoline
c. souring of milk
d. dissolving of sugar in water
e. melting of gold

(a) physical; (b) chemical; (c) chemical; (d) physical; (e) physical

Classify each of the following changes as physical or chemical:

a. coal burning
b. ice melting
c. mixing chocolate syrup with milk
d. explosion of a firecracker
e. magnetizing of a screwdriver

The volume of a sample of oxygen gas changed from 10 mL to 11 mL as the temperature changed. Is this a chemical or physical change?

physical

A 2.0-liter volume of hydrogen gas combined with 1.0 liter of oxygen gas to produce 2.0 liters of water vapor. Does oxygen undergo a chemical or physical change?

Explain the difference between extensive properties and intensive properties.

The value of an extensive property depends upon the amount of matter being considered, whereas the value of an intensive property is the same regardless of the amount of matter being considered.

Identify the following properties as either extensive or intensive.

a. volume
b. temperature
c. humidity
d. heat
e. boiling point

The density (d) of a substance is an intensive property that is defined as the ratio of its mass (m) to its volume (V).

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

Considering that mass and volume are both extensive properties, explain why their ratio, density, is intensive.

Being extensive properties, both mass and volume are directly proportional to the amount of substance under study. Dividing one extensive property by another will in effect “cancel” this dependence on amount, yielding a ratio that is independent of amount (an intensive property).

1.1.E.4: 1.4: Measurements

Is one liter about an ounce, a pint, a quart, or a gallon?

Is a meter about an inch, a foot, a yard, or a mile?

about a yard

Indicate the SI base units or derived units that are appropriate for the following measurements:

1. (a) the length of a marathon race (26 miles 385 yards)
2. (b) the mass of an automobile
3. (c) the volume of a swimming pool
4. (d) the speed of an airplane
5. (e) the density of gold
6. (f) the area of a football field
7. (g) the maximum temperature at the South Pole on April 1, 1913

Indicate the SI base units or derived units that are appropriate for the following measurements:

1. (a) the mass of the moon
2. (b) the distance from Dallas to Oklahoma City
3. (c) the speed of sound
4. (d) the density of air
5. (e) the temperature at which alcohol boils
6. (f) the area of the state of Delaware
7. (g) the volume of a flu shot or a measles vaccination

(a) kilograms; (b) meters; (c) kilometers/second; (d) kilograms/cubic meter; (e) kelvin; (f) square meters; (g) cubic meters

Give the name and symbol of the prefixes used with SI units to indicate multiplication by the following exact quantities.

1. (a) 10^3
2. (b) 10^{-2}

3. (c) 0.1
4. (d) 10^{-3}
5. (e) 1,000,000
6. (f) 0.000001

Give the name of the prefix and the quantity indicated by the following symbols that are used with SI base units.

1. (a) c
2. (b) d
3. (c) G
4. (d) k
5. (e) m
6. (f) n
7. (g) p
8. (h) T

(a) centi-, $\times 10^{-2}$; (b) deci-, $\times 10^{-1}$; (c) Giga-, $\times 10^{9}$; (d) kilo-, $\times 10^{3}$; (e) milli-, $\times 10^{-3}$; (f) nano-, $\times 10^{-9}$; (g) pico-, $\times 10^{-12}$; (h) tera-, $\times 10^{12}$

A large piece of jewelry has a mass of 132.6 g. A graduated cylinder initially contains 48.6 mL water. When the jewelry is submerged in the graduated cylinder, the total volume increases to 61.2 mL.

1. (a) Determine the density of this piece of jewelry.
2. (b) Assuming that the jewelry is made from only one substance, what substance is it likely to be? Explain.

Visit this PhET density simulation and select the Same Volume Blocks.

1. (a) What are the mass, volume, and density of the yellow block?
2. (b) What are the mass, volume and density of the red block?
3. (c) List the block colors in order from smallest to largest mass.
4. (d) List the block colors in order from lowest to highest density.
5. (e) How are mass and density related for blocks of the same volume?

(a) 8.00 kg, 5.00 L, 1.60 kg/L; (b) 2.00 kg, 5.00 L, 0.400 kg/L; (c) red < green < blue < yellow; (d) If the volumes are the same, then the density is directly proportional to the mass.

Visit this PhET density simulation and select Custom Blocks and then My Block.

1. (a) Enter mass and volume values for the block such that the mass in kg is *less than* the volume in L. What does the block do? Why? Is this always the case when mass < volume?
2. (b) Enter mass and volume values for the block such that the mass in kg is *more than* the volume in L. What does the block do? Why? Is this always the case when mass > volume?
3. (c) How would (a) and (b) be different if the liquid in the tank were ethanol instead of water?
4. (d) How would (a) and (b) be different if the liquid in the tank were mercury instead of water?

Visit this PhET density simulation and select Mystery Blocks.

1. (a) Pick one of the Mystery Blocks and determine its mass, volume, density, and its likely identity.
2. (b) Pick a different Mystery Block and determine its mass, volume, density, and its likely identity.
3. (c) Order the Mystery Blocks from least dense to most dense. Explain.

(a) (b) Answer is one of the following. A/yellow: mass = 65.14 kg, volume = 3.38 L, density = 19.3 kg/L, likely identity = gold. B/blue: mass = 0.64 kg, volume = 1.00 L, density = 0.64 kg/L, likely identity = apple. C/green: mass = 4.08 kg, volume = 5.83 L, density = 0.700 kg/L, likely identity = gasoline. D/red: mass = 3.10 kg, volume = 3.38 L, density = 0.920 kg/L, likely identity = ice; and E/purple: mass = 3.53 kg, volume = 1.00 L, density = 3.53 kg/L, likely identity = diamond. (c) B/blue/apple (0.64 kg/L) < C/green/gasoline (0.700 kg/L) < D/red/ice (0.920 kg/L) < E/purple/diamond (3.53 kg/L) < A/yellow/gold (19.3 kg/L)

1.1.E.5: 1.5: Measurement Uncertainty, Accuracy, and Precision

Express each of the following numbers in scientific notation with correct significant figures:

1. (a) 711.0

2. (b) 0.239
3. (c) 90743
4. (d) 134.2
5. (e) 0.05499
6. (f) 10000.0
7. (g) 0.000000738592

Express each of the following numbers in exponential notation with correct significant figures:

1. (a) 704
2. (b) 0.03344
3. (c) 547.9
4. (d) 22086
5. (e) 1000.00
6. (f) 0.0000000651
7. (g) 0.007157

(a) 7.04×10^{2}; (b) 3.344×10^{-2}; (c) 5.479×10^{2}; (d) 2.2086×10^{4}; (e) 1.00000×10^{3}; (f) 6.51×10^{-8}; (g) 7.157×10^{-3}

Indicate whether each of the following can be determined exactly or must be measured with some degree of uncertainty:

1. (a) the number of eggs in a basket
2. (b) the mass of a dozen eggs
3. (c) the number of gallons of gasoline necessary to fill an automobile gas tank
4. (d) the number of cm in 2 m
5. (e) the mass of a textbook
6. (f) the time required to drive from San Francisco to Kansas City at an average speed of 53 mi/h

Indicate whether each of the following can be determined exactly or must be measured with some degree of uncertainty:

1. (a) the number of seconds in an hour
2. (b) the number of pages in this book
3. (c) the number of grams in your weight
4. (d) the number of grams in 3 kilograms
5. (e) the volume of water you drink in one day
6. (f) the distance from San Francisco to Kansas City

(a) exact; (b) exact; (c) uncertain; (d) exact; (e) uncertain; (f) uncertain

How many significant figures are contained in each of the following measurements?

1. (a) 38.7 g
2. (b) 2×10^{18} m
3. (c) 3,486,002 kg
4. (d) 9.74150×10^{-4} J
5. (e) 0.0613 cm^3
6. (f) 17.0 kg
7. (g) 0.01400 g/mL

How many significant figures are contained in each of the following measurements?

1. (a) 53 cm
2. (b) 2.05×10^{8} m
3. (c) 86,002 J
4. (d) 9.740×10^{4} m/s
5. (e) 10.0613 m^3
6. (f) 0.17 g/mL
7. (g) 0.88400 s

(a) two; (b) three; (c) five; (d) four; (e) six; (f) two; (g) five

The following quantities were reported on the labels of commercial products. Determine the number of significant figures in each.

1. (a) 0.0055 g active ingredients
2. (b) 12 tablets
3. (c) 3% hydrogen peroxide
4. (d) 5.5 ounces
5. (e) 473 mL
6. (f) 1.75% bismuth
7. (g) 0.001% phosphoric acid
8. (h) 99.80% inert ingredients

Round off each of the following numbers to two significant figures:

1. (a) 0.436
2. (b) 9.000
3. (c) 27.2
4. (d) 135
5. (e) 1.497×10^{-3}
6. (f) 0.445

(a) 0.44; (b) 9.0; (c) 27; (d) 140; (e) 1.5×10^{-3}; (f) 0.44

Round off each of the following numbers to two significant figures:

1. (a) 517
2. (b) 86.3
3. (c) 6.382×10^{3}
4. (d) 5.0008
5. (e) 22.497
6. (f) 0.885

Perform the following calculations and report each answer with the correct number of significant figures.

1. (a) 628×342
2. (b) $(5.63 \times 10^{2}) \times (7.4 \times 10^{3})$
3. (c)
4. $\dfrac{28.0}{13.483}$
5. (d) 8119×0.000023
6. (e) 14.98 + 27,340 + 84.7593
7. (f) 42.7 + 0.259

(a) 2.15×10^{5}; (b) 4.2×10^{6}; (c) 2.08; (d) 0.19; (e) 27,440; (f) 43.0

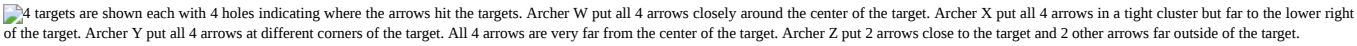
Perform the following calculations and report each answer with the correct number of significant figures.

1. (a) 62.8×34
2. (b) 0.147 + 0.0066 + 0.012
3. (c) $38 \times 95 \times 1.792$
4. (d) 15 – 0.15 – 0.6155
5. (e) $8.78 \times \left(\dfrac{0.0500}{0.478}\right)$
6. (f) 140 + 7.68 + 0.014
7. (g) 28.7 – 0.0483
8. (h) $\dfrac{(88.5 - 87.57)}{45.13}$

Consider the results of the archery contest shown in this figure.

1. (a) Which archer is most precise?
2. (b) Which archer is most accurate?

3. (c) Who is both least precise and least accurate?



(a) Archer X; (b) Archer W; (c) Archer Y

Classify the following sets of measurements as accurate, precise, both, or neither.

1. (a) Checking for consistency in the weight of chocolate chip cookies: 17.27 g, 13.05 g, 19.46 g, 16.92 g
2. (b) Testing the volume of a batch of 25-mL pipettes: 27.02 mL, 26.99 mL, 26.97 mL, 27.01 mL
3. (c) Determining the purity of gold: 99.9999%, 99.9998%, 99.9998%, 99.9999%

1.1.E.6: 1.6: Mathematical Treatment of Measurement Results

Write conversion factors (as ratios) for the number of:

a. yards in 1 meter
b. liters in 1 liquid quart
c. pounds in 1 kilogram

(a) $\frac{1.0936\ \text{yd}}{1\ \text{m}}$; (b) $\frac{0.94635\ \text{L}}{1\ \text{qt}}$; (c) $\frac{2.2046\ \text{lb}}{1\ \text{kg}}$

Write conversion factors (as ratios) for the number of:

1. (a) kilometers in 1 mile
2. (b) liters in 1 cubic foot
3. (c) grams in 1 ounce

The label on a soft drink bottle gives the volume in two units: 2.0 L and 67.6 fl oz. Use this information to derive a conversion factor between the English and metric units. How many significant figures can you justify in your conversion factor?

$$\frac{2.0\ \text{L}}{67.6\ \text{fl oz}} = \frac{0.030\ \text{L}}{1\ \text{fl oz}}$$

Only two significant figures are justified.

The label on a box of cereal gives the mass of cereal in two units: 978 grams and 34.5 oz. Use this information to find a conversion factor between the English and metric units. How many significant figures can you justify in your conversion factor?

Soccer is played with a round ball having a circumference between 27 and 28 in. and a weight between 14 and 16 oz. What are these specifications in units of centimeters and grams?

68–71 cm; 400–450 g

A woman's basketball has a circumference between 28.5 and 29.0 inches and a maximum weight of 20 ounces (two significant figures). What are these specifications in units of centimeters and grams?

How many milliliters of a soft drink are contained in a 12.0-oz can?

355 mL

A barrel of oil is exactly 42 gal. How many liters of oil are in a barrel?

The diameter of a red blood cell is about 3×10^{-4} in. What is its diameter in centimeters?

8×10^{-4} cm

The distance between the centers of the two oxygen atoms in an oxygen molecule is 1.21×10^{-8} cm. What is this distance in inches?

Is a 197-lb weight lifter light enough to compete in a class limited to those weighing 90 kg or less?

yes; weight = 89.4 kg

A very good 197-lb weight lifter lifted 192 kg in a move called the clean and jerk. What was the mass of the weight lifted in pounds?

Many medical laboratory tests are run using 5.0 μL blood serum. What is this volume in milliliters?

5.0×10^{-3} mL

If an aspirin tablet contains 325 mg aspirin, how many grams of aspirin does it contain?

Use scientific (exponential) notation to express the following quantities in terms of the SI base units in [link]:

1. (a) 0.13 g
2. (b) 232 Gg
3. (c) 5.23 pm
4. (d) 86.3 mg
5. (e) 37.6 cm
6. (f) 54 μm
7. (g) 1 Ts
8. (h) 27 ps
9. (i) 0.15 mK

(a) 1.3×10^{-4} kg; (b) 2.32×10^{8} kg; (c) 5.23×10^{-12} m; (d) 8.63×10^{-5} kg; (e) 3.76×10^{-1} m; (f) 5.4×10^{-5} m; (g) 1×10^{12} s; (h) 2.7×10^{-11} s; (i) 1.5×10^{-4} K

Complete the following conversions between SI units.

1. (a) 612 g = _____ mg
2. (b) 8.160 m = _____ cm
3. (c) 3779 μg = _____ g
4. (d) 781 mL = _____ L
5. (e) 4.18 kg = _____ g
6. (f) 27.8 m = _____ km
7. (g) 0.13 mL = _____ L
8. (h) 1738 km = _____ m
9. (i) 1.9 Gg = _____ g

Gasoline is sold by the liter in many countries. How many liters are required to fill a 12.0-gal gas tank?

45.4 L

Milk is sold by the liter in many countries. What is the volume of exactly 1/2 gal of milk in liters?

A long ton is defined as exactly 2240 lb. What is this mass in kilograms?

1.0160×10^{3} kg

Make the conversion indicated in each of the following:

1. (a) the men’s world record long jump, 29 ft 4¼ in., to meters
2. (b) the greatest depth of the ocean, about 6.5 mi, to kilometers
3. (c) the area of the state of Oregon, 96,981 mi^2, to square kilometers
4. (d) the volume of 1 gill (exactly 4 oz) to milliliters
5. (e) the estimated volume of the oceans, 330,000,000 mi^3, to cubic kilometers.
6. (f) the mass of a 3525-lb car to kilograms
7. (g) the mass of a 2.3-oz egg to grams

Make the conversion indicated in each of the following:

1. (a) the length of a soccer field, 120 m (three significant figures), to feet
2. (b) the height of Mt. Kilimanjaro, at 19,565 ft the highest mountain in Africa, to kilometers
3. (c) the area of an 8.5 t 11-inch sheet of paper in cm^2
4. (d) the displacement volume of an automobile engine, 161 $in.^3$, to liters
5. (e) the estimated mass of the atmosphere, 5.6 t 10^{15} tons, to kilograms
6. (f) the mass of a bushel of rye, 32.0 lb, to kilograms
7. (g) the mass of a 5.00-grain aspirin tablet to milligrams (1 grain = 0.00229 oz)

1. (a) 394 ft

2.
3. (b) 5.9634 km
4.
5. (c) 6.0×10^2
6.
7. (d) 2.64 L
8.
9. (e) 5.1×10^{18} kg
10.
11. (f) 14.5 kg
12.
13. (g) 324 mg

Many chemistry conferences have held a 50-Trillion Angstrom Run (two significant figures). How long is this run in kilometers and in miles? (1 Å = 1×10^{-10} m)

A chemist's 50-Trillion Angstrom Run (see Exercise) would be an archeologist's 10,900 cubit run. How long is one cubit in meters and in feet? (1 Å = 1×10^{-8} cm)

0.46 m; 1.5 ft/cubit

The gas tank of a certain luxury automobile holds 22.3 gallons according to the owner's manual. If the density of gasoline is 0.8206 g/mL, determine the mass in kilograms and pounds of the fuel in a full tank.

As an instructor is preparing for an experiment, he requires 225 g phosphoric acid. The only container readily available is a 150-mL Erlenmeyer flask. Is it large enough to contain the acid, whose density is 1.83 g/mL?

Yes, the acid's volume is 123 mL.

To prepare for a laboratory period, a student lab assistant needs 125 g of a compound. A bottle containing 1/4 lb is available. Did the student have enough of the compound?

A chemistry student is 159 cm tall and weighs 45.8 kg. What is her height in inches and weight in pounds?

62.6 in (about 5 ft 3 in.) and 101 lb

In a recent Grand Prix, the winner completed the race with an average speed of 229.8 km/h. What was his speed in miles per hour, meters per second, and feet per second?

Solve these problems about lumber dimensions.

(a) To describe to a European how houses are constructed in the US, the dimensions of "two-by-four" lumber must be converted into metric units. The thickness × width × length dimensions are 1.50 in. × 3.50 in. × 8.00 ft in the US. What are the dimensions in cm × cm × m?

(b) This lumber can be used as vertical studs, which are typically placed 16.0 in. apart. What is that distance in centimeters?

(a) 3.81 cm × 8.89 cm × 2.44 m; (b) 40.6 cm

The mercury content of a stream was believed to be above the minimum considered safe—1 part per billion (ppb) by weight. An analysis indicated that the concentration was 0.68 parts per billion. What quantity of mercury in grams was present in 15.0 L of the water, the density of which is 0.998 g/ml? $\left(1 \text{ ppb Hg} = \frac{1 \text{ ng Hg}}{1 \text{ g water}}\right)$

Calculate the density of aluminum if 27.6 cm^3 has a mass of 74.6 g.

2.70 g/cm^3

Osmium is one of the densest elements known. What is its density if 2.72 g has a volume of 0.121 cm^3?

Calculate these masses.

(a) What is the mass of 6.00 cm^3 of mercury, density = 13.5939 g/cm^3?

(b) What is the mass of 25.0 mL octane, density = 0.702 g/cm^3?

(a) 81.6 g; (b) 17.6 g

Calculate these masses.

1. (a) What is the mass of 4.00 cm^3 of sodium, density = 0.97 g/cm?
2. (b) What is the mass of 125 mL gaseous chlorine, density = 3.16 g/L?

Calculate these volumes.

1. (a) What is the volume of 25 g iodine, density = 4.93 g/cm^3?
2. (b) What is the volume of 3.28 g gaseous hydrogen, density = 0.089 g/L?

(a) 5.1 mL; (b) 37 L

Calculate these volumes.

1. (a) What is the volume of 11.3 g graphite, density = 2.25 g/cm^3?
2. (b) What is the volume of 39.657 g bromine, density = 2.928 g/cm^3?

Convert the boiling temperature of gold, 2966 °C, into degrees Fahrenheit and kelvin.

5371 °F, 3239 K

Convert the temperature of scalding water, 54 °C, into degrees Fahrenheit and kelvin.

Convert the temperature of the coldest area in a freezer, −10 °F, to degrees Celsius and kelvin.

−23 °C, 250 K

Convert the temperature of dry ice, −77 °C, into degrees Fahrenheit and kelvin.

Convert the boiling temperature of liquid ammonia, −28.1 °F, into degrees Celsius and kelvin.

−33.4 °C, 239.8 K

The label on a pressurized can of spray disinfectant warns against heating the can above 130 °F. What are the corresponding temperatures on the Celsius and kelvin temperature scales?

The weather in Europe was unusually warm during the summer of 1995. The TV news reported temperatures as high as 45 °C. What was the temperature on the Fahrenheit scale?

113 °F

1.1.E.7: Contributors and Attributions

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

This page titled 1.1.E: Essential Ideas of Chemistry (Exercises) is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

SECTION OVERVIEW

1.2: Atoms, Molecules, and Ions

A general chemistry Libretexts Textbook remixed and remastered from OpenStax's textbook:

General Chemistry

This chapter will describe some of the fundamental chemical principles related to the composition of matter, including those central to the concept of molecular identity.

1.2.1: Prelude to Atoms

1.2.2: Early Ideas in Atomic Theory

1.2.3: Evolution of Atomic Theory

1.2.4: Atomic Structure and Symbolism

1.2.5: Chemical Formulas

1.2.6: The Periodic Table

1.2.7: Molecular and Ionic Compounds

1.2.8: Chemical Nomenclature

1.2.E: Atoms, Molecules, and Ions (Exercises)

This page titled 1.2: Atoms, Molecules, and Ions is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

1.2.1: Prelude to Atoms

Your overall health and susceptibility to disease depends upon the complex interaction between your genetic makeup and environmental exposure, with the outcome difficult to predict. Early detection of biomarkers, substances that indicate an organism's disease or physiological state, could allow diagnosis and treatment before a condition becomes serious or irreversible. Recent studies have shown that your exhaled breath can contain molecules that may be biomarkers for recent exposure to environmental contaminants or for pathological conditions ranging from asthma to lung cancer.

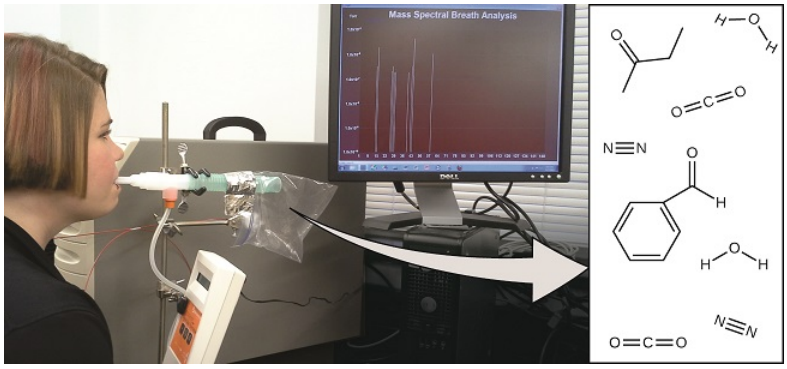


Figure 1.2.1.1: Analysis of molecules in an exhaled breath can provide valuable information, leading to early diagnosis of diseases or detection of environmental exposure to harmful substances. (credit: modification of work by Paul Flowers)

A person is shown blowing into a tube connected to a plastic bag. There is a computer screen displaying data that reads "Mass Spectral Breath Analysis." An arrow from the plastic bag points to an illustration of different molecular compounds contained in the person's exhalation

Scientists are working to develop biomarker "fingerprints" that could be used to diagnose a specific disease based on the amounts and identities of certain molecules in a patient's exhaled breath. An essential concept underlying this goal is that of a molecule's identity, which is determined by the numbers and types of atoms it contains, and how they are bonded together. This chapter will describe some of the fundamental chemical principles related to the composition of matter, including those central to the concept of molecular identity.

This page titled 1.2.1: Prelude to Atoms is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **2.1: Prelude to Atoms** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

1.2.2: Early Ideas in Atomic Theory

Learning Objectives

By the end of this section, you will be able to:

- State the postulates of Dalton's atomic theory
- Use postulates of Dalton's atomic theory to explain the laws of definite and multiple proportions

The language used in chemistry is seen and heard in many disciplines, ranging from medicine to engineering to forensics to art. The language of chemistry includes its own vocabulary as well as its own form of shorthand. Chemical symbols are used to represent atoms and elements. Chemical formulas depict molecules as well as the composition of compounds. Chemical equations provide information about the quality and quantity of the changes associated with chemical reactions.

This chapter will lay the foundation for our study of the language of chemistry. The concepts of this foundation include the atomic theory, the composition and mass of an atom, the variability of the composition of isotopes, ion formation, chemical bonds in ionic and covalent compounds, the types of chemical reactions, and the naming of compounds. We will also introduce one of the most powerful tools for organizing chemical knowledge: the periodic table.

1.2.2.1: Atomic Theory through the Nineteenth Century

The earliest recorded discussion of the basic structure of matter comes from ancient Greek philosophers, the scientists of their day. In the fifth century BC, Leucippus and Democritus argued that all matter was composed of small, finite particles that they called *atomos*, a term derived from the Greek word for "indivisible." They thought of atoms as moving particles that differed in shape and size, and which could join together. Later, Aristotle and others came to the conclusion that matter consisted of various combinations of the four "elements"—fire, earth, air, and water—and could be infinitely divided. Interestingly, these philosophers thought about atoms and "elements" as philosophical concepts, but apparently never considered performing experiments to test their ideas.

The Aristotelian view of the composition of matter held sway for over two thousand years, until English schoolteacher John Dalton helped to revolutionize chemistry with his hypothesis that the behavior of matter could be explained using an atomic theory. First published in 1807, many of Dalton's hypotheses about the microscopic features of matter are still valid in modern atomic theory. Here are the postulates of Dalton's atomic theory.

1. Matter is composed of exceedingly small particles called atoms. An atom is the smallest unit of an element that can participate in a chemical change.
2. An element consists of only one type of atom, which has a mass that is characteristic of the element and is the same for all atoms of that element (Figure 1.2.2.1). A macroscopic sample of an element contains an incredibly large number of atoms, all of which have identical chemical properties.

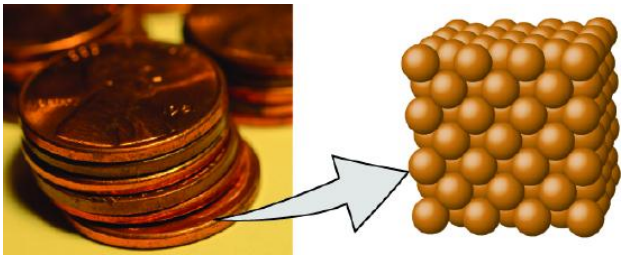


Figure 1.2.2.1: A pre-1982 copper penny (left) contains approximately 3×10^{22} copper atoms (several dozen are represented as brown spheres at the right), each of which has the same chemical properties. (credit: modification of work by "slgckgc"/Flickr)

The left image shows a photograph of a stack of pennies. The right image calls out an area of one of the pennies, which is made up of many sphere-shaped copper atoms. The atoms are densely organized.

3. Atoms of one element differ in properties from atoms of all other elements.
4. A compound consists of atoms of two or more elements combined in a small, whole-number ratio. In a given compound, the numbers of atoms of each of its elements are always present in the same ratio (Figure 1.2.2.2).

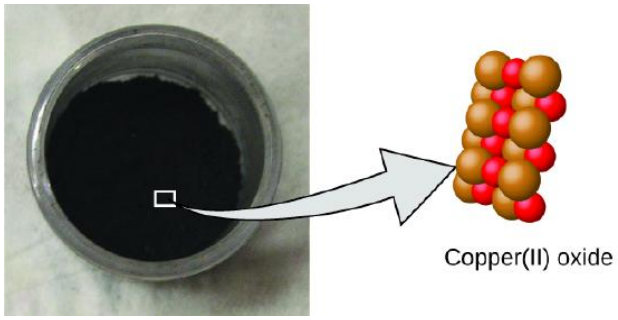


Figure 1.2.2.2: Copper(II) oxide, a powdery, black compound, results from the combination of two types of atoms—copper (brown spheres) and oxygen (red spheres)—in a 1:1 ratio. (credit: modification of work by "Chemicalinterest"/Wikimedia Commons)

The left image shows a container with a black, powdery compound. The right image calls out the molecular structure of the powder which contains copper atoms that are clustered together with an equal number of oxygen atoms.

5. *Atoms are neither created nor destroyed during a chemical change, but are instead rearranged to yield substances that are different from those present before the change (Figure* 1.2.2.3*).*

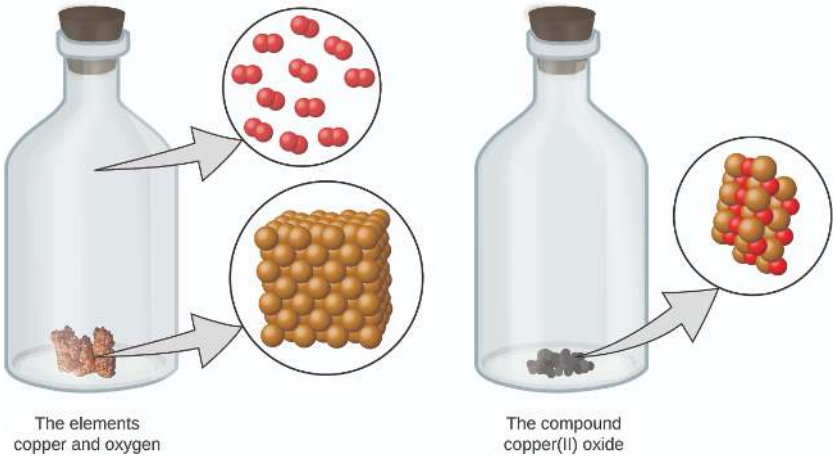


Figure 1.2.2.3: When the elements copper (a shiny, red-brown solid, shown here as brown spheres) and oxygen (a clear and colorless gas, shown here as red spheres) react, their atoms rearrange to form a compound containing copper and oxygen (a powdery, black solid). (credit copper: modification of work by Copper [images-of-elements.com]).

The left stoppered bottle contains copper and oxygen. There is a callout which shows that copper is made up of many sphere-shaped atoms. The atoms are densely organized. The open space of the bottle contains oxygen gas, which is made up of bonded pairs of oxygen atoms that are evenly spaced. The right stoppered bottle shows the compound copper two oxide. A callout from the powder shows a molecule of copper two oxide, which contains copper atoms that are clustered together with an equal number of oxygen atoms.

Dalton's atomic theory provides a microscopic explanation of the many macroscopic properties of matter that you've learned about. For example, if an element such as copper consists of only one kind of atom, then it cannot be broken down into simpler substances, that is, into substances composed of fewer types of atoms. And if atoms are neither created nor destroyed during a chemical change, then the total mass of matter present when matter changes from one type to another will remain constant (the law of conservation of matter).

Example 1.2.2.1: Testing Dalton's Atomic Theory

In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres touch, they are part of a single unit of a compound. Does the following chemical change represented by these symbols violate any of the ideas of Dalton's atomic theory? If so, which one?



This equation shows that the starting materials of the reaction are two bonded, green spheres, which are being combined with two smaller, bonded purple spheres. The product of the change is one purple sphere that is bonded to one green sphere.

Solution

The starting materials consist of two green spheres and two purple spheres. The products consist of only one green sphere and one purple sphere. This violates Dalton's postulate that atoms are neither created nor destroyed during a chemical change, but are merely redistributed. (In this case, atoms appear to have been destroyed.)

? Exercise 1.2.2.1

In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres touch, they are part of a single unit of a compound. Does the following chemical change represented by these symbols violate any of the ideas of Dalton's atomic theory? If so, which one



This equation shows that the starting materials of the reaction are two sets of bonded, green spheres which are each being combined with two smaller, bonded purple spheres. The products of the change are two molecules that each contain one purple sphere bonded between two green spheres.

Answer

The starting materials consist of four green spheres and two purple spheres. The products consist of four green spheres and two purple spheres. This does not violate any of Dalton's postulates: Atoms are neither created nor destroyed, but are redistributed in small, whole-number ratios.

Dalton knew of the experiments of French chemist Joseph Proust, who demonstrated that *all samples of a pure compound contain the same elements in the same proportion by mass*. This statement is known as the law of definite proportions or the law of constant composition. The suggestion that the numbers of atoms of the elements in a given compound always exist in the same ratio is consistent with these observations. For example, when different samples of isooctane (a component of gasoline and one of the standards used in the octane rating system) are analyzed, they are found to have a carbon-to-hydrogen mass ratio of 5.33:1, as shown in Table 1.2.2.1.

Table 1.2.2.1: Constant Composition of Isooctane

Sample	Carbon	Hydrogen	Mass Ratio
A	14.82 g	2.78 g	$\frac{14.82\text{ g carbon}}{2.78\text{ g hydrogen}} = \frac{5.33\text{ g carbo}}{1.00\text{ g hydrog}}$
B	22.33 g	4.19 g	$\frac{22.33\text{ g carbon}}{4.19\text{ g hydrogen}} = \frac{5.33\text{ g carbo}}{1.00\text{ g hydrog}}$
C	19.40 g	3.64 g	$\frac{19.40\text{ g carbon}}{3.63\text{ g hydrogen}} = \frac{5.33\text{ g carbo}}{1.00\text{ g hydrog}}$

It is worth noting that although all samples of a particular compound have the same mass ratio, the converse is not true in general. That is, samples that have the same mass ratio are not necessarily the same substance. For example, there are many compounds other than isooctane that also have a carbon-to-hydrogen mass ratio of 5.33:1.00.

Dalton also used data from Proust, as well as results from his own experiments, to formulate another interesting law. The law of multiple proportions states that *when two elements react to form more than one compound, a fixed mass of one element will react with masses of the other element in a ratio of small, whole numbers*. For example, copper and chlorine can form a green, crystalline solid with a mass ratio of 0.558 g chlorine to 1 g copper, as well as a brown crystalline solid with a mass ratio of 1.116 g chlorine to 1 g copper. These ratios by themselves may not seem particularly interesting or informative; however, if we take a ratio of these ratios, we obtain a useful and possibly surprising result: a small, whole-number ratio.

$$\frac{\frac{1.116\text{ g Cl}}{1\text{ g Cu}}}{\frac{0.558\text{ g Cl}}{1\text{ g Cu}}} = \frac{2}{1}$$

This 2-to-1 ratio means that the brown compound has twice the amount of chlorine per amount of copper as the green compound.

This can be explained by atomic theory if the copper-to-chlorine ratio in the brown compound is 1 copper atom to 2 chlorine atoms, and the ratio in the green compound is 1 copper atom to 1 chlorine atom. The ratio of chlorine atoms (and thus the ratio of their masses) is therefore 2 to 1 (Figure 1.2.2.4).

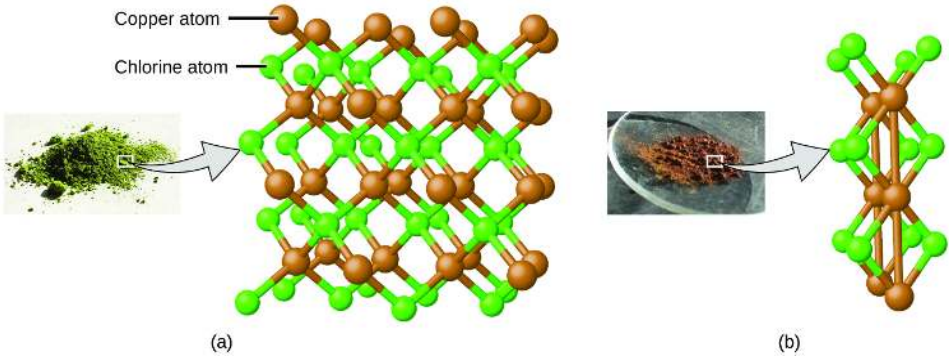


Figure 1.2.2.4: Compared to the copper chlorine compound in (a), where copper is represented by brown spheres and chlorine by green spheres, the copper chlorine compound in (b) has twice as many chlorine atoms per copper atom. (credit a: modification of work by "Benjah-bmm27"/Wikimedia Commons; credit b: modification of work by "Walkerma"/Wikimedia Commons)

Figure A shows a pile of green powder. A callout shows that the green powder is made up of a lattice of copper atoms interspersed with chlorine atoms. The atoms are color coded brown for copper and green for chlorine. The number of copper atoms is equal to the number of chlorine atoms in the molecule. Figure B shows a pile of brown powder. A callout shows that the brown powder is also made up of copper and chlorine atoms similar to the molecule shown in figure A.

Example 1.2.2.2: Laws of Definite and Multiple Proportions

A sample of compound A (a clear, colorless gas) is analyzed and found to contain 4.27 g carbon and 5.69 g oxygen. A sample of compound B (also a clear, colorless gas) is analyzed and found to contain 5.19 g carbon and 13.84 g oxygen. Are these data an example of the law of definite proportions, the law of multiple proportions, or neither? What do these data tell you about substances A and B?

Solution

In compound A, the mass ratio of carbon to oxygen is:

$$\frac{1.33\text{ g O}}{1\text{ g C}}$$

In compound B, the mass ratio of carbon to oxygen is:

$$\frac{2.67\text{ g O}}{1\text{ g C}}$$

The ratio of these ratios is:

$$\frac{\frac{1.33\text{ g O}}{1\text{ g C}}}{\frac{2.67\text{ g O}}{1\text{ g C}}} = \frac{1}{2}$$

This supports the law of multiple proportions. This means that A and B are different compounds, with A having one-half as much carbon per amount of oxygen (or twice as much oxygen per amount of carbon) as B. A possible pair of compounds that would fit this relationship would be A = CO_2 and B = CO.

Exercise 1.2.2.1

A sample of compound X (a clear, colorless, combustible liquid with a noticeable odor) is analyzed and found to contain 14.13 g carbon and 2.96 g hydrogen. A sample of compound Y (a clear, colorless, combustible liquid with a noticeable odor that is slightly different from X's odor) is analyzed and found to contain 19.91 g carbon and 3.34 g hydrogen. Are these data an example of the law of definite proportions, the law of multiple proportions, or neither? What do these data tell you about substances X and Y?

Answer

In compound X, the mass ratio of carbon to hydrogen is $\frac{14.13\text{ g C}}{2.96\text{ g H}}$.

In compound Y, the mass ratio of carbon to oxygen is $\frac{19.91\text{ g C}}{3.34\text{ g H}}$.

The ratio of these ratios is

$$\frac{\frac{14.13\text{ g C}}{2.96\text{ g H}}}{\frac{19.91\text{ g C}}{3.34\text{ g H}}} = \frac{4.77\text{ g C/g H}}{5.96\text{ g C/g H}} = 0.800 = \frac{4}{5}.$$

This small, whole-number ratio supports the law of multiple proportions. This means that X and Y are different compounds.

Summary

The ancient Greeks proposed that matter consists of extremely small particles called atoms. Dalton postulated that each element has a characteristic type of atom that differs in properties from atoms of all other elements, and that atoms of different elements can combine in fixed, small, whole-number ratios to form compounds. Samples of a particular compound all have the same elemental proportions by mass. When two elements form different compounds, a given mass of one element will combine with masses of the other element in a small, whole-number ratio. During any chemical change, atoms are neither created nor destroyed.

Glossary

Dalton's atomic theory
set of postulates that established the fundamental properties of atoms

law of constant composition
(also, law of definite proportions) all samples of a pure compound contain the same elements in the same proportions by mass

law of multiple proportions
when two elements react to form more than one compound, a fixed mass of one element will react with masses of the other element in a ratio of small whole numbers

law of definite proportions
(also, law of constant composition) all samples of a pure compound contain the same elements in the same proportions by mass

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

This page titled 1.2.2: Early Ideas in Atomic Theory is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **2.2: Early Ideas in Atomic Theory** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

1.2.3: Evolution of Atomic Theory

Learning Objectives

- Outline milestones in the development of modern atomic theory
- Summarize and interpret the results of the experiments of Thomson, Millikan, and Rutherford
- Describe the three subatomic particles that compose atoms
- Introduce the term isotopes

In the two centuries since Dalton developed his ideas, scientists have made significant progress in furthering our understanding of atomic theory. Much of this came from the results of several seminal experiments that revealed the details of the internal structure of atoms. Here, we will discuss some of those key developments, with an emphasis on application of the scientific method, as well as understanding how the experimental evidence was analyzed. While the historical persons and dates behind these experiments can be quite interesting, it is most important to understand the concepts resulting from their work.

1.2.3.1: Atomic Theory after the Nineteenth Century

If matter were composed of atoms, what were atoms composed of? Were they the smallest particles, or was there something smaller? In the late 1800s, a number of scientists interested in questions like these investigated the electrical discharges that could be produced in low-pressure gases, with the most significant discovery made by English physicist J. J. Thomson using a cathode ray tube. This apparatus consisted of a sealed glass tube from which almost all the air had been removed; the tube contained two metal electrodes. When high voltage was applied across the electrodes, a visible beam called a cathode ray appeared between them. This beam was deflected toward the positive charge and away from the negative charge, and was produced in the same way with identical properties when different metals were used for the electrodes. In similar experiments, the ray was simultaneously deflected by an applied magnetic field, and measurements of the extent of deflection and the magnetic field strength allowed Thomson to calculate the charge-to-mass ratio of the cathode ray particles. The results of these measurements indicated that these particles were much lighter than atoms (Figure 1.2.3.1).

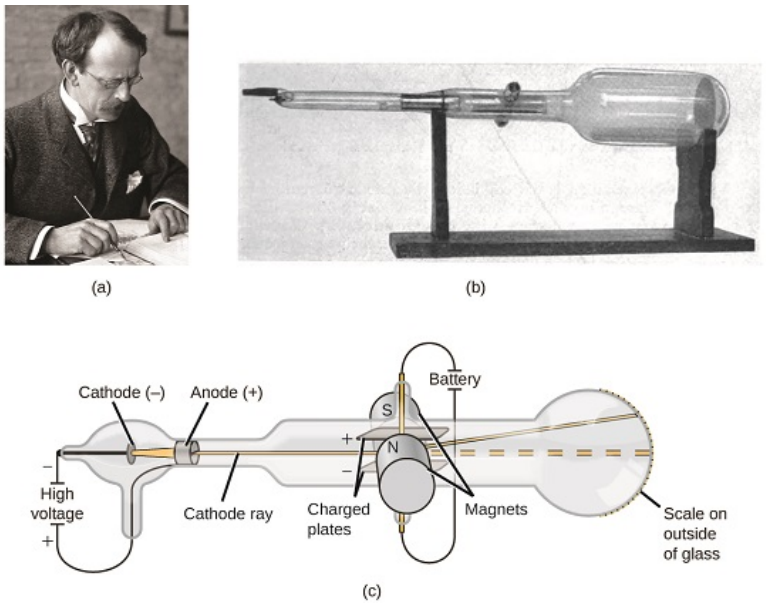
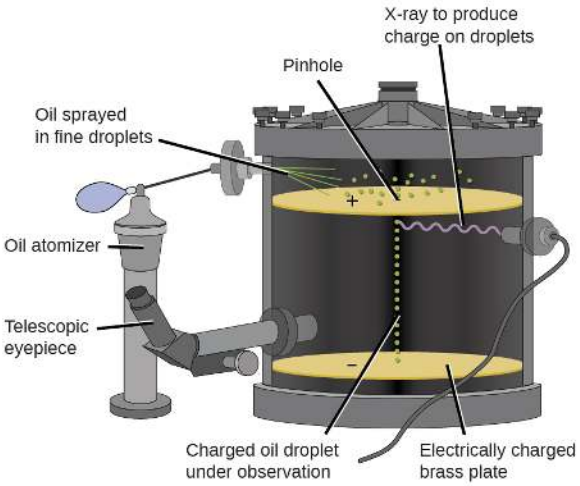


Figure 1.2.3.1: (a) J. J. Thomson produced a visible beam in a cathode ray tube. (b) This is an early cathode ray tube, invented in 1897 by Ferdinand Braun. (c) In the cathode ray, the beam (shown in yellow) comes from the cathode and is accelerated past the anode toward a fluorescent scale at the end of the tube. Simultaneous deflections by applied electric and magnetic fields permitted Thomson to calculate the mass-to-charge ratio of the particles composing the cathode ray. (credit a: modification of work by Nobel Foundation; credit b: modification of work by Eugen Nesper; credit c: modification of work by “Kurzon”/Wikimedia Commons).

Based on his observations, here is what Thomson proposed and why: The particles are attracted by positive (+) charges and repelled by negative (−) charges, so they must be negatively charged (like charges repel and unlike charges attract); they are less massive than atoms and indistinguishable, regardless of the source material, so they must be fundamental, subatomic constituents of all atoms. Although controversial at the time, Thomson’s idea was gradually accepted, and his cathode ray particle is what we

now call an electron, a negatively charged, subatomic particle with a mass more than one thousand-times less that of an atom. The term “electron” was coined in 1891 by Irish physicist George Stoney, from “*electr*ic i*on*.”

In 1909, more information about the electron was uncovered by American physicist Robert A. Millikan via his “oil drop” experiments. Millikan created microscopic oil droplets, which could be electrically charged by friction as they formed or by using X-rays. These droplets initially fell due to gravity, but their downward progress could be slowed or even reversed by an electric field lower in the apparatus. By adjusting the electric field strength and making careful measurements and appropriate calculations, Millikan was able to determine the charge on individual drops (Figure 1.2.3.2).



Oil drop	Charge in coulombs (C)
A	4.8×10^{-19} C
B	3.2×10^{-19} C
C	6.4×10^{-19} C
D	1.6×10^{-19} C
E	4.8×10^{-19} C

Figure 1.2.3.2: Millikan’s experiment measured the charge of individual oil drops. The tabulated data are examples of a few possible values.

Looking at the charge data that Millikan gathered, you may have recognized that the charge of an oil droplet is always a multiple of a specific charge, 1.6×10^{-19} C. Millikan concluded that this value must therefore be a fundamental charge—the charge of a single electron—with his measured charges due to an excess of one electron (1 times 1.6×10^{-19} C), two electrons (2 times 1.6×10^{-19} C), three electrons (3 times 1.6×10^{-19} C), and so on, on a given oil droplet. Since the charge of an electron was now known due to Millikan’s research, and the charge-to-mass ratio was already known due to Thomson’s research (1.759×10^{11} C/kg), it only required a simple calculation to determine the mass of the electron as well.

$$\text{Mass of electron} = 1.602 \times 10^{-19} \ \cancel{\text{C}} \times \frac{1 \text{ kg}}{1.759 \times 10^{11} \ \cancel{\text{C}}} = 9.107 \times 10^{-31} \text{ kg} \tag{2.3.1}$$

Scientists had now established that the atom was not indivisible as Dalton had believed, and due to the work of Thomson, Millikan, and others, the charge and mass of the negative, subatomic particles—the electrons—were known. However, the positively charged part of an atom was not yet well understood. In 1904, Thomson proposed the “plum pudding” model of atoms, which described a positively charged mass with an equal amount of negative charge in the form of electrons embedded in it, since all atoms are electrically neutral. A competing model had been proposed in 1903 by Hantaro Nagaoka, who postulated a Saturn-like atom, consisting of a positively charged sphere surrounded by a halo of electrons (Figure 1.2.3.3).

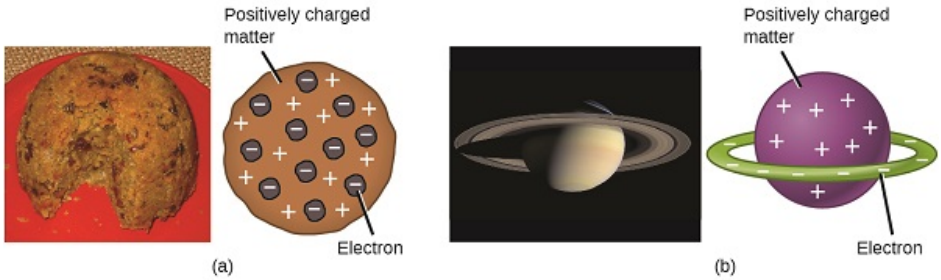


Figure 1.2.3.3: (a) Thomson suggested that atoms resembled plum pudding, an English dessert consisting of moist cake with embedded raisins (“plums”). (b) Nagaoka proposed that atoms resembled the planet Saturn, with a ring of electrons surrounding a positive “planet.” (credit a: modification of work by “Man vyi”/Wikimedia Commons; credit b: modification of work by “NASA”/Wikimedia Commons).

The next major development in understanding the atom came from Ernest Rutherford, a physicist from New Zealand who largely spent his scientific career in Canada and England. He performed a series of experiments using a beam of high-speed, positively charged alpha particles (α particles) that were produced by the radioactive decay of radium; α particles consist of two protons and two neutrons (you will learn more about radioactive decay in the chapter on nuclear chemistry). Rutherford and his colleagues Hans Geiger (later famous for the Geiger counter) and Ernest Marsden aimed a beam of α particles, the source of which was embedded in a lead block to absorb most of the radiation, at a very thin piece of gold foil and examined the resultant scattering of the α particles using a luminescent screen that glowed briefly where hit by an α particle.

What did they discover? Most particles passed right through the foil without being deflected at all. However, some were diverted slightly, and a very small number were deflected almost straight back toward the source (Figure 1.2.3.4). Rutherford described finding these results: “It was quite the most incredible event that has ever happened to me in my life. 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”[1] (p. 68).

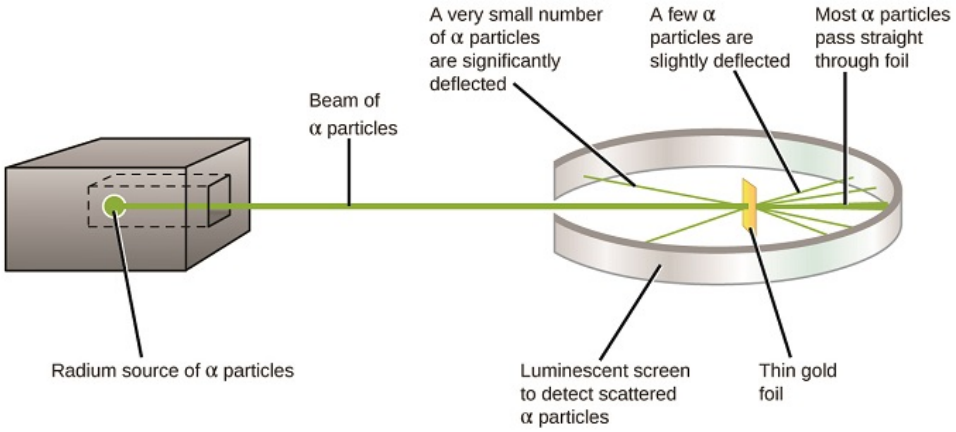


Figure 1.2.3.4: Geiger and Rutherford fired α particles at a piece of gold foil and detected where those particles went, as shown in this schematic diagram of their experiment. Most of the particles passed straight through the foil, but a few were deflected slightly and a very small number were significantly deflected.

Here is what Rutherford deduced: Because most of the fast-moving α particles passed through the gold atoms undeflected, they must have traveled through essentially empty space inside the atom. Alpha particles are positively charged, so deflections arose when they encountered another positive charge (like charges repel each other). Since like charges repel one another, the few positively charged α particles that changed paths abruptly must have hit, or closely approached, another body that also had a highly concentrated, positive charge. Since the deflections occurred a small fraction of the time, this charge only occupied a small amount of the space in the gold foil. Analyzing a series of such experiments in detail, Rutherford drew two conclusions:

1. The volume occupied by an atom must consist of a large amount of empty space.
2. A small, relatively heavy, positively charged body, the nucleus, must be at the center of each atom.

This analysis led Rutherford to propose a model in which an atom consists of a very small, positively charged nucleus, in which most of the mass of the atom is concentrated, surrounded by the negatively charged electrons, so that the atom is electrically neutral (Figure 1.2.3.5).

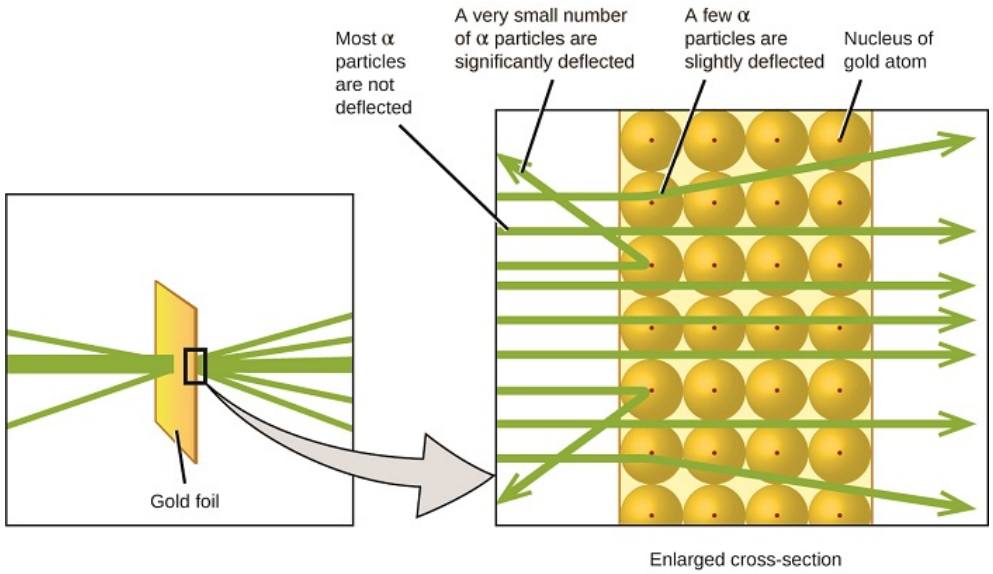


Figure 1.2.3.5: The α particles are deflected only when they collide with or pass close to the much heavier, positively charged gold nucleus. Because the nucleus is very small compared to the size of an atom, very few α particles are deflected. Most pass through the relatively large region occupied by electrons, which are too light to deflect the rapidly moving particles.

After many more experiments, Rutherford also discovered that the nuclei of other elements contain the hydrogen nucleus as a "building block," and he named this more fundamental particle the proton, the positively charged, subatomic particle found in the nucleus. With one addition, which you will learn next, this nuclear model of the atom, proposed over a century ago, is still used today.

Another important finding was the discovery of isotopes. During the early 1900s, scientists identified several substances that appeared to be new elements, isolating them from radioactive ores. For example, a "new element" produced by the radioactive decay of thorium was initially given the name mesothorium. However, a more detailed analysis showed that mesothorium was chemically identical to radium (another decay product), despite having a different atomic mass. This result, along with similar findings for other elements, led the English chemist Frederick Soddy to realize that an element could have types of atoms with different masses that were chemically indistinguishable. These different types are called isotopes—atoms of the same element that differ in mass. Soddy was awarded the Nobel Prize in Chemistry in 1921 for this discovery.

One puzzle remained: The nucleus was known to contain almost all of the mass of an atom, with the number of protons only providing half, or less, of that mass. Different proposals were made to explain what constituted the remaining mass, including the existence of neutral particles in the nucleus. As you might expect, detecting uncharged particles is very challenging, and it was not until 1932 that James Chadwick found evidence of neutrons, uncharged, subatomic particles with a mass approximately the same as that of protons. The existence of the neutron also explained isotopes: They differ in mass because they have different numbers of neutrons, but they are chemically identical because they have the same number of protons. This will be explained in more detail later in this chapter.

Summary

Although no one has actually seen the inside of an atom, experiments have demonstrated much about atomic structure. Thomson's cathode ray tube showed that atoms contain small, negatively charged particles called electrons. Millikan discovered that there is a fundamental electric charge—the charge of an electron. Rutherford's gold foil experiment showed that atoms have a small, dense, positively charged nucleus; the positively charged particles within the nucleus are called protons. Chadwick discovered that the nucleus also contains neutral particles called neutrons. Soddy demonstrated that atoms of the same element can differ in mass; these are called isotopes.

Footnotes

1. Ernest Rutherford, “The Development of the Theory of Atomic Structure,” ed. J. A. Ratcliffe, in *Background to Modern Science*, eds. Joseph Needham and Walter Pagel, (Cambridge, UK: Cambridge University Press, 1938), 61–74. Accessed September 22, 2014, https://ia600508.us.archive.org/3/it...e032734mbp.pdf.

Glossary

alpha particle (α particle)
positively charged particle consisting of two protons and two neutrons

electron
negatively charged, subatomic particle of relatively low mass located outside the nucleus

isotopes
atoms that contain the same number of protons but different numbers of neutrons

neutron
uncharged, subatomic particle located in the nucleus

proton
positively charged, subatomic particle located in the nucleus

nucleus
massive, positively charged center of an atom made up of protons and neutrons

---

This page titled 1.2.3: Evolution of Atomic Theory is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **2.3: Evolution of Atomic Theory** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

1.2.4: Atomic Structure and Symbolism

Learning Objectives

- Write and interpret symbols that depict the atomic number, mass number, and charge of an atom or ion
- Define the atomic mass unit and average atomic mass
- Calculate average atomic mass and isotopic abundance

The development of modern atomic theory revealed much about the inner structure of atoms. It was learned that an atom contains a very small nucleus composed of positively charged protons and uncharged neutrons, surrounded by a much larger volume of space containing negatively charged electrons. The nucleus contains the majority of an atom's mass because protons and neutrons are much heavier than electrons, whereas electrons occupy almost all of an atom's volume. The diameter of an atom is on the order of 10^{-10} m, whereas the diameter of the nucleus is roughly 10^{-15} m—about 100,000 times smaller. For a perspective about their relative sizes, consider this: If the nucleus were the size of a blueberry, the atom would be about the size of a football stadium (Figure 1.2.4.1).



Figure 1.2.4.1: If an atom could be expanded to the size of a football stadium, the nucleus would be the size of a single blueberry. (credit middle: modification of work by "babyknight"/Wikimedia Commons; credit right: modification of work by Paxson Woelber).

The diagram on the left shows a picture of an atom with a nucleus. The central figure shows a photograph of an American football stadium. The figure on the right shows a photograph of a handful of blueberries.

Atoms—and the protons, neutrons, and electrons that compose them—are extremely small. For example, a carbon atom weighs less than 2×10^{-23} g, and an electron has a charge of less than 2×10^{-19} C (coulomb). When describing the properties of tiny objects such as atoms, we use appropriately small units of measure, such as the atomic mass unit (amu) and the fundamental unit of charge (e). The amu was originally defined based on hydrogen, the lightest element, then later in terms of oxygen. Since 1961, it has been defined with regard to the most abundant isotope of carbon, atoms of which are assigned masses of exactly 12 amu. (This isotope is known as "carbon-12" as will be discussed later in this module.) Thus, one amu is exactly $1/12$ of the mass of one carbon-12 atom: 1 amu = 1.6605×10^{-24} g. (The Dalton (Da) and the unified atomic mass unit (u) are alternative units that are equivalent to the amu.) The fundamental unit of charge (also called the elementary charge) equals the magnitude of the charge of an electron (e) with e = 1.602×10^{-19} C.

A proton has a mass of 1.0073 amu and a charge of 1+. A neutron is a slightly heavier particle with a mass 1.0087 amu and a charge of zero; as its name suggests, it is neutral. The electron has a charge of 1− and is a much lighter particle with a mass of about 0.00055 amu (it would take about 1800 electrons to equal the mass of one proton. The properties of these fundamental particles are summarized in Table 1.2.4.1 (An observant student might notice that the sum of an atom's subatomic particles does not equal the atom's actual mass: The total mass of six protons, six neutrons, and six electrons is 12.0993 amu, slightly larger than the 12.00 amu of an actual carbon-12 atom. This "missing" mass is known as the mass defect, and you will learn about it in the chapter on nuclear chemistry.)

Table 1.2.4.1: Properties of Subatomic Particles

Name	Location	Charge (C)	Unit Charge	Mass (amu)	Mass (g)
electron	outside nucleus	-1.602×10^{-19}	1−	0.00055	0.00091×10^{-24}
proton	nucleus	1.602×10^{-19}	1+	1.00727	1.67262×10^{-24}

Name	Location	Charge (C)	Unit Charge	Mass (amu)	Mass (g)
neutron	nucleus	0	0	1.00866	1.67493×10^{-24}

The number of protons in the nucleus of an atom is its **atomic number** (Z). This is the defining trait of an element: Its value determines the identity of the atom. For example, any atom that contains six protons is the element carbon and has the atomic number 6, regardless of how many neutrons or electrons it may have. A neutral atom must contain the same number of positive and negative charges, so the number of protons equals the number of electrons. Therefore, the atomic number also indicates the number of electrons in an atom. The total number of protons and neutrons in an atom is called its mass number (A). The number of neutrons is therefore the difference between the mass number and the atomic number: A – Z = number of neutrons.

$$\begin{aligned} \text{atomic number (Z)} &= \text{number of protons} \\ \text{mass number (A)} &= \text{number of protons} + \text{number of neutrons} \\ \text{A} - \text{Z} &= \text{number of neutrons} \end{aligned}$$

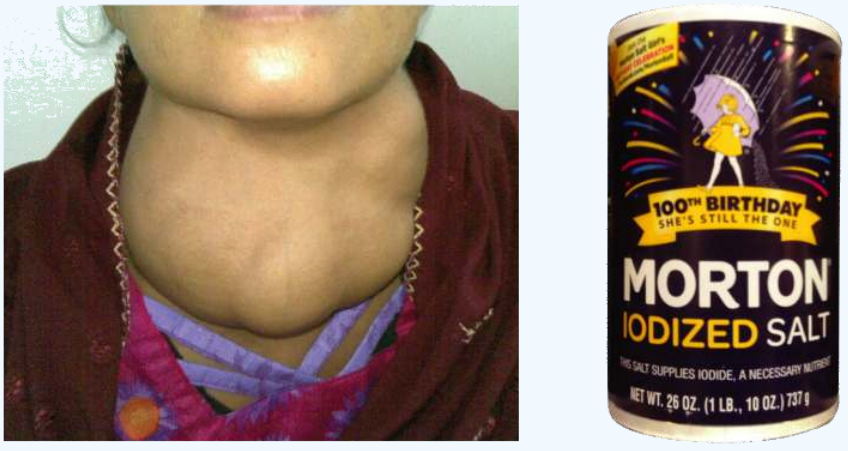
Atoms are electrically neutral if they contain the same number of positively charged protons and negatively charged electrons. When the numbers of these subatomic particles are *not* equal, the atom is electrically charged and is called an ion. The charge of an atom is defined as follows:

$$\text{Atomic charge} = \text{number of protons} - \text{number of electrons}$$

As will be discussed in more detail later in this chapter, atoms (and molecules) typically acquire charge by gaining or losing electrons. An atom that gains one or more electrons will exhibit a negative charge and is called an anion. Positively charged atoms called cations are formed when an atom loses one or more electrons. For example, a neutral sodium atom (Z = 11) has 11 electrons. If this atom loses one electron, it will become a cation with a 1+ charge (11 − 10 = 1+). A neutral oxygen atom (Z = 8) has eight electrons, and if it gains two electrons it will become an anion with a 2− charge (8 − 10 = 2−).

Example 1.2.4.1: Composition of an Atom

Iodine is an essential trace element in our diet; it is needed to produce thyroid hormone. Insufficient iodine in the diet can lead to the development of a goiter, an enlargement of the thyroid gland (Figure 1.2.4.2).



(a) (b)

Figure 1.2.4.2: (a) Insufficient iodine in the diet can cause an enlargement of the thyroid gland called a goiter. (b) The addition of small amounts of iodine to salt, which prevents the formation of goiters, has helped eliminate this concern in the US where salt consumption is high. (credit a: modification of work by “Almazi”/Wikimedia Commons; credit b: modification of work by Mike Mozart)

Figure A shows a photo of a person who has a very swollen thyroid in his or her neck. Figure B shows a photo of a canister of Morton iodized salt.

The addition of small amounts of iodine to table salt (iodized salt) has essentially eliminated this health concern in the United States, but as much as 40% of the world’s population is still at risk of iodine deficiency. The iodine atoms are added as anions,

and each has a 1− charge and a mass number of 127. Determine the numbers of protons, neutrons, and electrons in one of these iodine anions.

Solution

The atomic number of iodine (53) tells us that a neutral iodine atom contains 53 protons in its nucleus and 53 electrons outside its nucleus. Because the sum of the numbers of protons and neutrons equals the mass number, 127, the number of neutrons is 74 (127 − 53 = 74). Since the iodine is added as a 1− anion, the number of electrons is 54 [53 – (1–) = 54].

? Exercise 1.2.4.1

An ion of platinum has a mass number of 195 and contains 74 electrons. How many protons and neutrons does it contain, and what is its charge?

Answer

78 protons; 117 neutrons; charge is 4+

1.2.4.1: Chemical Symbols

A chemical symbol is an abbreviation that we use to indicate an element or an atom of an element. For example, the symbol for mercury is Hg (Figure 1.2.4.3). We use the same symbol to indicate one atom of mercury (microscopic domain) or to label a container of many atoms of the element mercury (macroscopic domain).



Figure 1.2.4.3: The symbol Hg represents the element mercury regardless of the amount; it could represent one atom of mercury or a large amount of mercury. from Wikipedia (user: Materialscientist).

The symbols for several common elements and their atoms are listed in Table 1.2.4.2 Some symbols are derived from the common name of the element; others are abbreviations of the name in another language. Symbols have one or two letters, for example, H for hydrogen and Cl for chlorine. To avoid confusion with other notations, only the first letter of a symbol is capitalized. For example, Co is the symbol for the element cobalt, but CO is the notation for the compound carbon monoxide, which contains atoms of the elements carbon (C) and oxygen (O). All known elements and their symbols are in the periodic table.

Table 1.2.4.2: Some Common Elements and Their Symbols

Element	Symbol	Element	Symbol
aluminum	Al	iron	Fe (from *ferrum*)
bromine	Br	lead	Pb (from *plumbum*)
calcium	Ca	magnesium	Mg
carbon	C	mercury	Hg (from *hydrargyrum*)
chlorine	Cl	nitrogen	N
chromium	Cr	oxygen	O

Element	Symbol	Element	Symbol
cobalt	Co	potassium	K (from *kalium*)
copper	Cu (from *cuprum*)	silicon	Si
fluorine	F	silver	Ag (from *argentum*)
gold	Au (from *aurum*)	sodium	Na (from *natrium*)
helium	He	sulfur	S
hydrogen	H	tin	Sn (from *stannum*)
iodine	I	zinc	Zn

Traditionally, the discoverer (or discoverers) of a new element names the element. However, until the name is recognized by the International Union of Pure and Applied Chemistry (IUPAC), the recommended name of the new element is based on the Latin word(s) for its atomic number. For example, element 106 was called unnilhexium (Unh), element 107 was called unnilseptium (Uns), and element 108 was called unniloctium (Uno) for several years. These elements are now named after scientists or locations; for example, element 106 is now known as *seaborgium* (Sg) in honor of Glenn Seaborg, a Nobel Prize winner who was active in the discovery of several heavy elements.

1.2.4.2: Isotopes

The symbol for a specific isotope of any element is written by placing the mass number as a superscript to the left of the element symbol (Figure 1.2.4.4). The atomic number is sometimes written as a subscript preceding the symbol, but since this number defines the element's identity, as does its symbol, it is often omitted. For example, magnesium exists as a mixture of three isotopes, each with an atomic number of 12 and with mass numbers of 24, 25, and 26, respectively. These isotopes can be identified as ^{24}Mg, ^{25}Mg, and ^{26}Mg. These isotope symbols are read as "element, mass number" and can be symbolized consistent with this reading. For instance, ^{24}Mg is read as "magnesium 24," and can be written as "magnesium-24" or "Mg-24." ^{25}Mg is read as "magnesium 25," and can be written as "magnesium-25" or "Mg-25." All magnesium atoms have 12 protons in their nucleus. They differ only because a ^{24}Mg atom has 12 neutrons in its nucleus, a ^{25}Mg atom has 13 neutrons, and a ^{26}Mg has 14 neutrons.

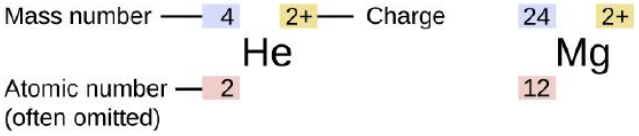


Figure 1.2.4.4: The symbol for an atom indicates the element via its usual two-letter symbol, the mass number as a left superscript, the atomic number as a left subscript (sometimes omitted), and the charge as a right superscript.

This diagram shows the symbol for helium, "H e." The number to the upper left of the symbol is the mass number, which is 4. The number to the upper right of the symbol is the charge which is positive 2. The number to the lower left of the symbol is the atomic number, which is 2. This number is often omitted. Also shown is "M g" which stands for magnesium It has a mass number of 24, a charge of positive 2, and an atomic number of 12.

Information about the naturally occurring isotopes of elements with atomic numbers 1 through 10 is given in Table 1.2.4.2 Note that in addition to standard names and symbols, the isotopes of hydrogen are often referred to using common names and accompanying symbols. Hydrogen-2, symbolized ^{2}H, is also called deuterium and sometimes symbolized D. Hydrogen-3, symbolized ^{3}H, is also called tritium and sometimes symbolized T.

Table 1.2.4.2: Nuclear Compositions of Atoms of the Very Light Elements

Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (amu)	% Natural Abundance
hydrogen	$^{1}_{1}$H (protium)	1	1	0	1.0078	99.989

Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (amu)	% Natural Abundance
	$^{2}_{1}\mathrm{H}$ (deuterium)	1	1	1	2.0141	0.0115
	$^{3}_{1}\mathrm{H}$ (tritium)	1	1	2	3.01605	— (trace)
helium	$^{3}_{2}\mathrm{He}$	2	2	1	3.01603	0.00013
	$^{4}_{2}\mathrm{He}$	2	2	2	4.0026	100
lithium	$^{6}_{3}\mathrm{Li}$	3	3	3	6.0151	7.59
	$^{7}_{3}\mathrm{Li}$	3	3	4	7.0160	92.41
beryllium	$^{9}_{4}\mathrm{Be}$	4	4	5	9.0122	100
boron	$^{10}_{5}\mathrm{B}$	5	5	5	10.0129	19.9
	$^{11}_{5}\mathrm{B}$	5	5	6	11.0093	80.1
carbon	$^{12}_{6}\mathrm{C}$	6	6	6	12.0000	98.89
	$^{13}_{6}\mathrm{C}$	6	6	7	13.0034	1.11
	$^{14}_{6}\mathrm{C}$	6	6	8	14.0032	— (trace)
nitrogen	$^{14}_{7}\mathrm{N}$	7	7	7	14.0031	99.63
	$^{15}_{7}\mathrm{N}$	7	7	8	15.0001	0.37
oxygen	$^{16}_{8}\mathrm{O}$	8	8	8	15.9949	99.757
	$^{17}_{8}\mathrm{O}$	8	8	9	16.9991	0.038
	$^{18}_{8}\mathrm{O}$	8	8	10	17.9992	0.205
fluorine	$^{19}_{9}\mathrm{F}$	9	9	10	18.9984	100
neon	$^{20}_{10}\mathrm{Ne}$	10	10	10	19.9924	90.48
	$^{21}_{10}\mathrm{Ne}$	10	10	11	20.9938	0.27
	$^{22}_{10}\mathrm{Ne}$	10	10	12	21.9914	9.25

1.2.4.3: Atomic Mass

Because each proton and each neutron contribute approximately one amu to the mass of an atom, and each electron contributes far less, the atomic mass of a single atom is approximately equal to its mass number (a whole number). However, the average masses of atoms of most elements are not whole numbers because most elements exist naturally as mixtures of two or more isotopes.

The mass of an element shown in a periodic table or listed in a table of atomic masses is a weighted, average mass of all the isotopes present in a naturally occurring sample of that element. This is equal to the sum of each individual isotope's mass multiplied by its fractional abundance.

$$\text{average mass} = \sum_i (\text{fractional abundance} \times \text{isotopic mass})_i$$

For example, the element boron is composed of two isotopes: About 19.9% of all boron atoms are ^{10}B with a mass of 10.0129 amu, and the remaining 80.1% are ^{11}B with a mass of 11.0093 amu. The average atomic mass for boron is calculated to be:

$$\begin{aligned}\text{boron average mass} &= (0.199 \times 10.0129\ \text{amu}) + (0.801 \times 11.0093\ \text{amu}) \\ &= 1.99\ \text{amu} + 8.82\ \text{amu} \\ &= 10.81\ \text{amu}\end{aligned}$$

It is important to understand that no single boron atom weighs exactly 10.8 amu; 10.8 amu is the average mass of all boron atoms, and individual boron atoms weigh either approximately 10 amu or 11 amu.

Example 1.2.4.2: Calculation of Average Atomic Mass

A meteorite found in central Indiana contains traces of the noble gas neon picked up from the solar wind during the meteorite's trip through the solar system. Analysis of a sample of the gas showed that it consisted of 91.84% ^{20}Ne (mass 19.9924 amu), 0.47% ^{21}Ne (mass 20.9940 amu), and 7.69% ^{22}Ne (mass 21.9914 amu). What is the average mass of the neon in the solar wind?

Solution

$$\begin{aligned}\text{average mass} &= (0.9184 \times 19.9924\ \text{amu}) + (0.0047 \times 20.9940\ \text{amu}) + (0.0769 \times 21.9914\ \text{amu}) \\ &= (18.36 + 0.099 + 1.69)\ \text{amu} \\ &= 20.15\ \text{amu}\end{aligned}$$

The average mass of a neon atom in the solar wind is 20.15 amu. (The average mass of a terrestrial neon atom is 20.1796 amu. This result demonstrates that we may find slight differences in the natural abundance of isotopes, depending on their origin.)

Exercise 1.2.4.2

A sample of magnesium is found to contain 78.70% of ^{24}Mg atoms (mass 23.98 amu), 10.13% of ^{25}Mg atoms (mass 24.99 amu), and 11.17% of ^{26}Mg atoms (mass 25.98 amu). Calculate the average mass of a Mg atom.

Answer

24.31 amu

We can also do variations of this type of calculation, as shown in the next example.

Example 1.2.4.3: Calculation of Percent Abundance

Naturally occurring chlorine consists of ^{35}Cl (mass 34.96885 amu) and ^{37}Cl (mass 36.96590 amu), with an average mass of 35.453 amu. What is the percent composition of Cl in terms of these two isotopes?

Solution

The average mass of chlorine is the fraction that is ^{35}Cl times the mass of ^{35}Cl plus the fraction that is ^{37}Cl times the mass of ^{37}Cl.

$$\text{average mass} = (\text{fraction of } ^{35}\text{Cl} \times \text{mass of } ^{35}\text{Cl}) + (\text{fraction of } ^{37}\text{Cl} \times \text{mass of } ^{37}\text{Cl})$$

If we let x represent the fraction that is ^{35}Cl, then the fraction that is ^{37}Cl is represented by 1.00 − x.

(The fraction that is ^{35}Cl + the fraction that is ^{37}Cl must add up to 1, so the fraction of ^{37}Cl must equal 1.00 − the fraction of ^{35}Cl.)

Substituting this into the average mass equation, we have:

$$\begin{aligned}35.453\ \text{amu} &= (x \times 34.96885\ \text{amu}) + [(1.00 - x) \times 36.96590\ \text{amu}] \\ 35.453 &= 34.96885x + 36.96590 - 36.96590x \\ 1.99705x &= 1.513 \\ x &= \frac{1.513}{1.99705} = 0.7576\end{aligned}$$

So solving yields: x = 0.7576, which means that 1.00 − 0.7576 = 0.2424. Therefore, chlorine consists of 75.76% ^{35}Cl and 24.24% ^{37}Cl.

? Exercise 1.2.4.3

Naturally occurring copper consists of ^{63}Cu (mass 62.9296 amu) and ^{65}Cu (mass 64.9278 amu), with an average mass of 63.546 amu. What is the percent composition of Cu in terms of these two isotopes?

Answer

69.15% Cu-63 and 30.85% Cu-65

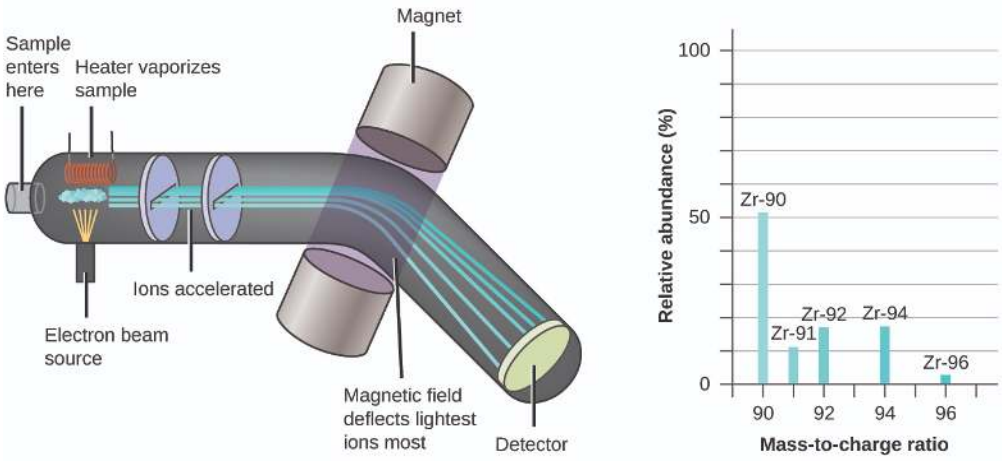


Figure 1.2.4.5: Analysis of zirconium in a mass spectrometer produces a mass spectrum with peaks showing the different isotopes of Zr.

The left diagram shows how a mass spectrometer works. The graph to the right of the spectrometer shows a mass spectrum of zirconium. The relative abundance, as a percentage from 0 to 100, is graphed on the y axis, and the mass to charge ratio is graphed on the x axis. The sample contains five different isomers of zirconium.

The occurrence and natural abundances of isotopes can be experimentally determined using an instrument called a mass spectrometer. Mass spectrometry (MS) is widely used in chemistry, forensics, medicine, environmental science, and many other fields to analyze and help identify the substances in a sample of material. In a typical mass spectrometer (Figure 1.2.4.5), the sample is vaporized and exposed to a high-energy electron beam that causes the sample's atoms (or molecules) to become electrically charged, typically by losing one or more electrons. These cations then pass through a (variable) electric or magnetic field that deflects each cation's path to an extent that depends on both its mass and charge (similar to how the path of a large steel ball bearing rolling past a magnet is deflected to a lesser extent that that of a small steel BB). The ions are detected, and a plot of the relative number of ions generated versus their mass-to-charge ratios (a *mass spectrum*) is made. The height of each vertical feature or peak in a mass spectrum is proportional to the fraction of cations with the specified mass-to-charge ratio. Since its initial use during the development of modern atomic theory, MS has evolved to become a powerful tool for chemical analysis in a wide range of applications.



***Video* 1.2.4.1** *: Watch this video from the Royal Society for Chemistry for a brief description of the rudiments of mass spectrometry.*

Summary

An atom consists of a small, positively charged nucleus surrounded by electrons. The nucleus contains protons and neutrons; its diameter is about 100,000 times smaller than that of the atom. The mass of one atom is usually expressed in atomic mass units (amu), which is referred to as the atomic mass. An amu is defined as exactly $1/12$ of the mass of a carbon-12 atom and is equal to 1.6605×10^{-24} g.

Protons are relatively heavy particles with a charge of 1+ and a mass of 1.0073 amu. Neutrons are relatively heavy particles with no charge and a mass of 1.0087 amu. Electrons are light particles with a charge of 1− and a mass of 0.00055 amu. The number of protons in the nucleus is called the atomic number (Z) and is the property that defines an atom's elemental identity. The sum of the numbers of protons and neutrons in the nucleus is called the mass number and, expressed in amu, is approximately equal to the mass of the atom. An atom is neutral when it contains equal numbers of electrons and protons.

Isotopes of an element are atoms with the same atomic number but different mass numbers; isotopes of an element, therefore, differ from each other only in the number of neutrons within the nucleus. When a naturally occurring element is composed of several isotopes, the atomic mass of the element represents the average of the masses of the isotopes involved. A chemical symbol identifies the atoms in a substance using symbols, which are one-, two-, or three-letter abbreviations for the atoms.

1.2.4.4: Key Equations

- $\text{average mass} = \sum_i (\text{fractional abundance} \times \text{isotopic mass})_i$

Glossary

anion
negatively charged atom or molecule (contains more electrons than protons)

atomic mass
average mass of atoms of an element, expressed in amu

atomic mass unit (amu)
(also, unified atomic mass unit, u, or Dalton, Da) unit of mass equal to $\frac{1}{12}$ of the mass of a ^{12}C atom

atomic number (Z)
number of protons in the nucleus of an atom

cation
positively charged atom or molecule (contains fewer electrons than protons)

chemical symbol
one-, two-, or three-letter abbreviation used to represent an element or its atoms

Dalton (Da)
alternative unit equivalent to the atomic mass unit

fundamental unit of charge
(also called the elementary charge) equals the magnitude of the charge of an electron (e) with e = 1.602×10^{-19} C

ion
electrically charged atom or molecule (contains unequal numbers of protons and electrons)

mass number (A)

sum of the numbers of neutrons and protons in the nucleus of an atom

unified atomic mass unit (u)

alternative unit equivalent to the atomic mass unit

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

This page titled 1.2.4: Atomic Structure and Symbolism is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **2.4: Atomic Structure and Symbolism** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

1.2.5: Chemical Formulas

Learning Objectives

- Symbolize the composition of molecules using molecular formulas and empirical formulas
- Represent the bonding arrangement of atoms within molecules using structural formulas

A molecular formula is a representation of a molecule that uses chemical symbols to indicate the types of atoms followed by subscripts to show the number of atoms of each type in the molecule. (A subscript is used only when more than one atom of a given type is present.) Molecular formulas are also used as abbreviations for the names of compounds.

The structural formula for a compound gives the same information as its molecular formula (the types and numbers of atoms in the molecule) but also shows how the atoms are connected in the molecule. The structural formula for methane contains symbols for one C atom and four H atoms, indicating the number of atoms in the molecule (Figure 1.2.5.1). The lines represent bonds that hold the atoms together. (A chemical bond is an attraction between atoms or ions that holds them together in a molecule or a crystal.) We will discuss chemical bonds and see how to predict the arrangement of atoms in a molecule later. For now, simply know that the lines are an indication of how the atoms are connected in a molecule. A ball-and-stick model shows the geometric arrangement of the atoms with atomic sizes not to scale, and a space-filling model shows the relative sizes of the atoms.

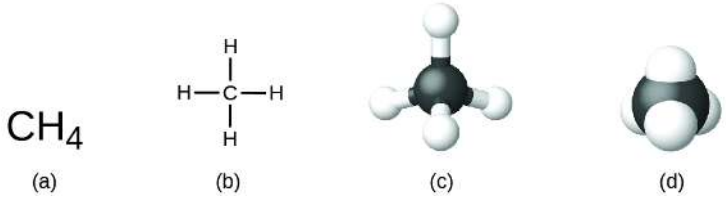


Figure 1.2.5.1: A methane molecule can be represented as (a) a molecular formula, (b) a structural formula, (c) a ball-and-stick model, and (d) a space-filling model. Carbon and hydrogen atoms are represented by black and white spheres, respectively.

Figure A shows C H subscript 4. Figure B shows a carbon atom that is bonded to four hydrogen atoms at right angles: one above, one to the left, one to the right, and one below. Figure C shows a 3-D, ball-and-stick model of the carbon atom bonded to four hydrogen atoms. Figure D shows a space-filling model of a carbon atom with hydrogen atoms partially embedded into the surface of the carbon atom.

Although many elements consist of discrete, individual atoms, some exist as molecules made up of two or more atoms of the element chemically bonded together. For example, most samples of the elements hydrogen, oxygen, and nitrogen are composed of molecules that contain two atoms each (called diatomic molecules) and thus have the molecular formulas H_2, O_2, and N_2, respectively. Other elements commonly found as diatomic molecules are fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2). 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 1.2.5.2).

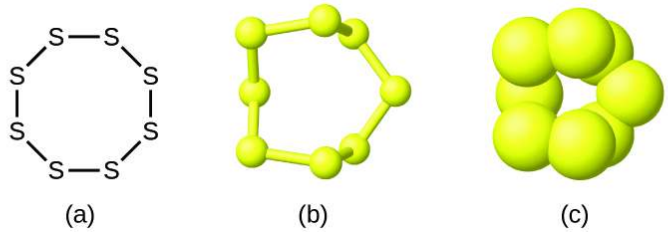


Figure 1.2.5.2: A molecule of sulfur is composed of eight sulfur atoms and is therefore written as S_8. It can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. Sulfur atoms are represented by yellow spheres.

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 1.2.5.3).

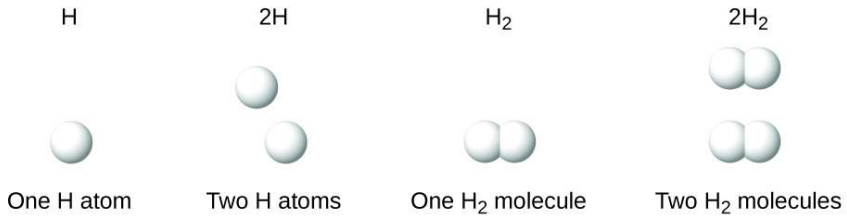


Figure 1.2.5.3: The symbols H, 2H, H_2, and $2H_2$ represent very different entities.

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.

Compounds are formed when two or more elements chemically combine, resulting in the formation of bonds. For example, hydrogen and oxygen can react to form water, and sodium and chlorine can react to form table salt. We sometimes describe the composition of these compounds with an empirical formula, which indicates the types of atoms present and *the simplest whole-number ratio of the number of atoms (or ions) in the compound*. For example, titanium dioxide (used as pigment in white paint and in the thick, white, blocking type of sunscreen) has an empirical formula of TiO_2. This identifies the elements titanium (Ti) and oxygen (O) as the constituents of titanium dioxide, and indicates the presence of twice as many atoms of the element oxygen as atoms of the element titanium (Figure 1.2.5.4).

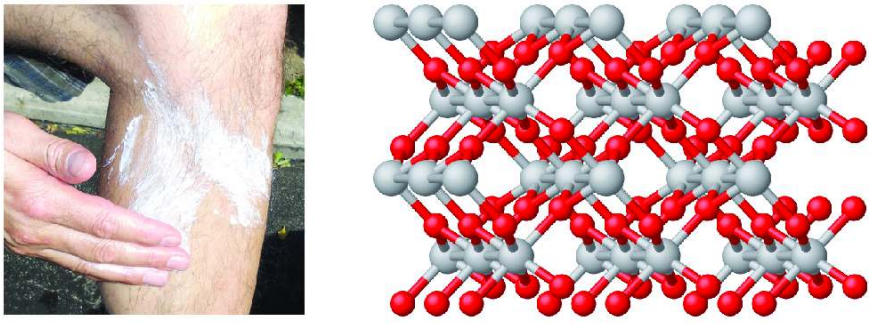


Figure 1.2.5.4: (a) The white compound titanium dioxide provides effective protection from the sun. (b) A crystal of titanium dioxide, TiO_2, contains titanium and oxygen in a ratio of 1 to 2. The titanium atoms are gray and the oxygen atoms are red. (credit a: modification of work by “osseous”/Flickr).

Figure A shows a photo of a person applying suntan lotion to his or her lower leg. Figure B shows a 3-D ball-and-stick model of the molecule titanium dioxide, which involves a complicated interlocking of many titanium and oxygen atoms. The titanium atoms in the molecule are shown as silver spheres and the oxygen atoms are shown as red spheres. There are twice as many oxygen atoms as titanium atoms in the molecule.

As discussed previously, we can describe a compound with a molecular formula, in which the subscripts indicate the *actual numbers of atoms* of each element in a molecule of the compound. In many cases, the molecular formula of a substance is derived from experimental determination of both its empirical formula and its molecular mass (the sum of atomic masses for all atoms composing the molecule). For example, it can be determined experimentally that benzene contains two elements, carbon (C) and hydrogen (H), and that for every carbon atom in benzene, there is one hydrogen atom. Thus, the empirical formula is CH. An experimental determination of the molecular mass reveals that a molecule of benzene contains six carbon atoms and six hydrogen atoms, so the molecular formula for benzene is C_6H_6 (Figure 1.2.5.5).

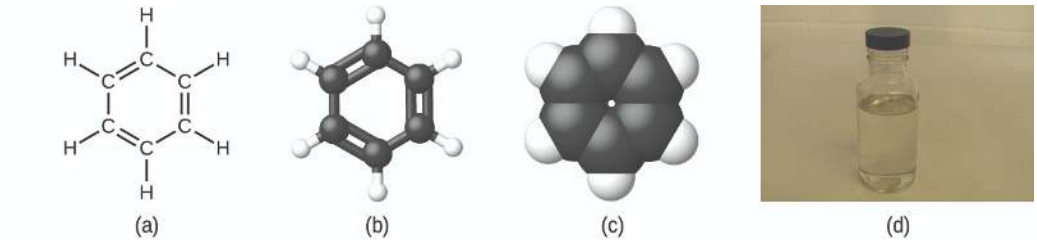


Figure 1.2.5.5: Benzene, C_6H_6, is produced during oil refining and has many industrial uses. A benzene molecule can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. (d) Benzene is a clear liquid. (credit d: modification of work by Sahar Atwa).

Figure A shows that benzene is composed of six carbons shaped like a hexagon. Every other bond between the carbon atoms is a double bond. Each carbon also has a single bonded hydrogen atom. Figure B shows a 3-D, ball-and-stick drawing of benzene. The six carbon atoms are black spheres while the six hydrogen atoms are smaller, white spheres. Figure C is a space-filling model of benzene which shows that most of the interior space is occupied by the carbon atoms. The hydrogen atoms are embedded in the outside surface of the carbon atoms. Figure d shows a small vial filled with benzene which appears to be clear.

If we know a compound's formula, we can easily determine the empirical formula. (This is somewhat of an academic exercise; the reverse chronology is generally followed in actual practice.) For example, the molecular formula for acetic acid, the component that gives vinegar its sharp taste, is $C_2H_4O_2$. This formula indicates that a molecule of acetic acid (Figure 1.2.5.6) contains two carbon atoms, four hydrogen atoms, and two oxygen atoms. The ratio of atoms is 2:4:2. Dividing by the lowest common denominator (2) gives the simplest, whole-number ratio of atoms, 1:2:1, so the empirical formula is CH_2O. Note that a molecular formula is always a whole-number multiple of an empirical formula.

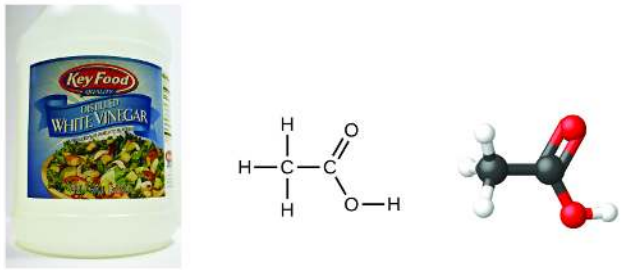


Figure 1.2.5.6: (a) Vinegar contains acetic acid, $C_2H_4O_2$, which has an empirical formula of CH_2O. It can be represented as (b) a structural formula and (c) as a ball-and-stick model. (credit a: modification of work by "HomeSpot HQ"/Flickr)

Figure A shows a jug of distilled, white vinegar. Figure B shows a structural formula for acetic acid which contains two carbon atoms connected by a single bond. The left carbon atom forms single bonds with three hydrogen atoms. The right carbon atom forms a double bond with an oxygen atom. The right carbon atom also forms a single bond with an oxygen atom. This oxygen forms a single bond with a hydrogen atom. Figure C shows a 3-D ball-and-stick model of acetic acid.

✔ Example 1.2.5.1: Empirical and Molecular Formulas

Molecules of glucose (blood sugar) contain 6 carbon atoms, 12 hydrogen atoms, and 6 oxygen atoms. What are the molecular and empirical formulas of glucose?

Solution

The molecular formula is $C_6H_{12}O_6$ because one molecule actually contains 6 C, 12 H, and 6 O atoms. The simplest whole-number ratio of C to H to O atoms in glucose is 1:2:1, so the empirical formula is CH_2O.

? Exercise 1.2.5.1

A molecule of metaldehyde (a pesticide used for snails and slugs) contains 8 carbon atoms, 16 hydrogen atoms, and 4 oxygen atoms. What are the molecular and empirical formulas of metaldehyde?

Answer

Molecular formula, $C_8H_{16}O_4$; empirical formula, C_2H_4O

It is important to be aware that it may be possible for the same atoms to be arranged in different ways: Compounds with the same molecular formula may have different atom-to-atom bonding and therefore different structures. For example, could there be another compound with the same formula as acetic acid, $C_2H_4O_2$? And if so, what would be the structure of its molecules?

If you predict that another compound with the formula $C_2H_4O_2$ could exist, then you demonstrated good chemical insight and are correct. Two C atoms, four H atoms, and two O atoms can also be arranged to form methyl formate, which is used in manufacturing, as an insecticide, and for quick-drying finishes. Methyl formate molecules have one of the oxygen atoms between the two carbon atoms, differing from the arrangement in acetic acid molecules. Acetic acid and methyl formate are examples of isomers—compounds with the same chemical formula but different molecular structures (Figure 1.2.5.7). Note that this small difference in the arrangement of the atoms has a major effect on their respective chemical properties. You would certainly not want to use a solution of methyl formate as a substitute for a solution of acetic acid (vinegar) when you make salad dressing.

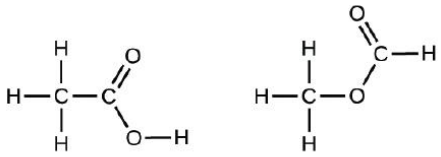


Figure 1.2.5.7: Molecules of (a) acetic acid and methyl formate (b) are structural isomers; they have the same formula ($C_2H_4O_2$) but different structures (and therefore different chemical properties).

Figure A shows a structural diagram of acetic acid, C subscript 2 H subscript 4 O subscript 2. Acetic acid contains two carbon atoms connected by a single bond. The left carbon atom forms single bonds with three hydrogen atoms. The carbon on the right forms a double bond with an oxygen atom. The right carbon atom also forms a single bond to an oxygen atom which forms a single bond with a hydrogen atom. Figure B shows a structural diagram of methyl formate, C subscript 2 H subscript 4 O subscript 2. This molecule contains a carbon atom which forms single bonds with three hydrogen atoms, and a single bond with an oxygen atom. The oxygen atom forms a single bond with another carbon atom which forms a double bond with another oxygen atom and a single bond with a hydrogen atom.

Many types of isomers exist (Figure 1.2.5.8). Acetic acid and methyl formate are structural isomers, compounds in which the molecules differ in how the atoms are connected to each other. There are also various types of spatial isomers, in which the relative orientations of the atoms in space can be different. For example, the compound carvone (found in caraway seeds, spearmint, and mandarin orange peels) consists of two isomers that are mirror images of each other. *S*-(+)-carvone smells like caraway, and *R*-(−)-carvone smells like spearmint.

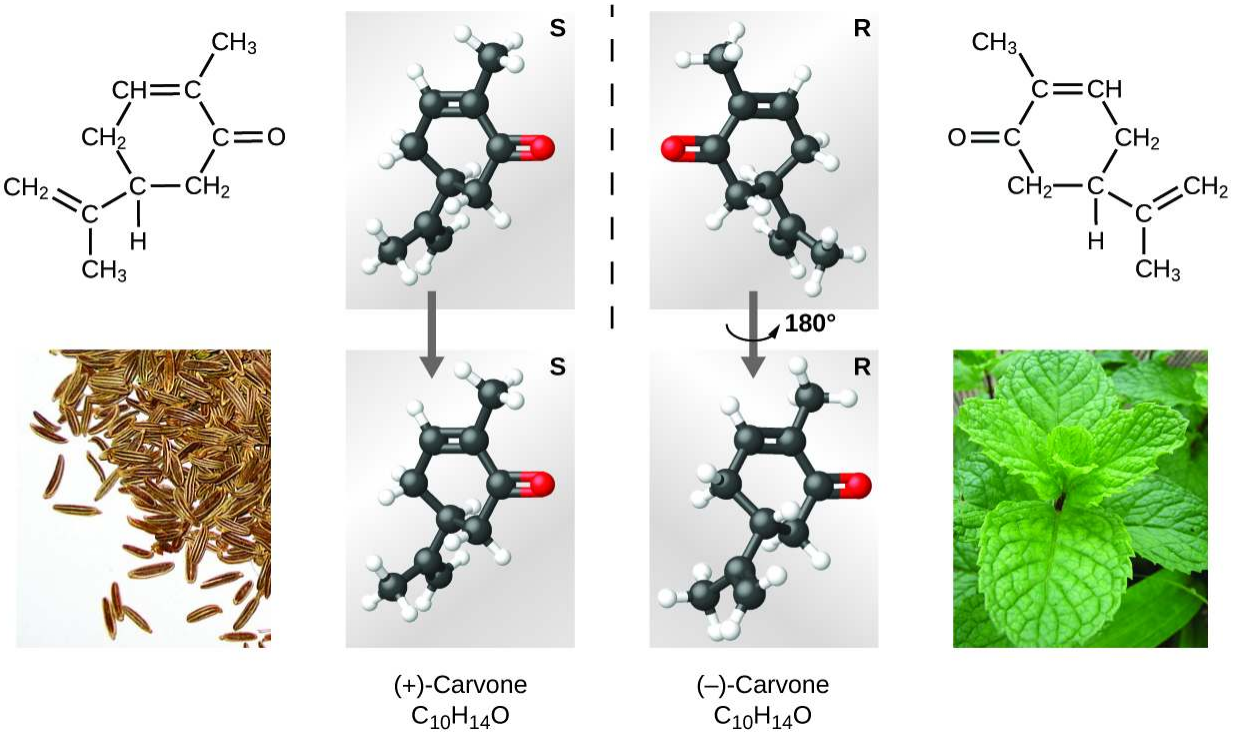


Figure 1.2.5.8: Molecules of carvone are spatial isomers; they only differ in the relative orientations of the atoms in space. (credit bottom left: modification of work by “Miansari66”/Wikimedia Commons; credit bottom right: modification of work by Forest & Kim Starr)

Summary

A molecular formula uses chemical symbols and subscripts to indicate the exact numbers of different atoms in a molecule or compound. An empirical formula gives the simplest, whole-number ratio of atoms in a compound. A structural formula indicates the bonding arrangement of the atoms in the molecule. Ball-and-stick and space-filling models show the geometric arrangement of atoms in a molecule. Isomers are compounds with the same molecular formula but different arrangements of atoms.

Glossary

empirical formula
formula showing the composition of a compound given as the simplest whole-number ratio of atoms

isomers
compounds with the same chemical formula but different structures

molecular formula
formula indicating the composition of a molecule of a compound and giving the actual number of atoms of each element in a molecule of the compound.

spatial isomers
compounds in which the relative orientations of the atoms in space differ

structural isomer
one of two substances that have the same molecular formula but different physical and chemical properties because their atoms are bonded differently

structural formula
shows the atoms in a molecule and how they are connected

This page titled 1.2.5: Chemical Formulas is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **2.5: Chemical Formulas** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

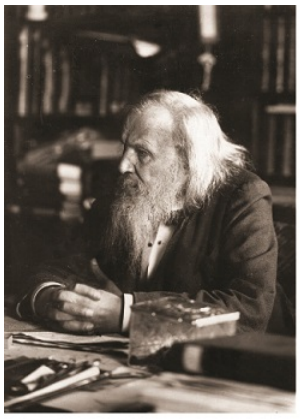
1.2.6: The Periodic Table

Learning Objectives

- State the periodic law and explain the organization of elements in the periodic table
- Predict the general properties of elements based on their location within the periodic table
- Identify metals, nonmetals, and metalloids by their properties and/or location on the periodic table

As early chemists worked to purify ores and discovered more elements, they realized that various elements could be grouped together by their similar chemical behaviors. One such grouping includes lithium (Li), sodium (Na), and potassium (K): These elements all are shiny, conduct heat and electricity well, and have similar chemical properties. A second grouping includes calcium (Ca), strontium (Sr), and barium (Ba), which also are shiny, good conductors of heat and electricity, and have chemical properties in common. However, the specific properties of these two groupings are notably different from each other. For example: Li, Na, and K are much more reactive than are Ca, Sr, and Ba; Li, Na, and K form compounds with oxygen in a ratio of two of their atoms to one oxygen atom, whereas Ca, Sr, and Ba form compounds with one of their atoms to one oxygen atom. Fluorine (F), chlorine (Cl), bromine (Br), and iodine (I) also exhibit similar properties to each other, but these properties are drastically different from those of any of the elements above.

Dimitri Mendeleev in Russia (1869) and Lothar Meyer in Germany (1870) independently recognized that there was a periodic relationship among the properties of the elements known at that time. Both published tables with the elements arranged according to increasing atomic mass. But Mendeleev went one step further than Meyer: He used his table to predict the existence of elements that would have the properties similar to aluminum and silicon, but were yet unknown. The discoveries of gallium (1875) and germanium (1886) provided great support for Mendeleev's work. Although Mendeleev and Meyer had a long dispute over priority, Mendeleev's contributions to the development of the periodic table are now more widely recognized (Figure 1.2.6.1).



Reihen	Gruppe I. — R²O	Gruppe II. — RO	Gruppe III. — R²O³	Gruppe IV. RH⁴ RO²	Gruppe V. RH³ R²O⁵	Gruppe VI. RH² RO³	Gruppe VII. RH R²O⁷	Gruppe VIII. — RO⁴
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=86	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

(a) (b)

Figure 1.2.6.1: (a) Dimitri Mendeleev is widely credited with creating (b) the first periodic table of the elements. (credit a: modification of work by Serge Lachinov; credit b: modification of work by “Den fjättrade ankan”/Wikimedia Commons)

Figure A shows a photograph of Dimitri Mendeleev. Figure B shows the first periodic table developed by Mendeleev, which had eight groups and twelve periods. In the first group (—, R superscript plus sign 0) is the following information: H = 1, L i = 7, N a = 23, K = 39, (C u = 63), R b = 85, (A g = 108), C a = 183, (—),—, (A u = 199) —. Note that each of these entries corresponds to one of the twelve periods respectively. The second group (—, R 0) contains the following information: (not entry for period 1) B o = 9, 4, M g = 24, C a = 40, Z n = 65, S r = 87, C d = 112, B a = 187, —, —, H g = 200, —. Note the ach of these entries corresponds to one of the twelve periods respectively. Group three (—, R superscript one 0 superscript nine) contains the information: (no entry for period 1), B = 11, A l = 27, 8. — = 44, — = 68, ? Y t = 88, I n = 113, ? D I = 138, —, ? E r = 178, T l = 204, —. Note that each of these entries corresponds to one of the twelve periods respectively. Group four (RH superscript four, R0 superscript eight) contains the following information: (no entry for period 1), C = 12, B i = 28, T i = 48, — = 72, Z r = 90, S n = 118, ? C o = 140, ? L a = 180, P b = 207, T h = 231. Note that each of these entries corresponds to one of the twelve periods respectively. Group five (R H superscript two, R superscript two 0 superscript five) contains the following information: (no entry for period 1), N = 14, P = 31, V = 51, A s = 75, N b = 94, S b = 122, —, —, T a = 182, B l = 208, —. Note that each of these entries corresponds to one of the twelve periods respectively. Group six (R H superscript two, R 0 superscript three) contains the following information: (no entry for period 1), O = 16, S = 32, C r = 52, S o = 78, M o = 96, T o = 125, —, —, W = 184, —, U = 240. Note that each of these entries corresponds to one of the twelve periods respectively. Group seven (R H , R superscript plus sing, 0 superscript 7) contains the following information: (no entry for period 1), F = 19, C l = 35, 5, M n = 55, B r = 80, — = 100, J = 127, —, —, —, —, —. Note that each of these entries corresponds to one of the twelve periods respectively. Group 8 (—, R 0 superscript four) contains the following information: (no entry for periods 1, 2, 3), in period 4: F o = 56, C o = 59, N i = 59, C u = 63, no entry for period five, in period 6: R u = 104, R h = 104, P d = 106, A g = 108, no entries for periods 7, 8 , or 9, in period 10: O s = 195, I r = 197, P t = 198, A u = 199, no entries for periods 11 or 12.

By the twentieth century, it became apparent that the periodic relationship involved atomic numbers rather than atomic masses. The modern statement of this relationship, the periodic law, is as follows: *the properties of the elements are periodic functions of their atomic numbers.* A modern periodic table arranges the elements in increasing order of their atomic numbers and groups atoms with similar properties in the same vertical column (Figure 1.2.6.2). Each box represents an element and contains its atomic number, symbol, average atomic mass, and (sometimes) name. The elements are arranged in seven horizontal rows, called periods or series, and 18 vertical columns, called groups. Groups are labeled at the top of each column. In the United States, the labels traditionally were numerals with capital letters. However, IUPAC recommends that the numbers 1 through 18 be used, and these labels are more common. For the table to fit on a single page, parts of two of the rows, a total of 14 columns, are usually written below the main body of the table.

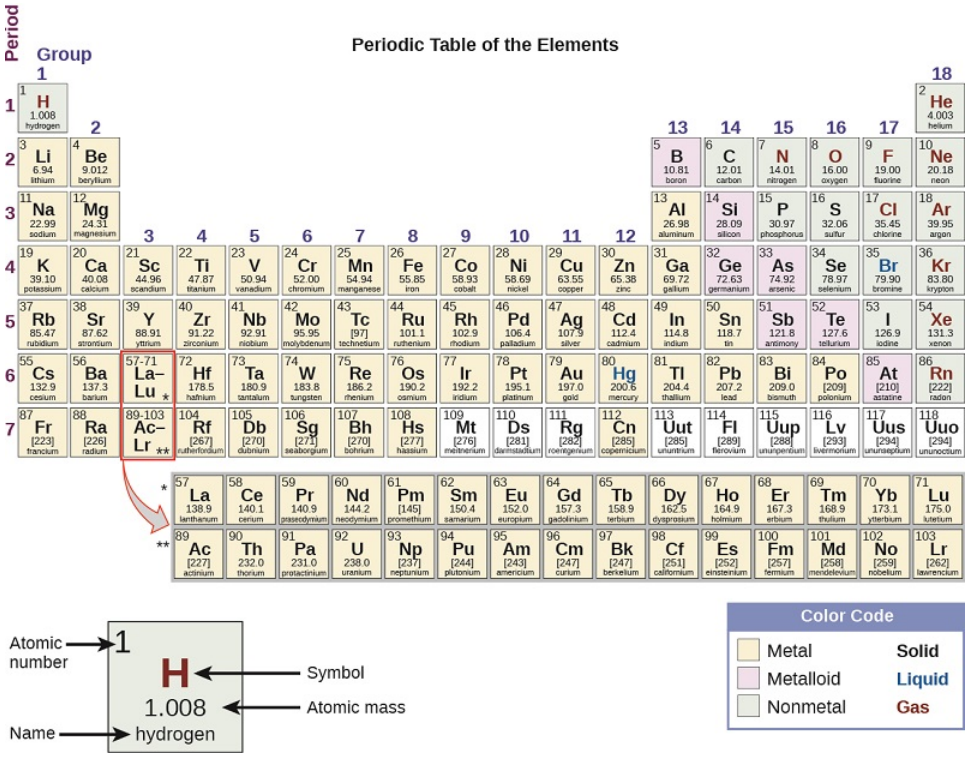


Figure 1.2.6.2: Elements in the periodic table are organized according to their properties.

The Periodic Table of Elements is shown. The 18 columns are labeled “Group” and the 7 rows are labeled “Period.” Below the table to the right is a box labeled “Color Code” with different colors for metals, metalloids, and nonmetals, as well as solids, liquids, and gases. To the left of this box is an enlarged picture of the upper-left most box on the table. The number 1 is in its upper-left hand corner and is labeled “Atomic number.” The letter “H” is in the middle in red indicating that it is a gas. It is labeled “Symbol.” Below that is the number 1.008 which is labeled “Atomic Mass.” Below that is the word hydrogen which is labeled “name.” The color of the box indicates that it is a nonmetal. Each element will be described in this order: atomic number; name; symbol; whether it is a metal, metalloid, or nonmetal; whether it is a solid, liquid, or gas; and atomic mass. Beginning at the top left of the table, or period 1, group 1, is a box containing “1; hydrogen; H; nonmetal; gas; and 1.008.” There is only one other element box in period 1, group 18, which contains “2; helium; H e; nonmetal; gas; and 4.003.” Period 2, group 1 contains “3; lithium; L i; metal; solid; and 6.94” Group 2 contains “4; beryllium; B e; metal; solid; and 9.012.” Groups 3 through 12 are skipped and group 13 contains “5; boron; B; metalloid; solid; 10.81.” Group 14 contains “6; carbon; C; nonmetal; solid; and 12.01.” Group 15 contains “7; nitrogen; N; nonmetal; gas; and 14.01.” Group 16 contains “8; oxygen; O; nonmetal; gas; and 16.00.” Group 17 contains “9; fluorine; F; nonmetal; gas; and 19.00.” Group 18 contains “10; neon; N e; nonmetal; gas; and 20.18.” Period 3, group 1 contains “11; sodium; N a; metal; solid; and 22.99.” Group 2 contains “12; magnesium; M g; metal; solid; and 24.31.” Groups 3 through 12 are skipped again in period 3 and group 13 contains “13; aluminum; A l; metal; solid; and 26.98.” Group 14 contains “14; silicon; S i; metalloid; solid; and 28.09.” Group 15 contains “15; phosphorous; P; nonmetal; solid; and 30.97.” Group 16 contains “16; sulfur; S; nonmetal; solid; and 32.06.” Group 17 contains “17; chlorine; C l; nonmetal; gas; and 35.45.” Group 18 contains “18; argon; A r; nonmetal; gas; and 39.95.” Period 4, group 1 contains “19; potassium; K; metal; solid; and 39.10.” Group 2 contains “20; calcium; C a; metal; solid; and 40.08.” Group 3 contains “21; scandium; S c; metal; solid; and 44.96.” Group 4 contains “22; titanium; T i; metal; solid; and 47.87.” Group 5 contains “23; vanadium; V; metal; solid; and 50.94.” Group 6 contains “24; chromium; C r; metal; solid; and 52.00.” Group 7 contains “25; manganese; M n; metal; solid; and 54.94.” Group 8 contains “26; iron; F e; metal; solid; and 55.85.” Group 9 contains “27; cobalt; C o; metal; solid; and 58.93.” Group 10 contains “28; nickel; N i; metal; solid; and 58.69.” Group 11 contains “29; copper; C u; metal; solid; and 63.55.” Group 12 contains “30; zinc; Z n; metal; solid; and 65.38.” Group 13 contains “31; gallium; G a; metal; solid; and 69.72.” Group 14 contains “32; germanium; G e; metalloid; solid; and 72.63.” Group 15 contains “33; arsenic; A s; metalloid; solid; and 74.92.” Group 16 contains “34; selenium; S e; nonmetal; solid; and 78.97.” Group 17 contains “35; bromine; B r; nonmetal; liquid; and 79.90.” Group 18 contains “36; krypton; K r; nonmetal; gas; and 83.80.” Period 5, group 1 contains “37; rubidium; R b; metal; solid; and 85.47.” Group 2 contains “38; strontium; S r; metal; solid; and 87.62.” Group 3 contains “39; yttrium; Y; metal; solid; and 88.91.” Group 4 contains “40; zirconium; Z r; metal; solid; and 91.22.” Group 5 contains “41; niobium; N b; metal; solid; and 92.91.” Group 6 contains “42; molybdenum; M o; metal; solid; and 95.95.” Group 7 contains “43; technetium; T c; metal; solid; and 97.” Group 8 contains “44; ruthenium; R u; metal; solid; and 101.1.” Group 9 contains “45; rhodium; R h; metal; solid; and 102.9.” Group 10 contains “46; palladium; P d; metal; solid; and 106.4.” Group 11 contains “47; silver; A g; metal; solid; and 107.9.” Group 12 contains “48; cadmium; C d; metal; solid; and 112.4.” Group 13 contains “49; indium; I n; metal; solid; and 114.8.” Group 14 contains “50; tin; S n; metal; solid; and 118.7.” Group 15 contains “51; antimony; S b; metalloid; solid; and 121.8.” Group 16 contains “52; tellurium; T e; metalloid; solid; and 127.6.” Group 17 contains “53; iodine; I; nonmetal; solid; and 126.9.” Group 18 contains “54; xenon; X e; nonmetal; gas; and 131.3.” Period 6, group 1 contains “55; cesium; C s; metal; solid; and 132.9.” Group 2 contains “56; barium; B a; metal; solid; and 137.3.” Group 3 breaks the pattern. The box has a large arrow pointing to a row of elements below the table with atomic numbers ranging from 57-71. In sequential order by atomic number, the first box in this row

contains “57; lanthanum; L a; metal; solid; and 138.9.” To its right, the next is “58; cerium; C e; metal; solid; and 140.1.” Next is “59; praseodymium; P r; metal; solid; and 140.9.” Next is “60; neodymium; N d; metal; solid; and 144.2.” Next is “61; promethium; P m; metal; solid; and 145.” Next is “62; samarium; S m; metal; solid; and 150.4.” Next is “63; europium; E u; metal; solid; and 152.0.” Next is “64; gadolinium; G d; metal; solid; and 157.3.” Next is “65; terbium; T b; metal; solid; and 158.9.” Next is “66; dysprosium; D y; metal; solid; and 162.5.” Next is “67; holmium; H o; metal; solid; and 164.9.” Next is “68; erbium; E r; metal; solid; and 167.3.” Next is “69; thulium; T m; metal; solid; and 168.9.” Next is “70; ytterbium; Y b; metal; solid; and 173.1.” The last in this special row is “71; lutetium; L u; metal; solid; and 175.0.” Continuing in period 6, group 4 contains “72; hafnium; H f; metal; solid; and 178.5.” Group 5 contains “73; tantalum; T a; metal; solid; and 180.9.” Group 6 contains “74; tungsten; W; metal; solid; and 183.8.” Group 7 contains “75; rhenium; R e; metal; solid; and 186.2.” Group 8 contains “76; osmium; O s; metal; solid; and 190.2.” Group 9 contains “77; iridium; I r; metal; solid; and 192.2.” Group 10 contains “78; platinum; P t; metal; solid; and 195.1.” Group 11 contains “79; gold; A u; metal; solid; and 197.0.” Group 12 contains “80; mercury; H g; metal; liquid; and 200.6.” Group 13 contains “81; thallium; T l; metal; solid; and 204.4.” Group 14 contains “82; lead; P b; metal; solid; and 207.2.” Group 15 contains “83; bismuth; B i; metal; solid; and 209.0.” Group 16 contains “84; polonium; P o; metal; solid; and 209.” Group 17 contains “85; astatine; A t; metalloid; solid; and 210.” Group 18 contains “86; radon; R n; nonmetal; gas; and 222.” Period 7, group 1 contains “87; francium; F r; metal; solid; and 223.” Group 2 contains “88; radium; R a; metal; solid; and 226.” Group 3 breaks the pattern much like what occurs in period 6. A large arrow points from the box in period 7, group 3 to a special row containing the elements with atomic numbers ranging from 89-103, just below the row which contains atomic numbers 57-71. In sequential order by atomic number, the first box in this row contains “89; actinium; A c; metal; solid; and 227.” To its right, the next is “90; thorium; T h; metal; solid; and 232.0.” Next is “91; protactinium; P a; metal; solid; and 231.0.” Next is “92; uranium; U; metal; solid; and 238.0.” Next is “93; neptunium; N p; metal; solid; and N p.” Next is “94; plutonium; P u; metal; solid; and 244.” Next is “95; americium; A m; metal; solid; and 243.” Next is “96; curium; C m; metal; solid; and 247.” Next is “97; berkelium; B k; metal; solid; and 247.” Next is “98; californium; C f; metal; solid; and 251.” Next is “99; einsteinium; E s; metal; solid; and 252.” Next is “100; fermium; F m; metal; solid; and 257.” Next is “101; mendelevium; M d; metal; solid; and 258.” Next is “102; nobelium; N o; metal; solid; and 259.” The last in this special row is “103; lawrencium; L r; metal; solid; and 262.” Continuing in period 7, group 4 contains “104; rutherfordium; R f; metal; solid; and 267.” Group 5 contains “105; dubnium; D b; metal; solid; and 270.” Group 6 contains “106; seaborgium; S g; metal; solid; and 271.” Group 7 contains “107; bohrium; B h; metal; solid; and 270.” Group 8 contains “108; hassium; H s; metal; solid; and 277.” Group 9 contains “109; meitnerium; M t; not indicated; solid; and 276.” Group 10 contains “110; darmstadtium; D s; not indicated; solid; and 281.” Group 11 contains “111; roentgenium; R g; not indicated; solid; and 282.” Group 12 contains “112; copernicium; C n; metal; liquid; and 285.” Group 13 contains “113; ununtrium; U u t; not indicated; solid; and 285.” Group 14 contains “114; flerovium; F l; not indicated; solid; and 289.” Group 15 contains “115; ununpentium; U u p; not indicated; solid; and 288.” Group 16 contains “116; livermorium; L v; not indicated; solid; and 293.” Group 17 contains “117; ununseptium; U u s; not indicated; solid; and 294.” Group 18 contains “118; ununoctium; U u o; not indicated; solid; and 294.”

Many elements differ dramatically in their chemical and physical properties, but some elements are similar in their behaviors. For example, many elements appear shiny, are malleable (able to be deformed without breaking) and ductile (can be drawn into wires), and conduct heat and electricity well. Other elements are not shiny, malleable, or ductile, and are poor conductors of heat and electricity. We can sort the elements into large classes with common properties: metals (elements that are shiny, malleable, good conductors of heat and electricity—shaded yellow); nonmetals (elements that appear dull, poor conductors of heat and electricity—shaded green); and metalloids (elements that conduct heat and electricity moderately well, and possess some properties of metals and some properties of nonmetals—shaded purple).

The elements can also be classified into the main-group elements (or representative elements) in the columns labeled 1, 2, and 13–18; the transition metals in the columns labeled 3–12; and inner transition metals in the two rows at the bottom of the table (the top-row elements are called lanthanides and the bottom-row elements are actinides; Figure 1.2.6.3). The elements can be subdivided further by more specific properties, such as the composition of the compounds they form. For example, the elements in group 1 (the first column) form compounds that consist of one atom of the element and one atom of hydrogen. These elements (except hydrogen) are known as alkali metals, and they all have similar chemical properties. The elements in group 2 (the second column) form compounds consisting of one atom of the element and two atoms of hydrogen: These are called alkaline earth metals, with similar properties among members of that group. Other groups with specific names are the pnictogens (group 15), chalcogens (group 16), halogens (group 17), and the noble gases (group 18, also known as inert gases). The groups can also be referred to by the first element of the group: For example, the chalcogens can be called the oxygen group or oxygen family. Hydrogen is a unique, nonmetallic element with properties similar to both group 1 and group 17 elements. For that reason, hydrogen may be shown at the top of both groups, or by itself.

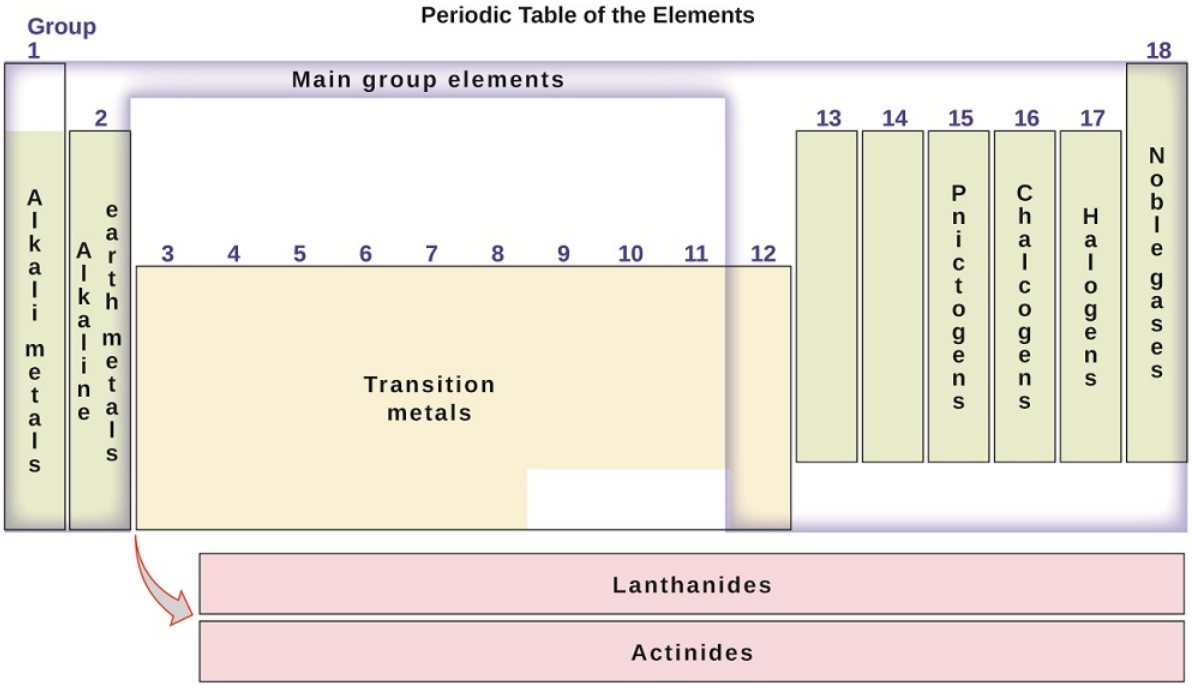


Figure 1.2.6.3: The periodic table organizes elements with similar properties into groups.

This diagram combines the groups and periods of the periodic table based on their similar properties. Group 1 contains the alkali metals, group 2 contains the earth alkaline metals, group 15 contains the pnictogens, group 16 contains the chalcogens, group 17 contains the halogens and group 18 contains the noble gases. The main group elements consist of groups 1, 2, and 12 through 18. Therefore, most of the transition metals, which are contained in groups 3 through 11, are not main group elements. The lanthanides and actinides are called out at the bottom of the periodic table.

✔ Example 1.2.6.1: Naming Groups of Elements

Atoms of each of the following elements are essential for life. Give the group name for the following elements:

a. chlorine
b. calcium
c. sodium
d. sulfur

Solution

The family names are as follows:

a. halogen
b. alkaline earth metal
c. alkali metal
d. chalcogen

? Exercise 1.2.6.1

Give the group name for each of the following elements:

a. krypton
b. selenium
c. barium
d. lithium

Answer a

noble gas

Answer b

chalcogen

Answer c

alkaline earth metal

Answer d

alkali metal

In studying the periodic table, you might have noticed something about the atomic masses of some of the elements. Element 43 (technetium), element 61 (promethium), and most of the elements with atomic number 84 (polonium) and higher have their atomic mass given in square brackets. This is done for elements that consist entirely of unstable, radioactive isotopes (you will learn more about radioactivity in the nuclear chemistry chapter). An average atomic weight cannot be determined for these elements because their radioisotopes may vary significantly in relative abundance, depending on the source, or may not even exist in nature. The number in square brackets is the atomic mass number (and approximate atomic mass) of the most stable isotope of that element.

Summary

The discovery of the periodic recurrence of similar properties among the elements led to the formulation of the periodic table, in which the elements are arranged in order of increasing atomic number in rows known as periods and columns known as groups. Elements in the same group of the periodic table have similar chemical properties. Elements can be classified as metals, metalloids, and nonmetals, or as a main-group elements, transition metals, and inner transition metals. Groups are numbered 1–18 from left to right. The elements in group 1 are known as the alkali metals; those in group 2 are the alkaline earth metals; those in 15 are the pnictogens; those in 16 are the chalcogens; those in 17 are the halogens; and those in 18 are the noble gases.

Glossary

actinide
inner transition metal in the bottom of the bottom two rows of the periodic table

alkali metal
element in group 1

alkaline earth metal
element in group 2

chalcogen
element in group 16

group
vertical column of the periodic table

halogen
element in group 17

inert gas
(also, noble gas) element in group 18

inner transition metal
(also, lanthanide or actinide) element in the bottom two rows; if in the first row, also called lanthanide, or if in the second row, also called actinide

lanthanide
inner transition metal in the top of the bottom two rows of the periodic table

main-group element
(also, representative element) element in columns 1, 2, and 12–18

metal
element that is shiny, malleable, good conductor of heat and electricity

metalloid
element that conducts heat and electricity moderately well, and possesses some properties of metals and some properties of nonmetals

noble gas
(also, inert gas) element in group 18

nonmetal
element that appears dull, poor conductor of heat and electricity

period
(also, series) horizontal row of the periodic table

periodic law
properties of the elements are periodic function of their atomic numbers.

periodic table
table of the elements that places elements with similar chemical properties close together

pnictogen
element in group 15

representative element
(also, main-group element) element in columns 1, 2, and 12–18

transition metal
element in columns 3–11

series
(also, period) horizontal row of the period table

This page titled 1.2.6: The Periodic Table is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **2.6: The Periodic Table** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

1.2.7: Molecular and Ionic Compounds

Learning Objectives

- Define ionic and molecular (covalent) compounds
- Predict the type of compound formed from elements based on their location within the periodic table
- Determine formulas for simple ionic compounds

In ordinary chemical reactions, the nucleus of each atom (and thus the identity of the element) remains unchanged. Electrons, however, can be added to atoms by transfer from other atoms, lost by transfer to other atoms, or shared with other atoms. The transfer and sharing of electrons among atoms govern the chemistry of the elements. During the formation of some compounds, atoms gain or lose electrons, and form electrically charged particles called ions (Figure 1.2.7.1).

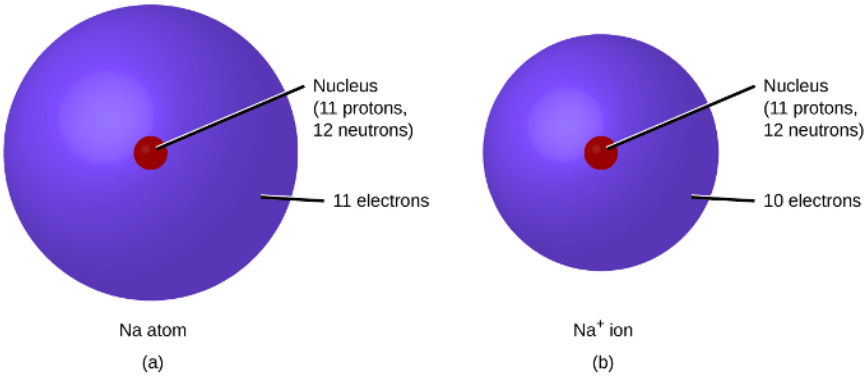


Figure 1.2.7.1: (a) A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. (b) A sodium cation (Na^+) has lost an electron, so it has one more proton (11) than electrons (10), giving it an overall positive charge, signified by a superscripted plus sign.

Figure A shows a sodium atom which has a nucleus containing 11 protons, 12 neutrons, and 11 electrons. Figure B shows a sodium ion. Its nucleus contains 11 protons, 12 neutrons, and 11 electrons.

You can use the periodic table to predict whether an atom will form an anion or a cation, and you can often predict the charge of the resulting ion. Atoms of many main-group metals lose enough electrons to leave them with the same number of electrons as an atom of the preceding noble gas. To illustrate, an atom of an alkali metal (group 1) loses one electron and forms a cation with a 1+ charge; an alkaline earth metal (group 2) loses two electrons and forms a cation with a 2+ charge, and so on. For example, a neutral calcium atom, with 20 protons and 20 electrons, readily loses two electrons. This results in a cation with 20 protons, 18 electrons, and a 2+ charge. It has the same number of electrons as atoms of the preceding noble gas, argon, and is symbolized Ca^{2+}. The name of a metal ion is the same as the name of the metal atom from which it forms, so Ca^{2+} is called a calcium ion.

When atoms of nonmetal elements form ions, they generally gain enough electrons to give them the same number of electrons as an atom of the next noble gas in the periodic table. Atoms of group 17 gain one electron and form anions with a 1− charge; atoms of group 16 gain two electrons and form ions with a 2− charge, and so on. For example, the neutral bromine atom, with 35 protons and 35 electrons, can gain one electron to provide it with 36 electrons. This results in an anion with 35 protons, 36 electrons, and a 1− charge. It has the same number of electrons as atoms of the next noble gas, krypton, and is symbolized Br^-. (A discussion of the theory supporting the favored status of noble gas electron numbers reflected in these predictive rules for ion formation is provided in a later chapter of this text.)

Note the usefulness of the periodic table in predicting likely ion formation and charge (Figure 1.2.7.2). Moving from the far left to the right on the periodic table, main-group elements tend to form cations with a charge equal to the group number. That is, group 1 elements form 1+ ions; group 2 elements form 2+ ions, and so on. Moving from the far right to the left on the periodic table, elements often form anions with a negative charge equal to the number of groups moved left from the noble gases. For example, group 17 elements (one group left of the noble gases) form 1− ions; group 16 elements (two groups left) form 2− ions, and so on. This trend can be used as a guide in many cases, but its predictive value decreases when moving toward the center of the periodic table. In fact, transition metals and some other metals often exhibit variable charges that are not predictable by their location in the table. For example, copper can form ions with a 1+ or 2+ charge, and iron can form ions with a 2+ or 3+ charge.

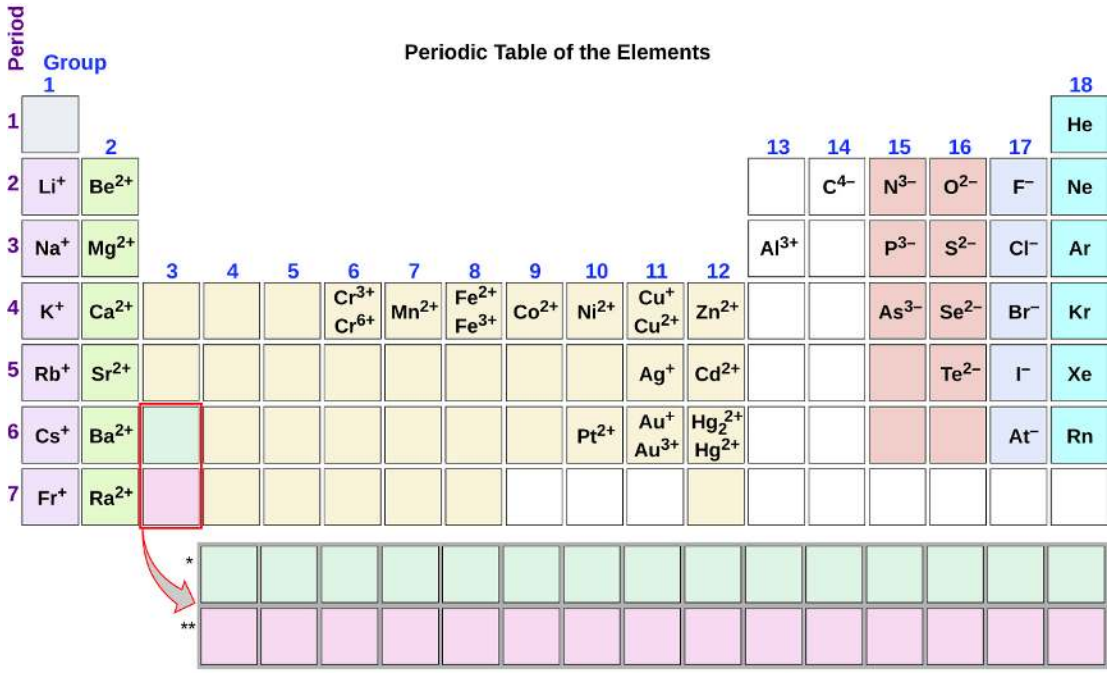


Figure 1.2.7.2: Some elements exhibit a regular pattern of ionic charge when they form ions.

This periodic table shows the charges of ions corresponding with the group number. Starting with a charge of positive one for group 1, positive 2 for group 2, and negative 4, 3, 2, and 1 for groups 14, 15, 16, and 17 respectively. Noble gases on the far right do not have any charges. Some of the ions of transition metals are shown, with multiple charges existing for certain metals.

✔ Example 1.2.7.1: Composition of Ions

An ion found in some compounds used as antiperspirants contains 13 protons and 10 electrons. What is its symbol?

Solution

Because the number of protons remains unchanged when an atom forms an ion, the atomic number of the element must be 13. Knowing this lets us use the periodic table to identify the element as Al (aluminum). The Al atom has lost three electrons and thus has three more positive charges (13) than it has electrons (10). This is the aluminum cation, Al^{3+}.

? Exercise 1.2.7.1

Give the symbol and name for the ion with 34 protons and 36 electrons.

Answer

Se^{2-}, the selenide ion

✔ Example 1.2.7.2: Formation of Ions

Magnesium and nitrogen react to form an ionic compound. Predict which forms an anion, which forms a cation, and the charges of each ion. Write the symbol for each ion and name them.

Solution

Magnesium's position in the periodic table (group 2) tells us that it is a metal. Metals form positive ions (cations). A magnesium atom must lose two electrons to have the same number electrons as an atom of the previous noble gas, neon. Thus, a magnesium atom will form a cation with two fewer electrons than protons and a charge of 2+. The symbol for the ion is Mg^{2+}, and it is called a magnesium ion.

Nitrogen's position in the periodic table (group 15) reveals that it is a nonmetal. Nonmetals form negative ions (anions). A nitrogen atom must gain three electrons to have the same number of electrons as an atom of the following noble gas, neon.

Thus, a nitrogen atom will form an anion with three more electrons than protons and a charge of 3−. The symbol for the ion is N^{3-}, and it is called a nitride ion.

? Exercise 1.2.7.2

Aluminum and carbon react to form an ionic compound. Predict which forms an anion, which forms a cation, and the charges of each ion. Write the symbol for each ion and name them.

Answer

Al will form a cation with a charge of 3+: Al^{3+}, an aluminum ion. Carbon will form an anion with a charge of 4−: C^{4-}, a carbide ion.

The ions that we have discussed so far are called monatomic ions, that is, they are ions formed from only one atom. We also find many polyatomic ions. These ions, which act as discrete units, are electrically charged molecules (a group of bonded atoms with an overall charge). Some of the more important polyatomic ions are listed in Table 1.2.7.1. Oxyanions are polyatomic ions that contain one or more oxygen atoms. At this point in your study of chemistry, you should memorize the names, formulas, and charges of the most common polyatomic ions. Because you will use them repeatedly, they will soon become familiar.

Table 1.2.7.1: Common Polyatomic Ions

Name	Formula	Related Acid	Formula
ammonium	NH_4^+		
hydronium	H_3O^+		
oxide	O^{2-}		
peroxide	O_2^{2-}		
hydroxide	OH^-		
acetate	CH_3COO^-	acetic acid	CH_3COOH
cyanide	CN^-	hydrocyanic acid	HCN
azide	N_3^-	hydrazoic acid	HN_3
carbonate	CO_3^{2-}	carbonic acid	H_2CO_3
bicarbonate	HCO_3^-		
nitrate	NO_3^-	nitric acid	HNO_3
nitrite	NO_2^-	nitrous acid	HNO_2
sulfate	SO_4^{2-}	sulfuric acid	H_2SO_4
hydrogen sulfate	HSO_4^-		
sulfite	SO_3^{2-}	sulfurous acid	H_2SO_3
hydrogen sulfite	HSO_3^-		
phosphate	PO_4^{3-}	phosphoric acid	H_3PO_4
hydrogen phosphate	HPO_4^{2-}		
dihydrogen phosphate	$H_2PO_4^-$		
perchlorate	ClO_4^-	perchloric acid	$HClO_4$
chlorate	ClO_3^-	chloric acid	$HClO_3$

Name	Formula	Related Acid	Formula
chlorite	ClO_2^-	chlorous acid	$HClO_2$
hypochlorite	ClO^-	hypochlorous acid	$HClO$
chromate	CrO_4^{2-}	chromic acid	H_2CrO_4
dichromate	$Cr_2O_7^{2-}$	dichromic acid	$H_2Cr_2O_7$
permanganate	MnO_4^-	permanganic acid	$HMnO_4$

Note that there is a system for naming some polyatomic ions; *-ate* and *-ite* are suffixes designating polyatomic ions containing more or fewer oxygen atoms. *Per-* (short for "hyper") and *hypo-* (meaning "under") are prefixes meaning more oxygen atoms than *-ate* and fewer oxygen atoms than *-ite*, respectively. For example, perchlorate is ClO_4^-, chlorate is ClO_3^-, chlorite is ClO_2^- and hypochlorite is ClO^-. Unfortunately, the number of oxygen atoms corresponding to a given suffix or prefix is not consistent; for example, nitrate is NO_3^- while sulfate is SO_4^{2-}. This will be covered in more detail in the next module on nomenclature.

The nature of the attractive forces that hold atoms or ions together within a compound is the basis for classifying chemical bonding. When electrons are transferred and ions form, ionic bonds result. Ionic bonds are electrostatic forces of attraction, that is, the attractive forces experienced between objects of opposite electrical charge (in this case, cations and anions). When electrons are "shared" and molecules form, covalent bonds result. Covalent bonds are the attractive forces between the positively charged nuclei of the bonded atoms and one or more pairs of electrons that are located between the atoms. Compounds are classified as ionic or molecular (covalent) on the basis of the bonds present in them.

1.2.7.1: Ionic Compounds

When an element composed of atoms that readily lose electrons (a metal) reacts with an element composed of atoms that readily gain electrons (a nonmetal), a transfer of electrons usually occurs, producing ions. The compound formed by this transfer is stabilized by the electrostatic attractions (ionic bonds) between the ions of opposite charge present in the compound. For example, when each sodium atom in a sample of sodium metal (group 1) gives up one electron to form a sodium cation, Na^+, and each chlorine atom in a sample of chlorine gas (group 17) accepts one electron to form a chloride anion, Cl^-, the resulting compound, NaCl, is composed of sodium ions and chloride ions in the ratio of one Na^+ ion for each Cl^- ion. Similarly, each calcium atom (group 2) can give up two electrons and transfer one to each of two chlorine atoms to form $CaCl_2$, which is composed of Ca^{2+} and Cl^- ions in the ratio of one Ca^{2+} ion to two Cl^- ions.

A compound that contains ions and is held together by ionic bonds is called an ionic compound. The periodic table can help us recognize many of the compounds that are ionic: When a metal is combined with one or more nonmetals, the compound is usually ionic. This guideline works well for predicting ionic compound formation for most of the compounds typically encountered in an introductory chemistry course. However, it is not always true (for example, aluminum chloride, $AlCl_3$, is not ionic).

You can often recognize ionic compounds because of their properties. Ionic compounds are solids that typically melt at high temperatures and boil at even higher temperatures. For example, sodium chloride melts at 801 °C and boils at 1413 °C. (As a comparison, the molecular compound water melts at 0 °C and boils at 100 °C.) In solid form, an ionic compound is not electrically conductive because its ions are unable to flow ("electricity" is the flow of charged particles). When molten, however, it can conduct electricity because its ions are able to move freely through the liquid (Figure 1.2.7.3).

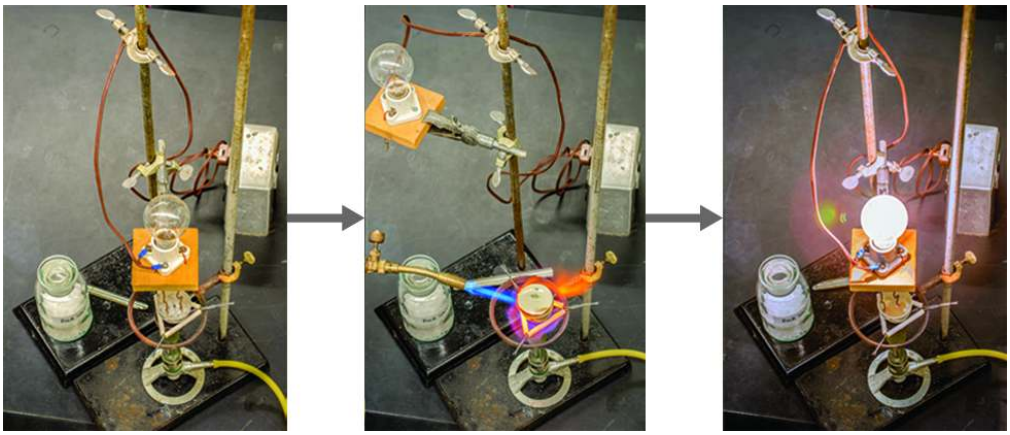


Figure 1.2.7.3: Sodium chloride melts at 801 °C and conducts electricity when molten. (credit: modification of work by Mark Blaser and Matt Evans)

This figure shows three photos connected by right-facing arrows. The first shows a light bulb as part of a complex lab equipment setup. The light bulb is not lit. The second photo shows a substances being heated or set on fire. The third shows the light bulb again which is lit.

In every ionic compound, the total number of positive charges of the cations equals the total number of negative charges of the anions. Thus, ionic compounds are electrically neutral overall, even though they contain positive and negative ions. We can use this observation to help us write the formula of an ionic compound. The formula of an ionic compound must have a ratio of ions such that the numbers of positive and negative charges are equal.

Example 1.2.7.3: Predicting the Formula of an Ionic Compound

The gemstone sapphire (Figure 1.2.7.4) is mostly a compound of aluminum and oxygen that contains aluminum cations, Al^{3+}, and oxygen anions, O^{2-}. What is the formula of this compound?



Figure 1.2.7.4: Although pure aluminum oxide is colorless, trace amounts of iron and titanium give blue sapphire its characteristic color. (credit: modification of work by Stanislav Doronenko)

Solution Because the ionic compound must be electrically neutral, it must have the same number of positive and negative charges. Two aluminum ions, each with a charge of 3+, would give us six positive charges, and three oxide ions, each with a charge of 2−, would give us six negative charges. The formula would be Al_2O_3.

Exercise 1.2.7.3

Predict the formula of the ionic compound formed between the sodium cation, Na^+, and the sulfide anion, S^{2-}.

Answer

Na_2S

Many ionic compounds contain polyatomic ions (Table 1.2.7.1) as the cation, the anion, or both. As with simple ionic compounds, these compounds must also be electrically neutral, so their formulas can be predicted by treating the polyatomic ions as discrete units. We use parentheses in a formula to indicate a group of atoms that behave as a unit. For example, the formula for calcium phosphate, one of the minerals in our bones, is $Ca_3(PO_4)_2$. This formula indicates that there are three calcium ions (Ca^{2+}) for every two phosphate $\left(PO_4^{3-}\right)$ groups. The PO_4^{3-} groups are discrete units, each consisting of one phosphorus atom and four oxygen

atoms, and having an overall charge of 3−. The compound is electrically neutral, and its formula shows a total count of three Ca, two P, and eight O atoms.

Example 1.2.7.4: Predicting the Formula of a Compound with a Polyatomic Anion

Baking powder contains calcium dihydrogen phosphate, an ionic compound composed of the ions Ca^{2+} and $H_2PO_4^-$. What is the formula of this compound?

Solution

The positive and negative charges must balance, and this ionic compound must be electrically neutral. Thus, we must have two negative charges to balance the 2+ charge of the calcium ion. This requires a ratio of one Ca^{2+} ion to two $H_2PO_4^-$ ions. We designate this by enclosing the formula for the dihydrogen phosphate ion in parentheses and adding a subscript 2. The formula is $Ca(H_2PO_4)_2$.

Exercise 1.2.7.4

Predict the formula of the ionic compound formed between the lithium ion and the peroxide ion, O_2^{2-} (Hint: Use the periodic table to predict the sign and the charge on the lithium ion.)

Answer

Li_2O_2

Because an ionic compound is not made up of single, discrete molecules, it may not be properly symbolized using a *molecular* formula. Instead, ionic compounds must be symbolized by a formula indicating the *relative numbers* of its constituent ions. For compounds containing only monatomic ions (such as NaCl) and for many compounds containing polyatomic ions (such as $CaSO_4$), these formulas are just the empirical formulas introduced earlier in this chapter. However, the formulas for some ionic compounds containing polyatomic ions are not empirical formulas. For example, the ionic compound sodium oxalate is comprised of Na^+ and $C_2O_4^{2-}$ ions combined in a 2:1 ratio, and its formula is written as $Na_2C_2O_4$. The subscripts in this formula are not the smallest-possible whole numbers, as each can be divided by 2 to yield the empirical formula, $NaCO_2$. This is not the accepted formula for sodium oxalate, however, as it does not accurately represent the compound's polyatomic anion, $C_2O_4^{2-}$.

1.2.7.2: Molecular Compounds

Many compounds do not contain ions but instead consist solely of discrete, neutral molecules. These molecular compounds (covalent compounds) result when atoms share, rather than transfer (gain or lose), electrons. Covalent bonding is an important and extensive concept in chemistry, and it will be treated in considerable detail in a later chapter of this text. We can often identify molecular compounds on the basis of their physical properties. Under normal conditions, molecular compounds often exist as gases, low-boiling liquids, and low-melting solids, although many important exceptions exist.

Whereas ionic compounds are usually formed when a metal and a nonmetal combine, covalent compounds are usually formed by a combination of nonmetals. Thus, the periodic table can help us recognize many of the compounds that are covalent. While we can use the positions of a compound's elements in the periodic table to predict whether it is ionic or covalent at this point in our study of chemistry, you should be aware that this is a very simplistic approach that does not account for a number of interesting exceptions. Shades of gray exist between ionic and molecular compounds, and you'll learn more about those later.

Example 1.2.7.5: Predicting the Type of Bonding in Compounds

Predict whether the following compounds are ionic or molecular:

a. KI, the compound used as a source of iodine in table salt
b. H_2O_2, the bleach and disinfectant hydrogen peroxide
c. $CHCl_3$, the anesthetic chloroform
d. Li_2CO_3, a source of lithium in antidepressants

Solution

a. Potassium (group 1) is a metal, and iodine (group 17) is a nonmetal; KI is predicted to be ionic.
b. Hydrogen (group 1) is a nonmetal, and oxygen (group 16) is a nonmetal; H_2O_2 is predicted to be molecular.
c. Carbon (group 14) is a nonmetal, hydrogen (group 1) is a nonmetal, and chlorine (group 17) is a nonmetal; $CHCl_3$ is predicted to be molecular.
d. Lithium (group 1) is a metal, and carbonate is a polyatomic ion; Li_2CO_3 is predicted to be ionic.

? Exercise 1.2.7.5

Using the periodic table, predict whether the following compounds are ionic or covalent:

a. SO_2
b. CaF_2
c. N_2H_4
d. $Al_2(SO_4)_3$

Answer a

molecular

Answer b

ionic

Answer c

molecular

Answer d

ionic

Summary

Metals (particularly those in groups 1 and 2) tend to lose the number of electrons that would leave them with the same number of electrons as in the preceding noble gas in the periodic table. By this means, a positively charged ion is formed. Similarly, nonmetals (especially those in groups 16 and 17, and, to a lesser extent, those in Group 15) can gain the number of electrons needed to provide atoms with the same number of electrons as in the next noble gas in the periodic table. Thus, nonmetals tend to form negative ions. Positively charged ions are called cations, and negatively charged ions are called anions. Ions can be either monatomic (containing only one atom) or polyatomic (containing more than one atom).

Compounds that contain ions are called ionic compounds. Ionic compounds generally form from metals and nonmetals. Compounds that do not contain ions, but instead consist of atoms bonded tightly together in molecules (uncharged groups of atoms that behave as a single unit), are called covalent compounds. Covalent compounds usually form from two or more nonmetals.

Glossary

covalent bond
attractive force between the nuclei of a molecule’s atoms and pairs of electrons between the atoms

covalent compound
(also, molecular compound) composed of molecules formed by atoms of two or more different elements

ionic bond
electrostatic forces of attraction between the oppositely charged ions of an ionic compound

ionic compound
compound composed of cations and anions combined in ratios, yielding an electrically neutral substance

molecular compound

(also, covalent compound) composed of molecules formed by atoms of two or more different elements

monatomic ion

ion composed of a single atom

polyatomic ion

ion composed of more than one atom

oxyanion

polyatomic anion composed of a central atom bonded to oxygen atoms

---

This page titled 1.2.7: Molecular and Ionic Compounds is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **2.7: Molecular and Ionic Compounds** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

1.2.8: Chemical Nomenclature

Learning Objectives

- Derive names for common types of inorganic compounds using a systematic approach.
- Describe how to name binary covalent compounds including acids and oxyacids.

Nomenclature, a collection of rules for naming things, is important in science and in many other situations. This module describes an approach that is used to name simple ionic and molecular compounds, such as NaCl, $CaCO_3$, and N_2O_4. The simplest of these are binary compounds, those containing only two elements, but we will also consider how to name ionic compounds containing polyatomic ions, and one specific, very important class of compounds known as acids (subsequent chapters in this text will focus on these compounds in great detail). We will limit our attention here to inorganic compounds, compounds that are composed principally of elements other than carbon, and will follow the nomenclature guidelines proposed by IUPAC. The rules for organic compounds, in which carbon is the principle element, will be treated in a later chapter on organic chemistry.

1.2.8.1: Ionic Compounds

To name an inorganic compound, we need to consider the answers to several questions. First, is the compound ionic or molecular? If the compound is ionic, does the metal form ions of only one type (fixed charge) or more than one type (variable charge)? Are the ions monatomic or polyatomic? If the compound is molecular, does it contain hydrogen? If so, does it also contain oxygen? From the answers we derive, we place the compound in an appropriate category and then name it accordingly. We will begin with the nomenclature rules for ionic compounds.

1.2.8.2: Compounds Containing Only Monatomic Ions

The name of a binary compound containing monatomic ions consists of the name of the cation (the name of the metal) followed by the name of the anion (the name of the nonmetallic element with its ending replaced by the suffix *–ide*). Some examples are given in Table 1.2.8.2

Table 1.2.8.1: Names of Some Ionic Compounds

NaCl, sodium chloride	Na_2O, sodium oxide
KBr, potassium bromide	CdS, cadmium sulfide
CaI_2, calcium iodide	Mg_3N_2, magnesium nitride
CsF, cesium fluoride	Ca_3P_2, calcium phosphide
LiCl, lithium chloride	Al_4C_3, aluminum carbide

1.2.8.3: Compounds Containing Polyatomic Ions

Compounds containing polyatomic ions are named similarly to those containing only monatomic ions, except there is no need to change to an *–ide* ending, since the suffix is already present in the name of the anion. Examples are shown in Table 1.2.8.2

CL, ammonium chloride, C a S O subscript 4 calcium sulfate, and M g subscript 3 (P O subscript 4) subscript 2 magnesium phosphate." data-quail-id="54" data-mt-width="1246">

Table 1.2.8.2: Names of Some Polyatomic Ionic Compounds

$KC_2H_3O_2$, potassium acetate	$(NH_4)Cl$, ammonium chloride
$NaHCO_3$, sodium bicarbonate	$CaSO_4$, calcium sulfate
$Al_2(CO_3)_3$, aluminum carbonate	$Mg_3(PO_4)_2$, magnesium phosphate

Ionic Compounds in Your Cabinets

Every day you encounter and use a large number of ionic compounds. Some of these compounds, where they are found, and what they are used for are listed in Table 1.2.8.3 Look at the label or ingredients list on the various products that you use during the next few days, and see if you run into any of those in this table, or find other ionic compounds that you could now name or write as a formula.

Table 1.2.8.3: Everyday Ionic Compounds

Ionic Compound	Name	Use
NaCl	sodium chloride	ordinary table salt
KI	potassium iodide	added to “iodized” salt for thyroid health
NaF	sodium fluoride	ingredient in toothpaste
$NaHCO_3$	sodium bicarbonate	baking soda; used in cooking (and in antacids)
Na_2CO_3	sodium carbonate	washing soda; used in cleaning agents
NaOCl	sodium hypochlorite	active ingredient in household bleach
$CaCO_3$	calcium carbonate	ingredient in antacids
$Mg(OH)_2$	magnesium hydroxide	ingredient in antacids
$Al(OH)_3$	aluminum hydroxide	ingredient in antacids
NaOH	sodium hydroxide	lye; used as drain cleaner
K_3PO_4	potassium phosphate	food additive (many purposes)
$MgSO_4$	magnesium sulfate	added to purified water
Na_2HPO_4	sodium hydrogen phosphate	anti-caking agent; used in powdered products
Na_2SO_3	sodium sulfite	preservative

1.2.8.4: Compounds Containing a Metal Ion with a Variable Charge

Most of the transition metals can form two or more cations with different charges. Compounds of these metals with nonmetals are named with the same method as compounds in the first category, except the charge of the metal ion is specified by a Roman numeral in parentheses after the name of the metal. The charge of the metal ion is determined from the formula of the compound and the charge of the anion. For example, consider binary ionic compounds of iron and chlorine. Iron typically exhibits a charge of either 2+ or 3+, and the two corresponding compound formulas are $FeCl_2$ and $FeCl_3$. The simplest name, “iron chloride,” will, in this case, be ambiguous, as it does not distinguish between these two compounds. In cases like this, the charge of the metal ion is included as a Roman numeral in parentheses immediately following the metal name. These two compounds are then unambiguously named iron(II) chloride and iron(III) chloride, respectively. Other examples are provided in Table 1.2.8.4

Table 1.2.8.4: Names of Some Transition Metal Ionic Compounds

Transition Metal Ionic Compound	Name
$FeCl_3$	iron(III) chloride
Hg_2O	mercury(I) oxide
HgO	mercury(II) oxide
$Cu_3(PO_4)_2$	copper(II) phosphate

Out-of-date nomenclature used the suffixes *–ic* and *–ous* to designate metals with higher and lower charges, respectively: Iron(III) chloride, $FeCl_3$, was previously called ferric chloride, and iron(II) chloride, $FeCl_2$, was known as ferrous chloride. Though this naming convention has been largely abandoned by the scientific community, it remains in use by some segments of industry. For example, you may see the words *stannous fluoride* on a tube of toothpaste. This represents the formula SnF_2, which is more properly named tin(II) fluoride. The other fluoride of tin is SnF_4, which was previously called stannic fluoride but is now named tin(IV) fluoride.

Example 1.2.8.1: Naming Ionic Compounds

Name the following ionic compounds, which contain a metal that can have more than one ionic charge:

a. Fe_2S_3
b. CuSe
c. GaN
d. $CrCl_3$
e. $Ti_2(SO_4)_3$

Solution

The anions in these compounds have a fixed negative charge (S^{2-}, Se^{2-}, N^{3-}, Cl^-, and SO_4^{2-}), and the compounds must be neutral. Because the total number of positive charges in each compound must equal the total number of negative charges, the positive ions must be Fe^{3+}, Cu^{2+}, Ga^{3+}, Cr^{3+}, and Ti^{3+}. These charges are used in the names of the metal ions:

a. iron(III) sulfide
b. copper(II) selenide
c. gallium(III) nitride
d. chromium(III) chloride
e. titanium(III) sulfate

Exercise 1.2.8.1

Write the formulas of the following ionic compounds:

a. chromium(III) phosphide
b. mercury(II) sulfide
c. manganese(II) phosphate
d. copper(I) oxide
e. chromium(VI) fluoride

Answer a

CrP

Answer b

HgS

Answer c

$Mn_3(PO_4)_2$

Answer d

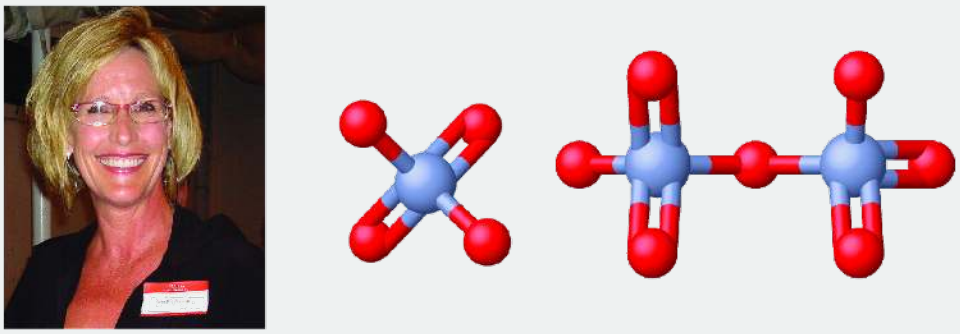
Cu_2O

Answer e

CrF_6

Erin Brokovich and Chromium Contamination

In the early 1990s, legal file clerk Erin Brockovich (Figure 1.2.8.2) discovered a high rate of serious illnesses in the small town of Hinckley, California. Her investigation eventually linked the illnesses to groundwater contaminated by Cr(VI) used by Pacific Gas & Electric (PG&E) to fight corrosion in a nearby natural gas pipeline. As dramatized in the film *Erin Brokovich* (for which Julia Roberts won an Oscar), Erin and lawyer Edward Masry sued PG&E for contaminating the water near Hinckley in 1993. The settlement they won in 1996—$333 million—was the largest amount ever awarded for a direct-action lawsuit in the US at that time.



(a) (b)

Figure **1.2.8.2**: (a) Erin Brockovich found that Cr(VI), used by PG&E, had contaminated the Hinckley, California, water supply. (b) The Cr(VI) ion is often present in water as the polyatomic ions chromate, CrO_4^{2-} (left), and dichromate, $Cr_2O_7^{2-}$ (right).

Chromium compounds are widely used in industry, such as for chrome plating, in dye-making, as preservatives, and to prevent corrosion in cooling tower water, as occurred near Hinckley. In the environment, chromium exists primarily in either the Cr(III) or Cr(VI) forms. Cr(III), an ingredient of many vitamin and nutritional supplements, forms compounds that are not very soluble in water, and it has low toxicity. Cr(VI), on the other hand, is much more toxic and forms compounds that are reasonably soluble in water. Exposure to small amounts of Cr(VI) can lead to damage of the respiratory, gastrointestinal, and immune systems, as well as the kidneys, liver, blood, and skin.

Despite cleanup efforts, Cr(VI) groundwater contamination remains a problem in Hinckley and other locations across the globe. A 2010 study by the Environmental Working Group found that of 35 US cities tested, 31 had higher levels of Cr(VI) in their tap water than the public health goal of 0.02 parts per billion set by the California Environmental Protection Agency.

1.2.8.5: Molecular (Covalent) Compounds

The bonding characteristics of inorganic molecular compounds are different from ionic compounds, and they are named using a different system as well. The charges of cations and anions dictate their ratios in ionic compounds, so specifying the names of the ions provides sufficient information to determine chemical formulas. However, because covalent bonding allows for significant variation in the combination ratios of the atoms in a molecule, the names for molecular compounds must explicitly identify these ratios.

1.2.8.6: Compounds Composed of Two Elements

When two nonmetallic elements form a molecular compound, several combination ratios are often possible. For example, carbon and oxygen can form the compounds CO and CO_2. Since these are different substances with different properties, they cannot both have the same name (they cannot both be called carbon oxide). To deal with this situation, we use a naming method that is somewhat similar to that used for ionic compounds, but with added prefixes to specify the numbers of atoms of each element. The name of the more metallic element (the one farther to the left and/or bottom of the periodic table) is first, followed by the name of the more nonmetallic element (the one farther to the right and/or top) with its ending changed to the suffix *–ide*. The numbers of atoms of each element are designated by the Greek prefixes shown in Table 1.2.8.5

Table 1.2.8.5: Nomenclature Prefixes

Number	Prefix	Number	Prefix

Number	Prefix		Number	Prefix
1 (sometimes omitted)	mono-		6	hexa-
2	di-		7	hepta-
3	tri-		8	octa-
4	tetra-		9	nona-
5	penta-		10	deca-

When only one atom of the first element is present, the prefix *mono-* is usually deleted from that part. Thus, CO is named carbon monoxide, and CO_2 is called carbon dioxide. When two vowels are adjacent, the *a* in the Greek prefix is usually dropped. Some other examples are shown in Table 1.2.8.6

Table 1.2.8.6: Names of Some Molecular Compounds Composed of Two Elements

Compound	Name		Compound	Name
SO_2	sulfur dioxide		BCl_3	boron trichloride
SO_3	sulfur trioxide		SF_6	sulfur hexafluoride
NO_2	nitrogen dioxide		PF_5	phosphorus pentafluoride
N_2O_4	dinitrogen tetroxide		P_4O_{10}	tetraphosphorus decaoxide
N_2O_5	dinitrogen pentoxide		IF_7	iodine heptafluoride

There are a few common names that you will encounter as you continue your study of chemistry. For example, although NO is often called nitric oxide, its proper name is nitrogen monoxide. Similarly, N_2O is known as nitrous oxide even though our rules would specify the name dinitrogen monoxide. (And H_2O is usually called water, not dihydrogen monoxide.) You should commit to memory the common names of compounds as you encounter them.

✔ Example 1.2.8.2: Naming Covalent Compounds

Name the following covalent compounds:

a. SF_6
b. N_2O_3
c. Cl_2O_7
d. P_4O_6

Solution

Because these compounds consist solely of nonmetals, we use prefixes to designate the number of atoms of each element:

a. sulfur hexafluoride
b. dinitrogen trioxide
c. dichlorine heptoxide
d. tetraphosphorus hexoxide

? Exercise 1.2.8.2

Write the formulas for the following compounds:

a. phosphorus pentachloride
b. dinitrogen monoxide
c. iodine heptafluoride
d. carbon tetrachloride

Answer a

PCl_5

Answer b

N_2O

Answer c

IF_7

Answer d

CCl_4

1.2.8.7: Binary Acids

Some compounds containing hydrogen are members of an important class of substances known as acids. The chemistry of these compounds is explored in more detail in later chapters of this text, but for now, it will suffice to note that many acids release hydrogen ions, H^+, when dissolved in water. To denote this distinct chemical property, a mixture of water with an acid is given a name derived from the compound's name. If the compound is a binary acid (comprised of hydrogen and one other nonmetallic element):

1. The word "hydrogen" is changed to the prefix *hydro-*
2. The other nonmetallic element name is modified by adding the suffix *-ic*
3. The word "acid" is added as a second word

For example, when the gas HCl (hydrogen chloride) is dissolved in water, the solution is called *hydrochloric acid*. Several other examples of this nomenclature are shown in Table 1.2.8.7.

Table 1.2.8.7: Names of Some Simple Acids

Name of Gas	Name of Acid
HF(*g*), hydrogen fluoride	HF(*aq*), hydrofluoric acid
HCl(*g*), hydrogen chloride	HCl(*aq*), hydrochloric acid
HBr(*g*), hydrogen bromide	HBr(*aq*), hydrobromic acid
HI(*g*), hydrogen iodide	HI(*aq*), hydroiodic acid
H_2S(*g*), hydrogen sulfide	H_2S(*aq*), hydrosulfuric acid

1.2.8.8: Oxyacids

Many compounds containing three or more elements (such as organic compounds or coordination compounds) are subject to specialized nomenclature rules that you will learn later. However, we will briefly discuss the important compounds known as oxyacids, compounds that contain hydrogen, oxygen, and at least one other element, and are bonded in such a way as to impart acidic properties to the compound (you will learn the details of this in a later chapter). Typical oxyacids consist of hydrogen combined with a polyatomic, oxygen-containing ion. To name oxyacids:

1. Omit "hydrogen"
2. Start with the root name of the anion
3. Replace *–ate* with *–ic*, or *–ite* with *–ous*
4. Add "acid"

For example, consider H_2CO_3 (which you might be tempted to call "hydrogen carbonate"). To name this correctly, "hydrogen" is omitted; the *–ate* of carbonate is replace with *–ic*; and acid is added—so its name is carbonic acid. Other examples are given in Table 1.2.8.8 There are some exceptions to the general naming method (e.g., H_2SO_4 is called sulfuric acid, not sulfic acid, and H_2SO_3 is sulfurous, not sulfous, acid).

Table 1.2.8.8: Names of Common Oxyacids

Formula	Anion Name	Acid Name
$HC_2H_3O_2$	acetate	acetic acid
HNO_3	nitrate	nitric acid
HNO_2	nitrite	nitrous acid
$HClO_4$	perchlorate	perchloric acid
H_2CO_3	carbonate	carbonic acid
H_2SO_4	sulfate	sulfuric acid
H_2SO_3	sulfite	sulfurous acid
H_3PO_4	phosphate	phosphoric acid

Summary

Chemists use nomenclature rules to clearly name compounds. Ionic and molecular compounds are named using somewhat-different methods. Binary ionic compounds typically consist of a metal and a nonmetal. The name of the metal is written first, followed by the name of the nonmetal with its ending changed to *–ide*. For example, K_2O is called potassium oxide. If the metal can form ions with different charges, a Roman numeral in parentheses follows the name of the metal to specify its charge. Thus, $FeCl_2$ is iron(II) chloride and $FeCl_3$ is iron(III) chloride. Some compounds contain polyatomic ions; the names of common polyatomic ions should be memorized. Molecular compounds can form compounds with different ratios of their elements, so prefixes are used to specify the numbers of atoms of each element in a molecule of the compound. Examples include SF_6, sulfur hexafluoride, and N_2O_4, dinitrogen tetroxide. Acids are an important class of compounds containing hydrogen and having special nomenclature rules. Binary acids are named using the prefix *hydro-*, changing the *–ide* suffix to *–ic*, and adding "acid;" HCl is hydrochloric acid. Oxyacids are named by changing the ending of the anion (*-ate* to *–ic*, and *-ite* to *-ous*) and adding "acid;" H_2CO_3 is carbonic acid.

Glossary

binary acid

compound that contains hydrogen and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H^+ ions when dissolved in water)

binary compound

compound containing two different elements.

oxyacid

compound that contains hydrogen, oxygen, and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H^+ ions when dissolved in water)

nomenclature

system of rules for naming objects of interest

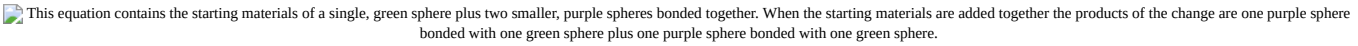
This page titled 1.2.8: Chemical Nomenclature is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **2.8: Chemical Nomenclature** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

1.2.E: Atoms, Molecules, and Ions (Exercises)

1.2.E.1: 2.1: Early Ideas in Atomic Theory

In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres of different elements touch, they are part of a single unit of a compound. The following chemical change represented by these spheres may violate one of the ideas of Dalton's atomic theory. Which one?


This equation contains the starting materials of a single, green sphere plus two smaller, purple spheres bonded together. When the starting materials are added together the products of the change are one purple sphere bonded with one green sphere plus one purple sphere bonded with one green sphere.

The starting materials consist of one green sphere and two purple spheres. The products consist of two green spheres and two purple spheres. This violates Dalton's postulate that that atoms are not created during a chemical change, but are merely redistributed.

Which postulate of Dalton's theory is consistent with the following observation concerning the weights of reactants and products? When 100 grams of solid calcium carbonate is heated, 44 grams of carbon dioxide and 56 grams of calcium oxide are produced.

Identify the postulate of Dalton's theory that is violated by the following observations: 59.95% of one sample of titanium dioxide is titanium; 60.10% of a different sample of titanium dioxide is titanium.

This statement violates Dalton's fourth postulate: In a given compound, the numbers of atoms of each type (and thus also the percentage) always have the same ratio.

Samples of compound X, Y, and Z are analyzed, with results shown here.

Compound	Description	Mass of Carbon	Mass of Hydrogen
X	clear, colorless, liquid with strong odor	1.776 g	0.148 g
Y	clear, colorless, liquid with strong odor	1.974 g	0.329 g
Z	clear, colorless, liquid with strong odor	7.812 g	0.651 g

Do these data provide example(s) of the law of definite proportions, the law of multiple proportions, neither, or both? What do these data tell you about compounds X, Y, and Z?

1.2.E.2: 2.2: Evolution of Atomic Theory

1.2.E.3: Exercises

1. The existence of isotopes violates one of the original ideas of Dalton's atomic theory. Which one?
2. How are electrons and protons similar? How are they different?
3. How are protons and neutrons similar? How are they different?
4. Predict and test the behavior of α particles fired at a "plum pudding" model atom.
    a. Predict the paths taken by α particles that are fired at atoms with a Thomson's plum pudding model structure. Explain why you expect the α particles to take these paths.
    b. If α particles of higher energy than those in (a) are fired at plum pudding atoms, predict how their paths will differ from the lower-energy α particle paths. Explain your reasoning.
    c. Now test your predictions from (a) and (b). Open the Rutherford Scattering simulation and select the "Plum Pudding Atom" tab. Set "Alpha Particles Energy" to "min," and select "show traces." Click on the gun to start firing α particles. Does this match your prediction from (a)? If not, explain why the actual path would be that shown in the simulation. Hit the pause button, or "Reset All." Set "Alpha Particles Energy" to "max," and start firing α particles. Does this match your prediction from (b)? If not, explain the effect of increased energy on the actual paths as shown in the simulation.

5. Predict and test the behavior of α particles fired at a Rutherford atom model.
    a. (a) Predict the paths taken by α particles that are fired at atoms with a Rutherford atom model structure. Explain why you expect the α particles to take these paths.
    b. (b) If α particles of higher energy than those in (a) are fired at Rutherford atoms, predict how their paths will differ from the lower-energy α particle paths. Explain your reasoning.
    c. (c) Predict how the paths taken by the α particles will differ if they are fired at Rutherford atoms of elements other than gold. What factor do you expect to cause this difference in paths, and why?
    d. (d) Now test your predictions from (a), (b), and (c). Open the Rutherford Scattering simulation and select the "Rutherford Atom" tab. Due to the scale of the simulation, it is best to start with a small nucleus, so select "20" for both protons and neutrons, "min" for energy, show traces, and then start firing α particles. Does this match your prediction from (a)? If not, explain why the actual path would be that shown in the simulation. Pause or reset, set energy to "max," and start firing α particles. Does this match your prediction from (b)? If not, explain the effect of increased energy on the actual path as shown in the simulation. Pause or reset, select "40" for both protons and neutrons, "min" for energy, show traces, and fire away. Does this match your prediction from (c)? If not, explain why the actual path would be that shown in the simulation. Repeat this with larger numbers of protons and neutrons. What generalization can you make regarding the type of atom and effect on the path of α particles? Be clear and specific.

1.2.E.3.1: Solutions

1 Dalton originally thought that all atoms of a particular element had identical properties, including mass. Thus, the concept of isotopes, in which an element has different masses, was a violation of the original idea. To account for the existence of isotopes, the second postulate of his atomic theory was modified to state that atoms of the same element must have identical chemical properties.

2 Both are subatomic particles that reside in an atom's nucleus. Both have approximately the same mass. Protons are positively charged, whereas neutrons are uncharged.

3 Both are subatomic particles that reside in an atom's nucleus. Both have approximately the same mass. Protons are positively charged, whereas neutrons are uncharged.

4. (a) The plum pudding model indicates that the positive charge is spread uniformly throughout the atom, so we expect the α particles to (perhaps) be slowed somewhat by the positive-positive repulsion, but to follow straight-line paths (i.e., not to be deflected) as they pass through the atoms. (b) Higher-energy α particles will be traveling faster (and perhaps slowed less) and will also follow straight-line paths through the atoms. (c) The α particles followed straight-line paths through the plum pudding atom. There was no apparent slowing of the α particles as they passed through the atoms.

5. (a) The Rutherford atom has a small, positively charged nucleus, so most α particles will pass through empty space far from the nucleus and be undeflected. Those α particles that pass near the nucleus will be deflected from their paths due to positive-positive repulsion. The more directly toward the nucleus the α particles are headed, the larger the deflection angle will be. (b) Higher-energy α particles that pass near the nucleus will still undergo deflection, but the faster they travel, the less the expected angle of deflection. (c) If the nucleus is smaller, the positive charge is smaller and the expected deflections are smaller—both in terms of how closely the α particles pass by the nucleus undeflected and the angle of deflection. If the nucleus is larger, the positive charge is larger and the expected deflections are larger—more α particles will be deflected, and the deflection angles will be larger. (d) The paths followed by the α particles match the predictions from (a), (b), and (c).

1.2.E.4: 2.3: Atomic Structure and Symbolism

In what way are isotopes of a given element always different? In what way(s) are they always the same?

Write the symbol for each of the following ions:

1. (a) the ion with a 1+ charge, atomic number 55, and mass number 133
2. (b) the ion with 54 electrons, 53 protons, and 74 neutrons
3. (c) the ion with atomic number 15, mass number 31, and a 3− charge
4. (d) the ion with 24 electrons, 30 neutrons, and a 3+ charge

1.

(a) $^{133}Cs^{+}$; (b) $^{127}I^{-}$; (c) $^{31}P^{3-}$; (d) $^{57}Co^{3+}$

Write the symbol for each of the following ions:

1. (a) the ion with a 3+ charge, 28 electrons, and a mass number of 71
2. (b) the ion with 36 electrons, 35 protons, and 45 neutrons
3. (c) the ion with 86 electrons, 142 neutrons, and a 4+ charge
4. (d) the ion with a 2+ charge, atomic number 38, and mass number 87

Open the Build an Atom simulation and click on the Atom icon.

1. (a) Pick any one of the first 10 elements that you would like to build and state its symbol.
2. (b) Drag protons, neutrons, and electrons onto the atom template to make an atom of your element. State the numbers of protons, neutrons, and electrons in your atom, as well as the net charge and mass number.
3. (c) Click on “Net Charge” and “Mass Number,” check your answers to (b), and correct, if needed.
4. (d) Predict whether your atom will be stable or unstable. State your reasoning.
5. (e) Check the “Stable/Unstable” box. Was your answer to (d) correct? If not, first predict what you can do to make a stable atom of your element, and then do it and see if it works. Explain your reasoning.

(a) Carbon-12, ^{12}C; (b) This atom contains six protons and six neutrons. There are six electrons in a neutral ^{12}C atom. The net charge of such a neutral atom is zero, and the mass number is 12. (c) The preceding answers are correct. (d) The atom will be stable since C-12 is a stable isotope of carbon. (e) The preceding answer is correct. Other answers for this exercise are possible if a different element of isotope is chosen.

Open the Build an Atom simulation

(a) Drag protons, neutrons, and electrons onto the atom template to make a neutral atom of Oxygen-16 and give the isotope symbol for this atom.

(b) Now add two more electrons to make an ion and give the symbol for the ion you have created.

Open the Build an Atom simulation

(a) Drag protons, neutrons, and electrons onto the atom template to make a neutral atom of Lithium-6 and give the isotope symbol for this atom.

(b) Now remove one electron to make an ion and give the symbol for the ion you have created.

(a) Lithium-6 contains three protons, three neutrons, and three electrons. The isotope symbol is ^{6}Li or $^{6}_{3}Li$. (b) $^{6}Li^{+}$ or $^{6}_{3}Li^{+}$

Determine the number of protons, neutrons, and electrons in the following isotopes that are used in medical diagnoses:

(a) atomic number 9, mass number 18, charge of 1−

(b) atomic number 43, mass number 99, charge of 7+

(c) atomic number 53, atomic mass number 131, charge of 1−

(d) atomic number 81, atomic mass number 201, charge of 1+

(e) Name the elements in parts (a), (b), (c), and (d).

The following are properties of isotopes of two elements that are essential in our diet. Determine the number of protons, neutrons and electrons in each and name them.

(a) atomic number 26, mass number 58, charge of 2+

(b) atomic number 53, mass number 127, charge of 1−

(a) Iron, 26 protons, 24 electrons, and 32 neutrons; (b) iodine, 53 protons, 54 electrons, and 74 neutrons

Give the number of protons, electrons, and neutrons in neutral atoms of each of the following isotopes:

(a) $^{10}_{5}\mathrm{B}$

(b) $^{199}_{80}\mathrm{Hg}$

(c) $^{63}_{29}\mathrm{Cu}$

(d) $^{13}_{6}\mathrm{C}$

(e) $^{77}_{34}\mathrm{Se}$

Give the number of protons, electrons, and neutrons in neutral atoms of each of the following isotopes:

(a) $^{7}_{3}\mathrm{Li}$

(b) $^{125}_{52}\mathrm{Te}$

(c) $^{109}_{47}\mathrm{Ag}$

(d) $^{15}_{7}\mathrm{N}$

(e) $^{31}_{15}\mathrm{P}$

(a) 3 protons, 3 electrons, 4 neutrons; (b) 52 protons, 52 electrons, 73 neutrons; (c) 47 protons, 47 electrons, 62 neutrons; (d) 7 protons, 7 electrons, 8 neutrons; (e) 15 protons, 15 electrons, 16 neutrons

Click on the site and select the “Mix Isotopes” tab, hide the “Percent Composition” and “Average Atomic Mass” boxes, and then select the element boron.

(a) Write the symbols of the isotopes of boron that are shown as naturally occurring in significant amounts.

(b) Predict the relative amounts (percentages) of these boron isotopes found in nature. Explain the reasoning behind your choice.

(c) Add isotopes to the black box to make a mixture that matches your prediction in (b). You may drag isotopes from their bins or click on “More” and then move the sliders to the appropriate amounts.

(d) Reveal the “Percent Composition” and “Average Atomic Mass” boxes. How well does your mixture match with your prediction? If necessary, adjust the isotope amounts to match your prediction.

(e) Select “Nature’s” mix of isotopes and compare it to your prediction. How well does your prediction compare with the naturally occurring mixture? Explain. If necessary, adjust your amounts to make them match “Nature’s” amounts as closely as possible.

Repeat Exercise using an element that has three naturally occurring isotopes.

Let us use neon as an example. Since there are three isotopes, there is no way to be sure to accurately predict the abundances to make the total of 20.18 amu average atomic mass. Let us guess that the abundances are 9% Ne-22, 91% Ne-20, and only a trace of Ne-21. The average mass would be 20.18 amu. Checking the nature’s mix of isotopes shows that the abundances are 90.48% Ne-20, 9.25% Ne-22, and 0.27% Ne-21, so our guessed amounts have to be slightly adjusted.

An element has the following natural abundances and isotopic masses: 90.92% abundance with 19.99 amu, 0.26% abundance with 20.99 amu, and 8.82% abundance with 21.99 amu. Calculate the average atomic mass of this element.

Average atomic masses listed by IUPAC are based on a study of experimental results. Bromine has two isotopes ^{79}Br and ^{81}Br, whose masses (78.9183 and 80.9163 amu) and abundances (50.69% and 49.31%) were determined in earlier experiments. Calculate the average atomic mass of bromine based on these experiments.

79.904 amu

Variations in average atomic mass may be observed for elements obtained from different sources. Lithium provides an example of this. The isotopic composition of lithium from naturally occurring minerals is 7.5% ^{6}Li and 92.5% ^{7}Li, which have masses of 6.01512 amu and 7.01600 amu, respectively. A commercial source of lithium, recycled from a military source, was 3.75% ^{6}Li (and the rest ^{7}Li). Calculate the average atomic mass values for each of these two sources.

The average atomic masses of some elements may vary, depending upon the sources of their ores. Naturally occurring boron consists of two isotopes with accurately known masses (^{10}B, 10.0129 amu and ^{11}B, 11.0931 amu). The actual atomic mass of boron can vary from 10.807 to 10.819, depending on whether the mineral source is from Turkey or the United States. Calculate the percent abundances leading to the two values of the average atomic masses of boron from these two countries.

Turkey source: 0.2649 (of 10.0129 amu isotope); US source: 0.2537 (of 10.0129 amu isotope)

The ^{18}O:^{16}O abundance ratio in some meteorites is greater than that used to calculate the average atomic mass of oxygen on earth. Is the average mass of an oxygen atom in these meteorites greater than, less than, or equal to that of a terrestrial oxygen atom?

1.2.E.5: 2.4: Chemical Formulas

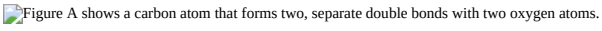
Explain why the symbol for an atom of the element oxygen and the formula for a molecule of oxygen differ.

The symbol for the element oxygen, O, represents both the element and one atom of oxygen. A molecule of oxygen, O_2, contains two oxygen atoms; the subscript 2 in the formula must be used to distinguish the diatomic molecule from two single oxygen atoms.

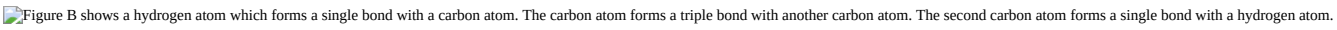
Explain why the symbol for the element sulfur and the formula for a molecule of sulfur differ.

Write the molecular and empirical formulas of the following compounds:

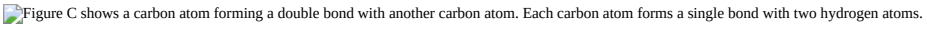
(a)


Figure A shows a carbon atom that forms two, separate double bonds with two oxygen atoms.

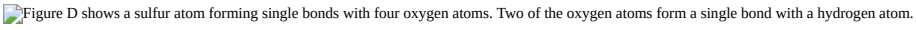
(b)


Figure B shows a hydrogen atom which forms a single bond with a carbon atom. The carbon atom forms a triple bond with another carbon atom. The second carbon atom forms a single bond with a hydrogen atom.

(c)


Figure C shows a carbon atom forming a double bond with another carbon atom. Each carbon atom forms a single bond with two hydrogen atoms.

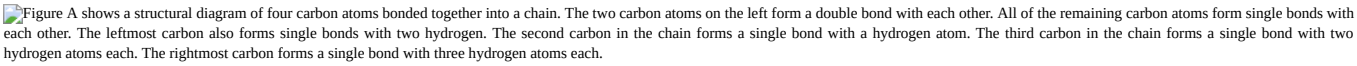
(d)


Figure D shows a sulfur atom forming single bonds with four oxygen atoms. Two of the oxygen atoms form a single bond with a hydrogen atom.

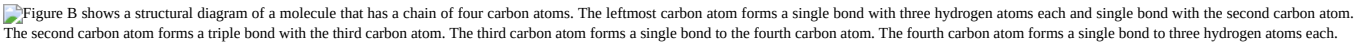
(a) molecular CO_2, empirical CO_2; (b) molecular C_2H_2, empirical CH; (c) molecular C_2H_4, empirical CH_2; (d) molecular H_2SO_4, empirical H_2SO_4

Write the molecular and empirical formulas of the following compounds:

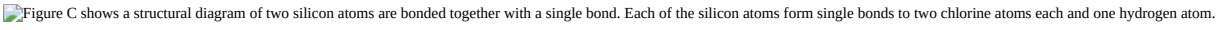
(a)


Figure A shows a structural diagram of four carbon atoms bonded together into a chain. The two carbon atoms on the left form a double bond with each other. All of the remaining carbon atoms form single bonds with each other. The leftmost carbon also forms single bonds with two hydrogen. The second carbon in the chain forms a single bond with a hydrogen atom. The third carbon in the chain forms a single bond with two hydrogen atoms each. The rightmost carbon forms a single bond with three hydrogen atoms each.

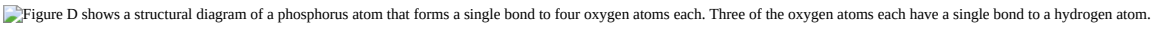
(b)


Figure B shows a structural diagram of a molecule that has a chain of four carbon atoms. The leftmost carbon atom forms a single bond with three hydrogen atoms each and single bond with the second carbon atom. The second carbon atom forms a triple bond with the third carbon atom. The third carbon atom forms a single bond to the fourth carbon atom. The fourth carbon atom forms a single bond to three hydrogen atoms each.

(c)


Figure C shows a structural diagram of two silicon atoms are bonded together with a single bond. Each of the silicon atoms form single bonds to two chlorine atoms each and one hydrogen atom.

(d)


Figure D shows a structural diagram of a phosphorus atom that forms a single bond to four oxygen atoms each. Three of the oxygen atoms each have a single bond to a hydrogen atom.

Determine the empirical formulas for the following compounds:

1. (a) caffeine, $C_8H_{10}N_4O_2$

2. (b) fructose, $C_{12}H_{22}O_{11}$
3. (c) hydrogen peroxide, H_2O_2
4. (d) glucose, $C_6H_{12}O_6$
5. (e) ascorbic acid (vitamin C), $C_6H_8O_6$

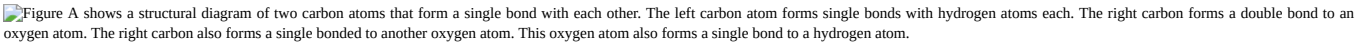
(a) $C_4H_5N_2O$; (b) $C_{12}H_{22}O_{11}$; (c) HO; (d) CH_2O; (e) $C_3H_4O_3$

Determine the empirical formulas for the following compounds:

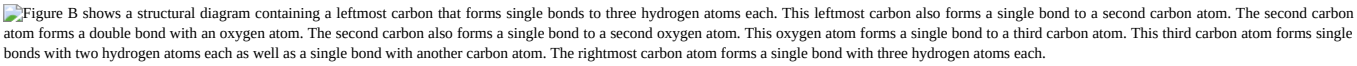
1. (a) acetic acid, $C_2H_4O_2$
2. (b) citric acid, $C_6H_8O_7$
3. (c) hydrazine, N_2H_4
4. (d) nicotine, $C_{10}H_{14}N_2$
5. (e) butane, C_4H_{10}

Write the empirical formulas for the following compounds:

(a)


Figure A shows a structural diagram of two carbon atoms that form a single bond with each other. The left carbon atom forms single bonds with hydrogen atoms each. The right carbon forms a double bond to an oxygen atom. The right carbon also forms a single bonded to another oxygen atom. This oxygen atom also forms a single bond to a hydrogen atom.

(b)


Figure B shows a structural diagram containing a leftmost carbon that forms single bonds to three hydrogen atoms each. This leftmost carbon also forms a single bond to a second carbon atom. The second carbon atom forms a double bond with an oxygen atom. The second carbon also forms a single bond to a second oxygen atom. This oxygen atom forms a single bond to a third carbon atom. This third carbon atom forms single bonds with two hydrogen atoms each as well as a single bond with another carbon atom. The rightmost carbon atom forms a single bond with three hydrogen atoms each.

(a) CH_2O; (b) C_2H_4O

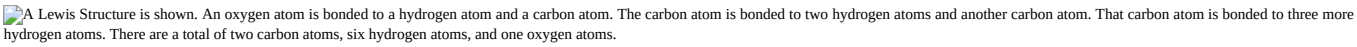
Open the Build a Molecule simulation and select the “Larger Molecules” tab. Select an appropriate atoms “Kit” to build a molecule with two carbon and six hydrogen atoms. Drag atoms into the space above the “Kit” to make a molecule. A name will appear when you have made an actual molecule that exists (even if it is not the one you want). You can use the scissors tool to separate atoms if you would like to change the connections. Click on “3D” to see the molecule, and look at both the space-filling and ball-and-stick possibilities.

1. (a) Draw the structural formula of this molecule and state its name.
2. (b) Can you arrange these atoms in any way to make a different compound?

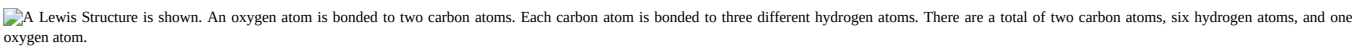
Use the Build a Molecule simulation to repeat Exercise, but build a molecule with two carbons, six hydrogens, and one oxygen.

1. (a) Draw the structural formula of this molecule and state its name.
2. (b) Can you arrange these atoms to make a different molecule? If so, draw its structural formula and state its name.
3. (c) How are the molecules drawn in (a) and (b) the same? How do they differ? What are they called (the type of relationship between these molecules, not their names).

(a) ethanol


A Lewis Structure is shown. An oxygen atom is bonded to a hydrogen atom and a carbon atom. The carbon atom is bonded to two hydrogen atoms and another carbon atom. That carbon atom is bonded to three more hydrogen atoms. There are a total of two carbon atoms, six hydrogen atoms, and one oxygen atoms.

(b) methoxymethane, more commonly known as dimethyl ether


A Lewis Structure is shown. An oxygen atom is bonded to two carbon atoms. Each carbon atom is bonded to three different hydrogen atoms. There are a total of two carbon atoms, six hydrogen atoms, and one oxygen atom.

(c) These molecules have the same chemical composition (types and number of atoms) but different chemical structures. They are structural isomers.

Use the Build a Molecule simulation to repeat Exercise, but build a molecule with three carbons, seven hydrogens, and one chlorine.

a. Draw the structural formula of this molecule and state its name.
b. Can you arrange these atoms to make a different molecule? If so, draw its structural formula and state its name.
c. How are the molecules drawn in (a) and (b) the same? How do they differ? What are they called (the type of relationship between these molecules, not their names)?

1.2.E.6: 2.5: The Periodic Table

Using the periodic table, classify each of the following elements as a metal or a nonmetal, and then further classify each as a main-group (representative) element, transition metal, or inner transition metal:

a. uranium
b. bromine
c. strontium
d. neon
e. gold
f. americium
g. rhodium
h. sulfur
i. carbon
j. potassium

(a) metal, inner transition metal; (b) nonmetal, representative element; (c) metal, representative element; (d) nonmetal, representative element; (e) metal, transition metal; (f) metal, inner transition metal; (g) metal, transition metal; (h) nonmetal, representative element; (i) nonmetal, representative element; (j) metal, representative element

Using the periodic table, classify each of the following elements as a metal or a nonmetal, and then further classify each as a main-group (representative) element, transition metal, or inner transition metal:

1. (a) cobalt
2. (b) europium
3. (c) iodine
4. (d) indium
5. (e) lithium
6. (f) oxygen
7. (g) cadmium
8. (h) terbium
9. (i) rhenium

Using the periodic table, identify the lightest member of each of the following groups:

1. (a) noble gases
2. (b) alkaline earth metals
3. (c) alkali metals
4. (d) chalcogens

(a) He; (b) Be; (c) Li; (d) O

Using the periodic table, identify the heaviest member of each of the following groups:

1. (a) alkali metals
2. (b) chalcogens
3. (c) noble gases
4. (d) alkaline earth metals

1. Use the periodic table to give the name and symbol for each of the following elements:
2. (a) the noble gas in the same period as germanium

3. (b) the alkaline earth metal in the same period as selenium
4. (c) the halogen in the same period as lithium
5. (d) the chalcogen in the same period as cadmium

(a) krypton, Kr; (b) calcium, Ca; (c) fluorine, F; (d) tellurium, Te

Use the periodic table to give the name and symbol for each of the following elements:

1. (a) the halogen in the same period as the alkali metal with 11 protons
2. (b) the alkaline earth metal in the same period with the neutral noble gas with 18 electrons
3. (c) the noble gas in the same row as an isotope with 30 neutrons and 25 protons
4. (d) the noble gas in the same period as gold

Write a symbol for each of the following neutral isotopes. Include the atomic number and mass number for each.

1. (a) the alkali metal with 11 protons and a mass number of 23
2. (b) the noble gas element with and 75 neutrons in its nucleus and 54 electrons in the neutral atom
3. (c) the isotope with 33 protons and 40 neutrons in its nucleus
4. (d) the alkaline earth metal with 88 electrons and 138 neutrons

(a) $^{23}_{11}\text{Na}$; (b) $^{129}_{54}\text{Xe}$; (c) $^{73}_{33}\text{As}$; (d) $^{226}_{88}\text{Ra}$

Write a symbol for each of the following neutral isotopes. Include the atomic number and mass number for each.

1. (a) the chalcogen with a mass number of 125
2. (b) the halogen whose longest-lived isotope is radioactive
3. (c) the noble gas, used in lighting, with 10 electrons and 10 neutrons
4. (d) the lightest alkali metal with three neutrons

1.2.E.7: 2.6: Molecular and Ionic Compounds

Using the periodic table, predict whether the following chlorides are ionic or covalent: KCl, NCl_3, ICl, $MgCl_2$, PCl_5, and CCl_4.

Ionic: KCl, $MgCl_2$; Covalent: NCl_3, ICl, PCl_5, CCl_4

Using the periodic table, predict whether the following chlorides are ionic or covalent: $SiCl_4$, PCl_3, $CaCl_2$, CsCl, $CuCl_2$, and $CrCl_3$.

For each of the following compounds, state whether it is ionic or covalent. If it is ionic, write the symbols for the ions involved:

1. (a) NF_3
2. (b) BaO,
3. (c) $(NH_4)_2CO_3$
4. (d) $Sr(H_2PO_4)_2$
5. (e) IBr
6. (f) Na_2O

(a) covalent; (b) ionic, Ba^{2+}, O^{2-}; (c) ionic, NH_4^+, CO_3^{2-}; (d) ionic, Sr^{2+}, $H_2PO_4^-$; (e) covalent; (f) ionic, Na^+, O^{2-}

For each of the following compounds, state whether it is ionic or covalent, and if it is ionic, write the symbols for the ions involved:

1. (a) $KClO_4$
2. (b) $MgC_2H_3O_2$
3. (c) H_2S
4. (d) Ag_2S

5. (e) N_2Cl_4
6. (f) $Co(NO_3)_2$

For each of the following pairs of ions, write the symbol for the formula of the compound they will form:

1. (a) Ca^{2+}, S^{2-}
2. (b) NH_4^+, SO_4^{2-}
3. (c) Al^{3+}, Br^-
4. (d) Na^+, HPO_4^{2-}
5. (e) Mg^{2+}, PO_4^{3-}

(a) CaS; (b) $(NH_4)_2CO_3$; (c) $AlBr_3$; (d) Na_2HPO_4; (e) $Mg_3(PO_4)_2$

For each of the following pairs of ions, write the symbol for the formula of the compound they will form:

1. (a) K^+, O^{2-}
2. (b) NH_4^+, PO_4^{3-}
3. (c) Al^{3+}, O^{2-}
4. (d) Na^+, CO_3^{2-}
5. (e) Ba^{2+}, PO_4^{3-}

1.2.E.8: 2.7: Chemical Nomenclature

Name the following compounds:

1. (a) CsCl
2. (b) BaO
3. (c) K_2S
4. (d) $BeCl_2$
5. (e) HBr
6. (f) AlF_3

(a) cesium chloride; (b) barium oxide; (c) potassium sulfide; (d) beryllium chloride; (e) hydrogen bromide; (f) aluminum fluoride

Name the following compounds:

1. (a) NaF
2. (b) Rb_2O
3. (c) BCl_3
4. (d) H_2Se
5. (e) P_4O_6
6. (f) ICl_3

Write the formulas of the following compounds:

1. (a) rubidium bromide
2. (b) magnesium selenide
3. (c) sodium oxide
4. (d) calcium chloride
5. (e) hydrogen fluoride
6. (f) gallium phosphide
7. (g) aluminum bromide
8. (h) ammonium sulfate

(a) RbBr; (b) MgSe; (c) Na_2O; (d) $CaCl_2$; (e) HF; (f) GaP; (g) $AlBr_3$; (h) $(NH_4)_2SO_4$

Write the formulas of the following compounds:

1. (a) lithium carbonate
2. (b) sodium perchlorate
3. (c) barium hydroxide
4. (d) ammonium carbonate
5. (e) sulfuric acid
6. (f) calcium acetate
7. (g) magnesium phosphate
8. (h) sodium sulfite

Write the formulas of the following compounds:

1. (a) chlorine dioxide
2. (b) dinitrogen tetraoxide
3. (c) potassium phosphide
4. (d) silver(I) sulfide
5. (e) aluminum nitride
6. (f) silicon dioxide

(a) ClO_2; (b) N_2O_4; (c) K_3P; (d) Ag_2S; (e) AlN; (f) SiO_2

Write the formulas of the following compounds:

1. (a) barium chloride
2. (b) magnesium nitride
3. (c) sulfur dioxide
4. (d) nitrogen trichloride
5. (e) dinitrogen trioxide
6. (f) tin(IV) chloride

Each of the following compounds contains a metal that can exhibit more than one ionic charge. Name these compounds:

1. (a) Cr_2O_3
2. (b) $FeCl_2$
3. (c) CrO_3
4. (d) $TiCl_4$
5. (e) CoO
6. (f) MoS_2

(a) chromium(III) oxide; (b) iron(II) chloride; (c) chromium(VI) oxide; (d) titanium(IV) chloride; (e) cobalt(II) oxide; (f) molybdenum(IV) sulfide

Each of the following compounds contains a metal that can exhibit more than one ionic charge. Name these compounds:

1. (a) $NiCO_3$
2. (b) MoO_3
3. (c) $Co(NO_3)_2$
4. (d) V_2O_5
5. (e) MnO_2
6. (f) Fe_2O_3

The following ionic compounds are found in common household products. Write the formulas for each compound:

1. (a) potassium phosphate

2. (b) copper(II) sulfate
3. (c) calcium chloride
4. (d) titanium dioxide
5. (e) ammonium nitrate
6. (f) sodium bisulfate (the common name for sodium hydrogen sulfate)

(a) K_3PO_4; (b) $CuSO_4$; (c) $CaCl_2$; (d) TiO_2; (e) NH_4NO_3; (f) $NaHSO_4$

The following ionic compounds are found in common household products. Name each of the compounds:

1. (a) $Ca(H_2PO_4)_2$
2. (b) $FeSO_4$
3. (c) $CaCO_3$
4. (d) MgO
5. (e) $NaNO_2$
6. (f) KI

Exercise 1.2.E.1

What are the IUPAC names of the following compounds?

Answer

(a) manganese dioxide (b) mercurous chloride (Hg_2Cl_2) (c) ferric nitrate [$Fe(NO_3)_3$] (d) titanium tetrachloride (e) cupric bromide ($CuBr_2$)

Does this make *chemical sense*?

Yes Because

Strategy Map 1.2.E.1.1

Add exercises text here.

HINT

Add texts here. Do not delete this text first.

HINT

Add texts here. Do not delete this text first.

HINT

Add texts here. Do not delete this text first.

Complete/Guided Solution

Add texts here. Do not delete this text first.

? Layer 21.2.E.1

Add exercises text here.

Answer

Add texts here. Do not delete this text first.

? Layer 3 1.2.E.1

Add exercises text here.

Answer

Add texts here. Do not delete this text first.

***Hint**

Add texts here. Do not delete this text first.

What are the IUPAC names of the following compounds?

1. (a) manganese dioxide
2. (b) mercurous chloride (Hg_2Cl_2)
3. (c) ferric nitrate [$Fe(NO_3)_3$]
4. (d) titanium tetrachloride
5. (e) cupric bromide ($CuBr_2$)

(a) manganese(IV) oxide; (b) mercury(I) chloride; (c) iron(III) nitrate; (d) titanium(IV) chloride; (e) copper(II) bromide

This page titled 1.2.E: Atoms, Molecules, and Ions (Exercises) is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

CHAPTER OVERVIEW

2: Quantum Theory and Electronic Structure of Atoms

Topic hierarchy

2.1: Electromagnetic Energy
2.2: Atomic Spectroscopy and The Bohr Model
2.3: The Wavelength Nature of Matter
2.4: Quantum Mechanics and The Atom
2.5: The Shape of Atomic Orbitals
2.6: Electronic Structure of Atoms (Electron Configurations)
2.E: Quantum Theory and Electronic Structure (Exercises)
2.S: Study Guide

2: Quantum Theory and Electronic Structure of Atoms is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

2.1: Electromagnetic Energy

Learning Objectives

- Explain the basic behavior of waves, including traveling waves and standing waves
- Describe the wave nature of light
- Use appropriate equations to calculate related light-wave properties such as period, frequency, wavelength, and energy
- Distinguish between line and continuous emission spectra
- Describe the particle nature of light

The nature of light has been a subject of inquiry since antiquity. In the seventeenth century, Isaac Newton performed experiments with lenses and prisms and was able to demonstrate that white light consists of the individual colors of the rainbow combined together. Newton explained his optics findings in terms of a "corpuscular" view of light, in which light was composed of streams of extremely tiny particles travelling at high speeds according to Newton's laws of motion. Others in the seventeenth century, such as Christiaan Huygens, had shown that optical phenomena such as reflection and refraction could be equally well explained in terms of light as waves travelling at high speed through a medium called "luminiferous aether" that was thought to permeate all space. Early in the nineteenth century, Thomas Young demonstrated that light passing through narrow, closely spaced slits produced interference patterns that could not be explained in terms of Newtonian particles but could be easily explained in terms of waves. Later in the nineteenth century, after James Clerk Maxwell developed his theory of electromagnetic radiation and showed that light was the visible part of a vast spectrum of electromagnetic waves, the particle view of light became thoroughly discredited. By the end of the nineteenth century, scientists viewed the physical universe as roughly comprising two separate domains: matter composed of particles moving according to Newton's laws of motion, and electromagnetic radiation consisting of waves governed by Maxwell's equations. Today, these domains are referred to as classical mechanics and classical electrodynamics (or classical electromagnetism). Although there were a few physical phenomena that could not be explained within this framework, scientists at that time were so confident of the overall soundness of this framework that they viewed these aberrations as puzzling paradoxes that would ultimately be resolved somehow within this framework. As we shall see, these paradoxes led to a contemporary framework that intimately connects particles and waves at a fundamental level called wave-particle duality, which has superseded the classical view.

Visible light and other forms of electromagnetic radiation play important roles in chemistry, since they can be used to infer the energies of electrons within atoms and molecules. Much of modern technology is based on electromagnetic radiation. For example, radio waves from a mobile phone, X-rays used by dentists, the energy used to cook food in your microwave, the radiant heat from red-hot objects, and the light from your television screen are forms of electromagnetic radiation that all exhibit wavelike behavior.

2.1.1: Waves

A wave is an oscillation or periodic movement that can transport energy from one point in space to another. Common examples of waves are all around us. Shaking the end of a rope transfers energy from your hand to the other end of the rope, dropping a pebble into a pond causes waves to ripple outward along the water's surface, and the expansion of air that accompanies a lightning strike generates sound waves (thunder) that can travel outward for several miles. In each of these cases, kinetic energy is transferred through matter (the rope, water, or air) while the matter remains essentially in place. An insightful example of a wave occurs in sports stadiums when fans in a narrow region of seats rise simultaneously and stand with their arms raised up for a few seconds before sitting down again while the fans in neighboring sections likewise stand up and sit down in sequence. While this wave can quickly encircle a large stadium in a few seconds, none of the fans actually travel with the wave-they all stay in or above their seats.

Waves need not be restricted to travel through matter. As Maxwell showed, electromagnetic waves consist of an electric field oscillating in step with a perpendicular magnetic field, both of which are perpendicular to the direction of travel. These waves can travel through a vacuum at a constant speed of 2.998×10^8 m/s, the speed of light (denoted by c).

All waves, including forms of electromagnetic radiation, are characterized by, a wavelength (denoted by λ, the lowercase Greek letter lambda), a frequency (denoted by ν, the lowercase Greek letter nu), and an amplitude. As can be seen in Figure 2.1.1, the wavelength is the distance between two consecutive peaks or troughs in a wave (measured in meters in the SI system). Electromagnetic waves have wavelengths that fall within an enormous range-wavelengths of kilometers (10^3 m) to picometers (10^{-12} m) have been observed. The frequency is the number of wave cycles that pass a specified point in space in a specified

amount of time (in the SI system, this is measured in seconds). A cycle corresponds to one complete wavelength. The unit for frequency, expressed as cycles per second [s^{-1}], is the hertz (Hz). Common multiples of this unit are megahertz, (1 MHz = 1 × 10^6 Hz) and gigahertz (1 GHz = 1 × 10^9 Hz). The amplitude corresponds to the magnitude of the wave's displacement and so, in Figure, this corresponds to one-half the height between the peaks and troughs. The amplitude is related to the intensity of the wave, which for light is the brightness, and for sound is the loudness.

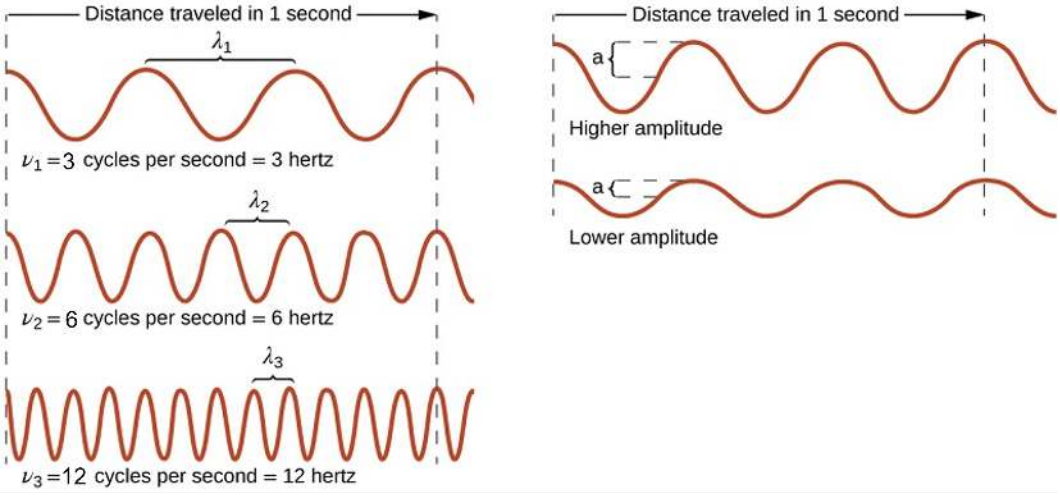


Figure 2.1.1: One-dimensional sinusoidal waves show the relationship among wavelength, frequency, and speed. The wave with the shortest wavelength has the highest frequency. Amplitude is one-half the height of the wave from peak to trough. (CC BY 4.0; OpenStax)

The product of a wave's wavelength (λ) and its frequency (ν), $\lambda\nu$, is the speed of the wave. Thus, for electromagnetic radiation in a vacuum:

$$c = 2.998 \times 10^8 \text{ ms}^{-1} = \lambda\nu \tag{2.1.1}$$

2.1.2: Electromagnetic Radiation

Water waves transmit energy through space by the periodic oscillation of matter (the water). In contrast, energy that is transmitted, or radiated, through space in the form of periodic oscillations of electric and magnetic fields is known as **electromagnetic radiation**. 2.1.2. Some forms of electromagnetic radiation are shown in Figure 2.1.3. In a vacuum, all forms of electromagnetic radiation—whether microwaves, visible light, or gamma rays—travel at the speed of light (c), which turns out to be a fundamental physical constant with a value of 2.99792458 × 10^8 m/s (about 3.00 ×10^8 m/s or 1.86 × 10^5 mi/s). This is about a million times faster than the speed of sound.

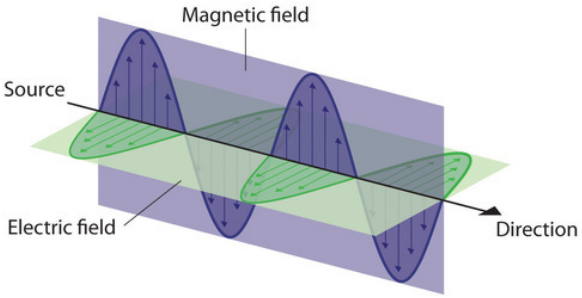


Figure 2.1.2: The Nature of Electromagnetic Radiation. All forms of electromagnetic radiation consist of perpendicular oscillating electric and magnetic fields.

Wavelength and frequency are inversely proportional: As the wavelength increases, the frequency decreases. The inverse proportionality is illustrated in Figure 2.1.3. This figure also shows the electromagnetic spectrum, the range of all types of electromagnetic radiation. Each of the various colors of visible light has specific frequencies and wavelengths associated with them, and you can see that visible light makes up only a small portion of the electromagnetic spectrum. Because the technologies

developed to work in various parts of the electromagnetic spectrum are different, for reasons of convenience and historical legacies, different units are typically used for different parts of the spectrum. For example, radio waves are usually specified as frequencies (typically in units of MHz), while the visible region is usually specified in wavelengths (typically in units of nm or angstroms).

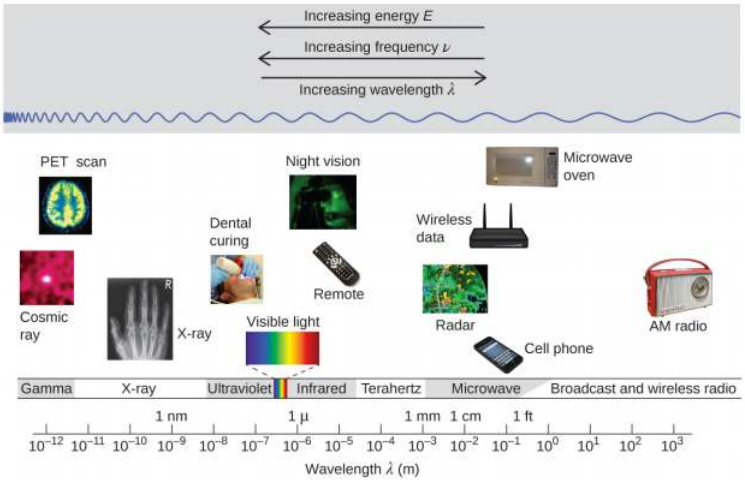


Figure 2.1.3: Portions of the electromagnetic spectrum are shown in order of decreasing frequency and increasing wavelength. Examples of some applications for various wavelengths include positron emission tomography (PET) scans, X-ray imaging, remote controls, wireless Internet, cellular telephones, and radios. (credit “Cosmic ray": modification of work by NASA; credit “PET scan": modification of work by the National Institute of Health; credit “X-ray": modification of work by Dr. Jochen Lengerke; credit “Dental curing": modification of work by the Department of the Navy; credit “Night vision": modification of work by the Department of the Army; credit “Remote": modification of work by Emilian Robert Vicol; credit “Cell phone": modification of work by Brett Jordan; credit “Microwave oven": modification of work by Billy Mabray; credit “Ultrasound": modification of work by Jane Whitney; credit “AM radio": modification of work by Dave Clausen)

Example 2.1.1: Determining the Frequency and Wavelength of Radiation

A sodium streetlight gives off yellow light that has a wavelength of 589 nm (1 nm = 1×10^{-9} m). What is the frequency of this light?

Solution

We can rearrange the Equation 2.1.1 to solve for the frequency:

$$\nu = \frac{c}{\lambda}$$

Since c is expressed in meters per second, we must also convert 589 nm to meters.

$$\nu = \left(\frac{2.998 \times 10^{8} \ \cancel{\text{m}}\,\text{s}^{-1}}{589 \ \cancel{\text{nm}}}\right)\left(\frac{1 \times 10^{9} \ \cancel{\text{nm}}}{1 \ \cancel{\text{m}}}\right) = 5.09 \times 10^{14}\,\text{s}^{-1}$$

Exercise 2.1.1

One of the frequencies used to transmit and receive cellular telephone signals in the United States is 850 MHz. What is the wavelength in meters of these radio waves?

Answer

0.353 m = 35.3 cm

2.1.3: Wireless Communication

Many valuable technologies operate in the radio (3 kHz-300 GHz) frequency region of the electromagnetic spectrum. At the low frequency (low energy, long wavelength) end of this region are AM (amplitude modulation) radio signals (540-2830 kHz) that can travel long distances. FM (frequency modulation) radio signals are used at higher frequencies (87.5-108.0 MHz). In AM radio, the

information is transmitted by varying the amplitude of the wave (Figure 2.1.5). In FM radio, by contrast, the amplitude is constant and the instantaneous frequency varies.



Figure 2.1.4: Radio and cell towers are typically used to transmit long-wavelength electromagnetic radiation. Increasingly, cell towers are designed to blend in with the landscape, as with the Tucson, Arizona, cell tower (right) disguised as a palm tree. (credit left: modification of work by Sir Mildred Pierce; credit middle: modification of work by M.O. Stevens)

Other technologies also operate in the radio-wave portion of the electromagnetic spectrum. For example, 4G cellular telephone signals are approximately 880 MHz, while Global Positioning System (GPS) signals operate at 1.228 and 1.575 GHz, local area wireless technology (Wi-Fi) networks operate at 2.4 to 5 GHz, and highway toll sensors operate at 5.8 GHz. The frequencies associated with these applications are convenient because such waves tend not to be absorbed much by common building materials.

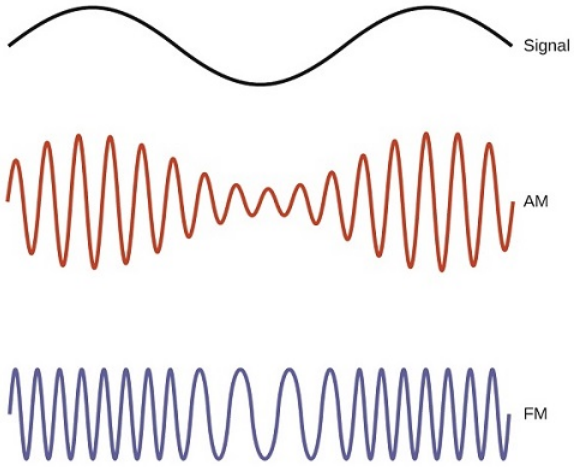


Figure 2.1.5: This schematic depicts how amplitude modulation (AM) and frequency modulation (FM) can be used to transmit a radio wave.

One particularly characteristic phenomenon of waves results when two or more waves come into contact: They interfere with each other. Figure 2.1.6 shows the interference patterns that arise when light passes through narrow slits closely spaced about a wavelength apart. The fringe patterns produced depend on the wavelength, with the fringes being more closely spaced for shorter wavelength light passing through a given set of slits. When the light passes through the two slits, each slit effectively acts as a new source, resulting in two closely spaced waves coming into contact at the detector (the camera in this case). The dark regions in Figure 2.1.6 correspond to regions where the peaks for the wave from one slit happen to coincide with the troughs for the wave from the other slit (destructive interference), while the brightest regions correspond to the regions where the peaks for the two waves (or their two troughs) happen to coincide (constructive interference). Likewise, when two stones are tossed close together into a pond, interference patterns are visible in the interactions between the waves produced by the stones. Such interference patterns cannot be explained by particles moving according to the laws of classical mechanics.

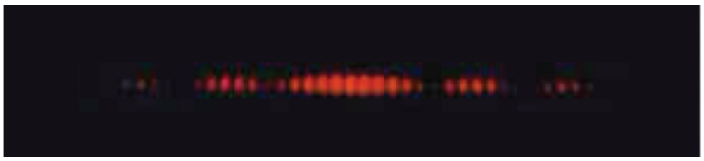


Figure 2.1.6: Interference fringe patterns are shown for light passing through two closely spaced, narrow slits. The spacing of the fringes depends on the wavelength, with the fringes being more closely spaced for the shorter-wavelength blue light. (credit: PASCO)

Dorothy Hodgkin

Because the wavelengths of X-rays (10-10,000 picometers [pm]) are comparable to the size of atoms, X-rays can be used to determine the structure of molecules. When a beam of X-rays is passed through molecules packed together in a crystal, the X-rays collide with the electrons and scatter. Constructive and destructive interference of these scattered X-rays creates a specific diffraction pattern. Calculating backward from this pattern, the positions of each of the atoms in the molecule can be determined very precisely. One of the pioneers who helped create this technology was Dorothy Crowfoot Hodgkin.

She was born in Cairo, Egypt, in 1910, where her British parents were studying archeology. Even as a young girl, she was fascinated with minerals and crystals. When she was a student at Oxford University, she began researching how X-ray crystallography could be used to determine the structure of biomolecules. She invented new techniques that allowed her and her students to determine the structures of vitamin B_{12}, penicillin, and many other important molecules. Diabetes, a disease that affects 382 million people worldwide, involves the hormone insulin. Hodgkin began studying the structure of insulin in 1934, but it required several decades of advances in the field before she finally reported the structure in 1969. Understanding the structure has led to better understanding of the disease and treatment options.

Not all waves are travelling waves. Standing waves (also known as stationary waves) remain constrained within some region of space. As we shall see, standing waves play an important role in our understanding of the electronic structure of atoms and molecules. The simplest example of a standing wave is a one-dimensional wave associated with a vibrating string that is held fixed at its two end points. Figure 2.1.7 shows the four lowest-energy standing waves (the fundamental wave and the lowest three harmonics) for a vibrating string at a particular amplitude. Although the string's motion lies mostly within a plane, the wave itself is considered to be one dimensional, since it lies along the length of the string. The motion of string segments in a direction perpendicular to the string length generates the waves and so the amplitude of the waves is visible as the maximum displacement of the curves seen in Figure 2.1.7. The key observation from the figure is that only those waves having an integer number, n, of half-wavelengths between the end points can form. A system with fixed end points such as this restricts the number and type of the possible waveforms. This is an example of quantization, in which only discrete values from a more general set of continuous values of some property are observed. Another important observation is that the harmonic waves (those waves displaying more than one-half wavelength) all have one or more points between the two end points that are not in motion. These special points are nodes. The energies of the standing waves with a given amplitude in a vibrating string increase with the number of half-wavelengths *n*. Since the number of nodes is $n - 1$, the energy can also be said to depend on the number of nodes, generally increasing as the number of nodes increases.

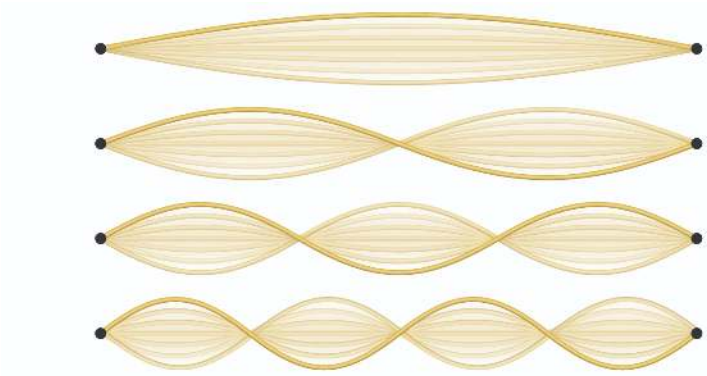


Figure 2.1.7: A vibrating string shows some one-dimensional standing waves. Since the two end points of the string are held fixed, only waves having an integer number of half-wavelengths can form. The points on the string between the end points that are not moving are called the nodes.

An example of two-dimensional standing waves is shown in Figure 2.1.8 which shows the vibrational patterns on a flat surface. Although the vibrational amplitudes cannot be seen like they could in the vibrating string, the nodes have been made visible by sprinkling the drum surface with a powder that collects on the areas of the surface that have minimal displacement. For one-dimensional standing waves, the nodes were points on the line, but for two-dimensional standing waves, the nodes are lines on the surface (for three-dimensional standing waves, the nodes are two-dimensional surfaces within the three-dimensional volume). Because of the circular symmetry of the drum surface, its boundary conditions (the drum surface being tightly constrained to the circumference of the drum) result in two types of nodes: radial nodes that sweep out all angles at constant radii and, thus, are seen as circles about the center, and angular nodes that sweep out all radii at constant angles and, thus, are seen as lines passing through the center. The upper left image in Figure 2.1.8 shows two radial nodes, while the image in the lower right shows the vibrational pattern associated with three radial nodes and two angular nodes.

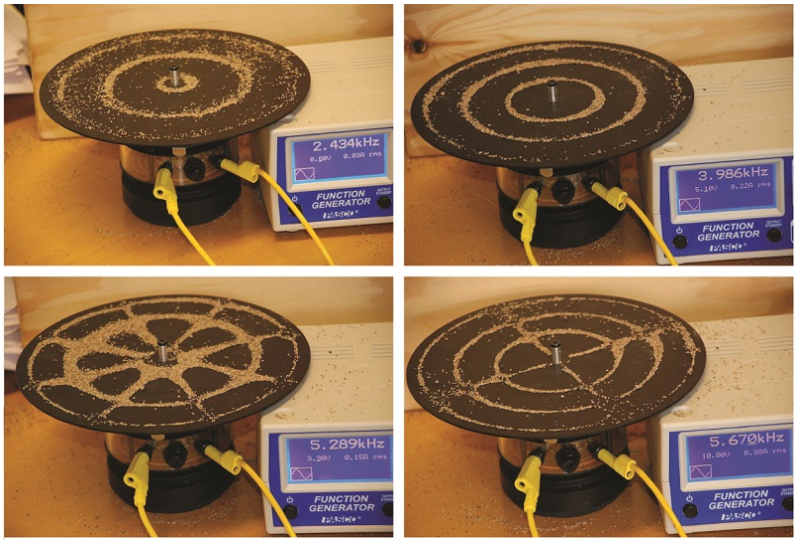


Figure 2.1.8: *Two-dimensional standing waves can be visualized on a vibrating surface. The surface has been sprinkled with a powder that collects near the nodal lines. There are two types of nodes visible: radial nodes (circles) and angular nodes (radii). For a more animated video, check this link out.*

2.1.4: Blackbody Radiation and the Ultraviolet Catastrophe

The last few decades of the nineteenth century witnessed intense research activity in commercializing newly discovered electric lighting. This required obtaining a better understanding of the distributions of light emitted from various sources being considered. Artificial lighting is usually designed to mimic natural sunlight within the limitations of the underlying technology. Such lighting consists of a range of broadly distributed frequencies that form a continuous spectrum. Figure 2.1.9 shows the wavelength distribution for sunlight. The most intense radiation is in the visible region, with the intensity dropping off rapidly for shorter wavelength ultraviolet (UV) light, and more slowly for longer wavelength infrared (IR) light.

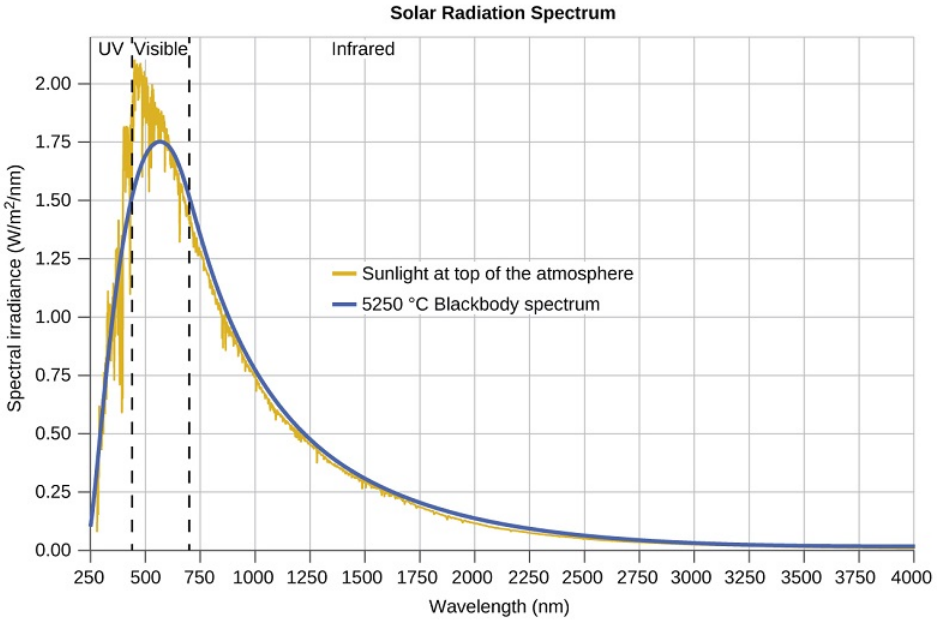


Figure 2.1.9: The spectral distribution (light intensity vs. wavelength) of sunlight reaches the Earth's atmosphere as UV light, visible light, and IR light. The unabsorbed sunlight at the top of the atmosphere has a distribution that approximately matches the theoretical distribution of a blackbody at 5250 °C, represented by the blue curve. (credit: modification of work by American Society for Testing and Materials (ASTM) Terrestrial Reference Spectra for Photovoltaic Performance Evaluation)

In Figure 2.1.9, the solar distribution is compared to a representative distribution, called a blackbody spectrum, that corresponds to a temperature of 5250 °C. The blackbody spectrum matches the solar spectrum quite well. A blackbody is a convenient, ideal emitter that approximates the behavior of many materials when heated. It is “ideal” in the same sense that an ideal gas is a convenient, simple representation of real gases that works well, provided that the pressure is not too high nor the temperature too low. A good approximation of a blackbody that can be used to observe blackbody radiation is a metal oven that can be heated to very high temperatures. The oven has a small hole allowing for the light being emitted within the oven to be observed with a spectrometer so that the wavelengths and their intensities can be measured. Figure 2.1.9 shows the resulting curves for some representative temperatures. Each distribution depends only on a single parameter: the temperature. The maxima in the blackbody curves, λ_{max}, shift to shorter wavelengths as the temperature increases, reflecting the observation that metals being heated to high temperatures begin to glow a darker red that becomes brighter as the temperature increases, eventually becoming white hot at very high temperatures as the intensities of all of the visible wavelengths become appreciable. This common observation was at the heart of the first paradox that showed the fundamental limitations of classical physics that we will examine.

Physicists derived mathematical expressions for the blackbody curves using well-accepted concepts from the theories of classical mechanics and classical electromagnetism. The theoretical expressions as functions of temperature fit the observed experimental blackbody curves well at longer wavelengths, but showed significant discrepancies at shorter wavelengths. Not only did the theoretical curves not show a peak, they absurdly showed the intensity becoming infinitely large as the wavelength became smaller, which would imply that everyday objects at room temperature should be emitting large amounts of UV light. This became known as the “ultraviolet catastrophe” because no one could find any problems with the theoretical treatment that could lead to such unrealistic short-wavelength behavior. Finally, around 1900, Max Planck derived a theoretical expression for blackbody radiation that fit the experimental observations exactly (within experimental error). Planck developed his theoretical treatment by extending the earlier work that had been based on the premise that the atoms composing the oven vibrated at increasing frequencies (or decreasing wavelengths) as the temperature increased, with these vibrations being the source of the emitted electromagnetic radiation. But where the earlier treatments had allowed the vibrating atoms to have any energy values obtained from a continuous set of energies (perfectly reasonable, according to classical physics), Planck found that by restricting the vibrational energies to discrete values for each frequency, he could derive an expression for blackbody radiation that correctly had the intensity dropping rapidly for the short wavelengths in the UV region.

$$E = nh\nu,\ n = 1, 2, 3,\ \ldots$$

The quantity h is a constant now known as Planck's constant, in his honor. Although Planck was pleased he had resolved the blackbody radiation paradox, he was disturbed that to do so, he needed to assume the vibrating atoms required quantized energies,

which he was unable to explain. The value of Planck's constant is very small, 6.626×10^{-34} joule seconds (J s), which helps explain why energy quantization had not been observed previously in macroscopic phenomena.

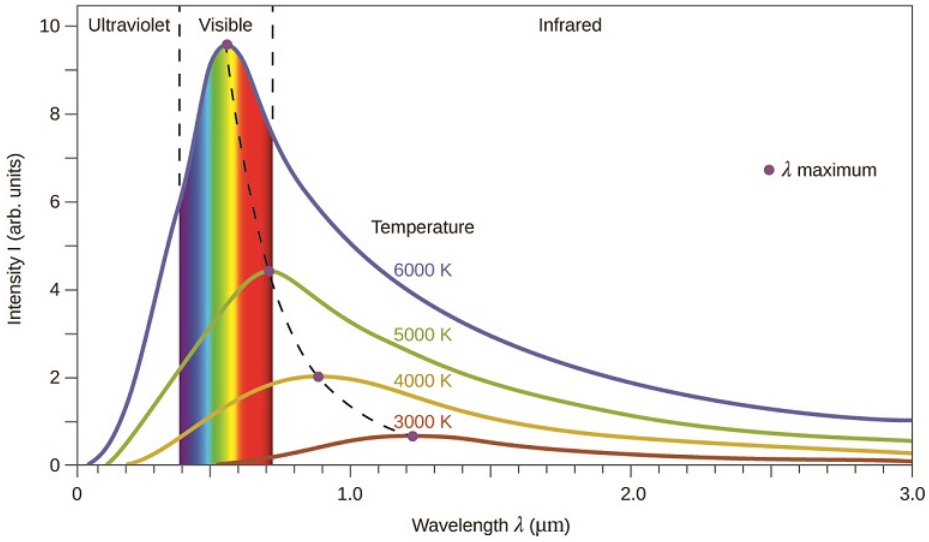


Figure 2.1.10: Blackbody spectral distribution curves are shown for some representative temperatures.

2.1.5: The Photoelectric Effect

The next paradox in the classical theory to be resolved concerned the photoelectric effect (Figure 2.1.11). It had been observed that electrons could be ejected from the clean surface of a metal when light having a frequency greater than some threshold frequency was shone on it. Surprisingly, the kinetic energy of the ejected electrons did not depend on the brightness of the light, but increased with increasing frequency of the light. Since the electrons in the metal had a certain amount of binding energy keeping them there, the incident light needed to have more energy to free the electrons. According to classical wave theory, a wave's energy depends on its intensity (which depends on its amplitude), not its frequency. One part of these observations was that the number of electrons ejected within in a given time period was seen to increase as the brightness increased. In 1905, Albert Einstein was able to resolve the paradox by incorporating Planck's quantization findings into the discredited particle view of light (Einstein actually won his Nobel prize for this work, and not for his theories of relativity for which he is most famous).

Einstein argued that the quantized energies that Planck had postulated in his treatment of blackbody radiation could be applied to the light in the photoelectric effect so that the light striking the metal surface should not be viewed as a wave, but instead as a stream of particles (later called photons) whose energy depended on their frequency, according to Planck's formula, $E = h\nu$ (or, in terms of wavelength using $c = \nu\lambda$, $E = \frac{hc}{\lambda}$). Electrons were ejected when hit by photons having sufficient energy (a frequency greater than the threshold). The greater the frequency, the greater the kinetic energy imparted to the escaping electrons by the collisions. Einstein also argued that the light intensity did not depend on the amplitude of the incoming wave, but instead corresponded to the number of photons striking the surface within a given time period. This explains why the number of ejected electrons increased with increasing brightness, since the greater the number of incoming photons, the greater the likelihood that they would collide with some of the electrons.

With Einstein's findings, the nature of light took on a new air of mystery. Although many light phenomena could be explained either in terms of waves or particles, certain phenomena, such as the interference patterns obtained when light passed through a double slit, were completely contrary to a particle view of light, while other phenomena, such as the photoelectric effect, were completely contrary to a wave view of light. Somehow, at a deep fundamental level still not fully understood, light is both wavelike and particle-like. This is known as wave-particle duality.

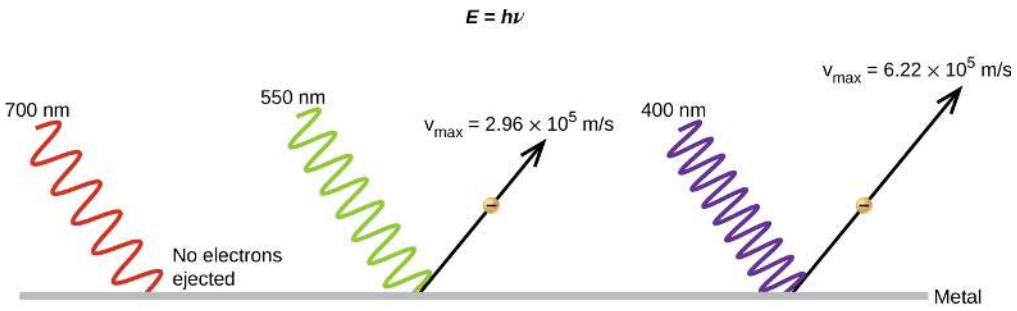


Figure 2.1.11: Photons with low frequencies do not have enough energy to cause electrons to be ejected via the photoelectric effect. For any frequency of light above the threshold frequency, the kinetic energy of an ejected electron will increase linearly with the energy of the incoming photon.

Example 2.1.2: Calculating the Energy of Radiation

When we see light from a neon sign, we are observing radiation from excited neon atoms. If this radiation has a wavelength of 640 nm, what is the energy of the photon being emitted?

Solution

We use the part of Planck's equation that includes the wavelength, λ, and convert units of nanometers to meters so that the units of λ and c are the same.

$$\begin{aligned} E &= \frac{hc}{\lambda} \\ &= \frac{(6.626 \times 10^{-34}\ \text{J}\ \cancel{\text{s}})(2.998 \times 10^{8}\ \text{m}\ \cancel{\text{s}}^{-1})}{(640\ \cancel{\text{nm}}) \left(\dfrac{1\ \text{m}}{10^{9}\ \cancel{\text{nm}}} \right)} \\ &= 3.10 \times 10^{-19}\ \text{J} \end{aligned}$$

Exercise 2.1.2

The microwaves in an oven are of a specific frequency that will heat the water molecules contained in food. (This is why most plastics and glass do not become hot in a microwave oven-they do not contain water molecules.) This frequency is about 3×10^9 Hz. What is the energy of one photon in these microwaves?

Answer

2×10^{-24} J

Example 2.1.3: Photoelectric Effect

Identify which of the following statements are false and, where necessary, change the italicized word or phrase to make them true, consistent with Einstein's explanation of the photoelectric effect.

a. Increasing the brightness of incoming light *increases* the kinetic energy of the ejected electrons.
b. Increasing the *wavelength* of incoming light increases the kinetic energy of the ejected electrons.
c. Increasing the brightness of incoming light *increases* the number of ejected electrons.
d. Increasing the *frequency* of incoming light can increase the number of ejected electrons.

Solution

a. False. Increasing the brightness of incoming light *has no effect* on the kinetic energy of the ejected electrons. Only energy, not the number or amplitude, of the photons influences the kinetic energy of the electrons.

b. False. Increasing the *frequency* of incoming light increases the kinetic energy of the ejected electrons. Frequency is proportional to energy and inversely proportional to wavelength. Frequencies above the threshold value transfer the excess energy into the kinetic energy of the electrons.
c. True. Because the number of collisions with photons increases with brighter light, the number of ejected electrons increases.
d. True with regard to the threshold energy binding the electrons to the metal. Below this threshold, electrons are not emitted and above it they are. Once over the threshold value, further increasing the frequency does not increase the number of ejected electrons

? Exercise 2.1.3

Calculate the threshold energy in kJ/mol of electrons in aluminum, given that the lowest frequency photon for which the photoelectric effect is observed is $9.87 \times 10^{14}\ Hz$.

Answer

$394\ kJ/mol$

2.1.6: Line Spectra

Another paradox within the classical electromagnetic theory that scientists in the late nineteenth century struggled with concerned the light emitted from atoms and molecules. When solids, liquids, or condensed gases are heated sufficiently, they radiate some of the excess energy as light. Photons produced in this manner have a range of energies, and thereby produce a continuous spectrum in which an unbroken series of wavelengths is present. Most of the light generated from stars (including our sun) is produced in this fashion. You can see all the visible wavelengths of light present in sunlight by using a prism to separate them. As can be seen in Figure 2.1.9, sunlight also contains UV light (shorter wavelengths) and IR light (longer wavelengths) that can be detected using instruments but that are invisible to the human eye. Incandescent (glowing) solids such as tungsten filaments in incandescent lights also give off light that contains all wavelengths of visible light. These continuous spectra can often be approximated by blackbody radiation curves at some appropriate temperature, such as those shown in Figure 2.1.10.

In contrast to continuous spectra, light can also occur as discrete or line spectra having very narrow line widths interspersed throughout the spectral regions such as those shown in Figure 2.1.6. Exciting a gas at low partial pressure using an electrical current, or heating it, will produce line spectra. Fluorescent light bulbs and neon signs operate in this way (Figure 2.1.12). Each element displays its own characteristic set of lines, as do molecules, although their spectra are generally much more complicated.



Figure 2.1.12: Neon signs operate by exciting a gas at low partial pressure using an electrical current. This sign shows the elaborate artistic effects that can be achieved. (credit: Dave Shaver)

Each emission line consists of a single wavelength of light, which implies that the light emitted by a gas consists of a set of discrete energies. For example, when an electric discharge passes through a tube containing hydrogen gas at low pressure, the H_2 molecules are broken apart into separate H atoms, and we see a blue-pink color. Passing the light through a prism produces a line spectrum, indicating that this light is composed of photons of four visible wavelengths, as shown in Figure 2.1.13.

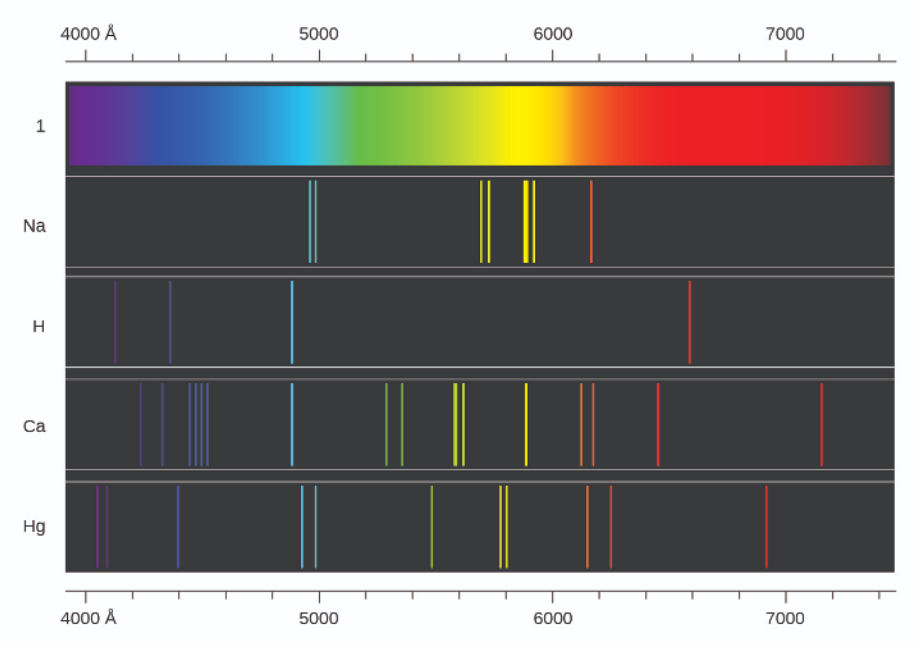


Figure 2.1.13: Line spectra of select gas. Compare the two types of emission spectra: continuous spectrum of white light (top) and the line spectra of the light from excited sodium, hydrogen, calcium, and mercury atoms.

The origin of discrete spectra in atoms and molecules was extremely puzzling to scientists in the late nineteenth century, since according to classical electromagnetic theory, only continuous spectra should be observed. Even more puzzling, in 1885, Johann Balmer was able to derive an empirical equation that related the four visible wavelengths of light emitted by hydrogen atoms to whole integers. That equation is the following one, in which k is a constant:

$$\frac{1}{\lambda} = k\left(\frac{1}{4} - \frac{1}{n^2}\right),\ n = 3,\ 4,\ 5,\ 6$$

Other discrete lines for the hydrogen atom were found in the UV and IR regions. Johannes Rydberg generalized Balmer's work and developed an empirical formula that predicted all of hydrogen's emission lines, not just those restricted to the visible range, where, n_1 and n_2 are integers, $n_1 < n_2$, and R_∞ is the Rydberg constant ($1.097 \times 10^7\ \text{m}^{-1}$).

$$\frac{1}{\lambda} = R_\infty\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Even in the late nineteenth century, spectroscopy was a very precise science, and so the wavelengths of hydrogen were measured to very high accuracy, which implied that the Rydberg constant could be determined very precisely as well. That such a simple formula as the Rydberg formula could account for such precise measurements seemed astounding at the time, but it was the eventual explanation for emission spectra by Neils Bohr in 1913 that ultimately convinced scientists to abandon classical physics and spurred the development of modern quantum mechanics.

Summary

Light and other forms of electromagnetic radiation move through a vacuum with a constant speed, c, of $2.998 \times 10^8\ \text{m s}^{-1}$. This radiation shows wavelike behavior, which can be characterized by a frequency, ν, and a wavelength, λ, such that $c = \lambda\nu$. Light is an example of a travelling wave. Other important wave phenomena include standing waves, periodic oscillations, and vibrations. Standing waves exhibit quantization, since their wavelengths are limited to discrete integer multiples of some characteristic lengths. Electromagnetic radiation that passes through two closely spaced narrow slits having dimensions roughly similar to the wavelength will show an interference pattern that is a result of constructive and destructive interference of the waves. Electromagnetic radiation also demonstrates properties of particles called photons. The energy of a photon is related to the frequency (or alternatively, the wavelength) of the radiation as $E = h\nu$ (or $E = \frac{hc}{\lambda}$), where h is Planck's constant. That light demonstrates both wavelike and particle-like behavior is known as wave-particle duality. All forms of electromagnetic radiation share these properties, although various forms including X-rays, visible light, microwaves, and radio waves interact differently with matter and have very different

practical applications. Electromagnetic radiation can be generated by exciting matter to higher energies, such as by heating it. The emitted light can be either continuous (incandescent sources like the sun) or discrete (from specific types of excited atoms). Continuous spectra often have distributions that can be approximated as blackbody radiation at some appropriate temperature. The line spectrum of hydrogen can be obtained by passing the light from an electrified tube of hydrogen gas through a prism. This line spectrum was simple enough that an empirical formula called the Rydberg formula could be derived from the spectrum. Three historically important paradoxes from the late 19th and early 20th centuries that could not be explained within the existing framework of classical mechanics and classical electromagnetism were the blackbody problem, the photoelectric effect, and the discrete spectra of atoms. The resolution of these paradoxes ultimately led to quantum theories that superseded the classical theories.

2.1.7: Key Equations

- $c = \lambda\nu$
- $E = h\nu = \frac{hc}{\lambda}$, where $h = 6.626 \times 10^{-34}$ J s
- $\frac{1}{\lambda} = R_\infty \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$

Glossary

amplitude
extent of the displacement caused by a wave (for sinusoidal waves, it is one-half the difference from the peak height to the trough depth, and the intensity is proportional to the square of the amplitude)

blackbody
idealized perfect absorber of all incident electromagnetic radiation; such bodies emit electromagnetic radiation in characteristic continuous spectra called blackbody radiation

continuous spectrum
electromagnetic radiation given off in an unbroken series of wavelengths (e.g., white light from the sun)

electromagnetic radiation
energy transmitted by waves that have an electric-field component and a magnetic-field component

electromagnetic spectrum
range of energies that electromagnetic radiation can comprise, including radio, microwaves, infrared, visible, ultraviolet, X-rays, and gamma rays; since electromagnetic radiation energy is proportional to the frequency and inversely proportional to the wavelength, the spectrum can also be specified by ranges of frequencies or wavelengths

frequency (ν)
number of wave cycles (peaks or troughs) that pass a specified point in space per unit time

hertz (Hz)
the unit of frequency, which is the number of cycles per second, s^{-1}

intensity
property of wave-propagated energy related to the amplitude of the wave, such as brightness of light or loudness of sound

interference pattern
pattern typically consisting of alternating bright and dark fringes; it results from constructive and destructive interference of waves

line spectrum
electromagnetic radiation emitted at discrete wavelengths by a specific atom (or atoms) in an excited state

node

any point of a standing wave with zero amplitude

photon

smallest possible packet of electromagnetic radiation, a particle of light

quantization

occurring only in specific discrete values, not continuous

standing wave

(also, stationary wave) localized wave phenomenon characterized by discrete wavelengths determined by the boundary conditions used to generate the waves; standing waves are inherently quantized

wave

oscillation that can transport energy from one point to another in space

wavelength (λ)

distance between two consecutive peaks or troughs in a wave

wave-particle duality

term used to describe the fact that elementary particles including matter exhibit properties of both particles (including localized position, momentum) and waves (including nonlocalization, wavelength, frequency)

This page titled 2.1: Electromagnetic Energy is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **6.1: Electromagnetic Energy** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.2: Atomic Spectroscopy and The Bohr Model

Learning Objectives

- To know the relationship between atomic spectra and the electronic structure of atoms.

The concept of the photon emerged from experimentation with *thermal radiation*, electromagnetic radiation emitted as the result of a source's temperature, which produces a continuous spectrum of energies.The photoelectric effect provided indisputable evidence for the existence of the photon and thus the particle-like behavior of electromagnetic radiation. However, more direct evidence was needed to verify the quantized nature of energy in all matter. In this section, we describe how observation of the interaction of atoms with visible light provided this evidence.

Line Spectra

Although objects at high temperature emit a continuous spectrum of electromagnetic radiation, a different kind of spectrum is observed when pure samples of individual elements are heated. For example, when a high-voltage electrical discharge is passed through a sample of hydrogen gas at low pressure, the resulting individual isolated hydrogen atoms caused by the dissociation of H_2 emit a red light. Unlike blackbody radiation, the color of the light emitted by the hydrogen atoms does not depend greatly on the temperature of the gas in the tube. When the emitted light is passed through a prism, only a few narrow lines of particular wavelengths, called a **line spectrum**, are observed rather than a continuous range of wavelengths (Figure 2.2.1). The light emitted by hydrogen atoms is red because, of its four characteristic lines, the most intense line in its spectrum is in the red portion of the visible spectrum, at 656 nm. With sodium, however, we observe a yellow color because the most intense lines in its spectrum are in the yellow portion of the spectrum, at about 589 nm.

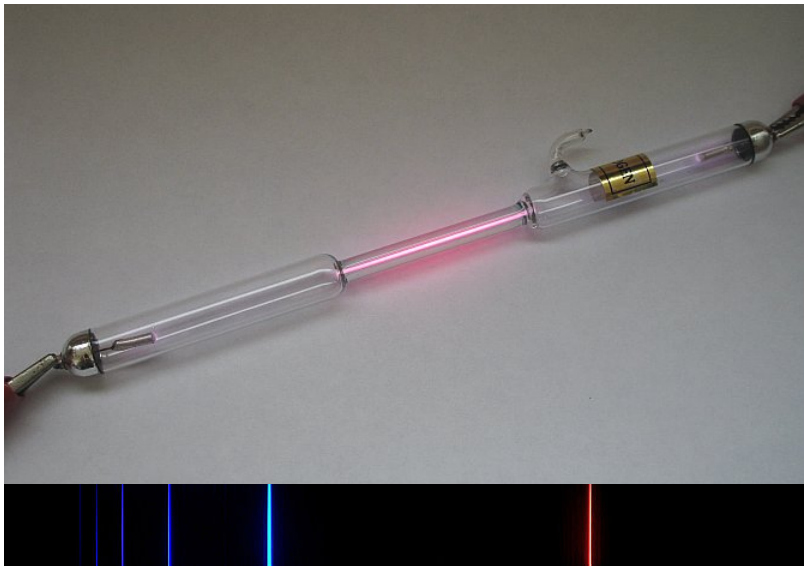


Figure 2.2.1: The Emission of Light by Hydrogen Atoms. (a) A sample of excited hydrogen atoms emits a characteristic red light. (CC BY-SA 3.0 Unported; Science Made Alive via Wikipedia) (b) When the light emitted by a sample of excited hydrogen atoms is split into its component wavelengths by a prism, four characteristic violet, blue, green, and red emission lines can be observed, the most intense of which is at 656 nm. (CC BY-SA 3.0; Jan Homann via Wikipedia)

Such *emission spectra* were observed for many other elements in the late 19th century, which presented a major challenge because classical physics was unable to explain them. Part of the explanation is provided by Planck's equation: the observation of only a few values of λ (or ν) in the line spectrum meant that only a few values of E were possible. Thus *the energy levels of a hydrogen atom had to be quantized*; in other words, only states that had certain values of energy were possible, or *allowed*. If a hydrogen atom could have *any* value of energy, then a continuous spectrum would have been observed, similar to blackbody radiation.

Bohr's Model

In 1913, a Danish physicist, Niels Bohr (1885–1962; Nobel Prize in Physics, 1922), proposed a theoretical model for the hydrogen atom that explained its emission spectrum. Bohr's model required only one assumption: *The electron moves around the nucleus in*

circular orbits that can have only certain allowed radii. Rutherford's earlier model of the atom had also assumed that electrons moved in circular orbits around the nucleus and that the atom was held together by the electrostatic attraction between the positively charged nucleus and the negatively charged electron. Although we now know that the assumption of circular orbits was incorrect, Bohr's insight was to propose that *the electron could occupy only certain regions of space*.

Using classical physics, Niels Bohr showed that the energy of an electron in a particular orbit is given by

Rydberg's phenomenological equation is as follows:

$$E_n = -R_{\mathrm{H}} \left(\frac{1}{n^2} \right) \tag{2.2.1}$$

where R_H is the **Rydberg constant** and is equal to $2.18 \times 10^{-18}\, J$ and n is a positive integer corresponding to the number assigned to the orbit, with n = 1 corresponding to the orbit closest to the nucleus. In this model n = ∞ corresponds to the level where the energy holding the electron and the nucleus together is zero. In that level, the electron is unbound from the nucleus and the atom has been separated into a negatively charged (the electron) and a positively charged (the nucleus) ion. In this state the radius of the orbit is also infinite. The atom has been ionized.

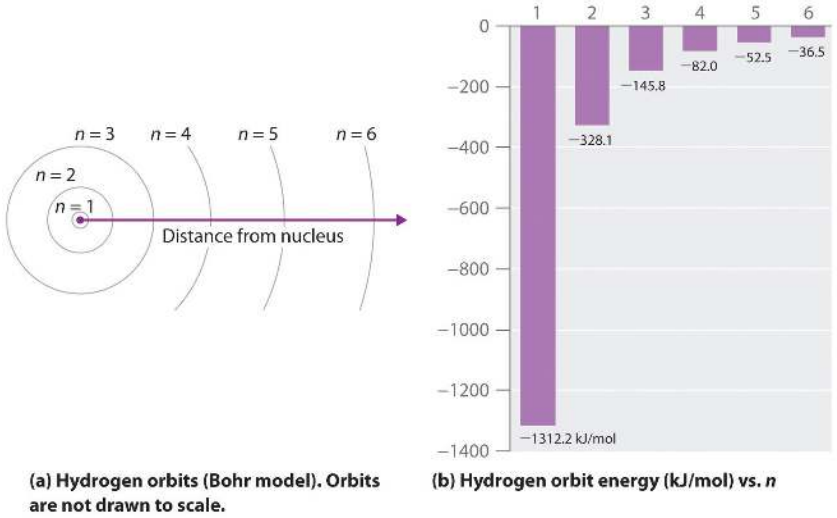
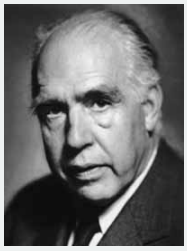


Figure 2.2.2: The Bohr Model of the Hydrogen Atom (a) The distance of the orbit from the nucleus increases with increasing *n*. (b) The energy of the orbit becomes increasingly less negative with increasing *n*.

Niels Bohr (1885–1962)

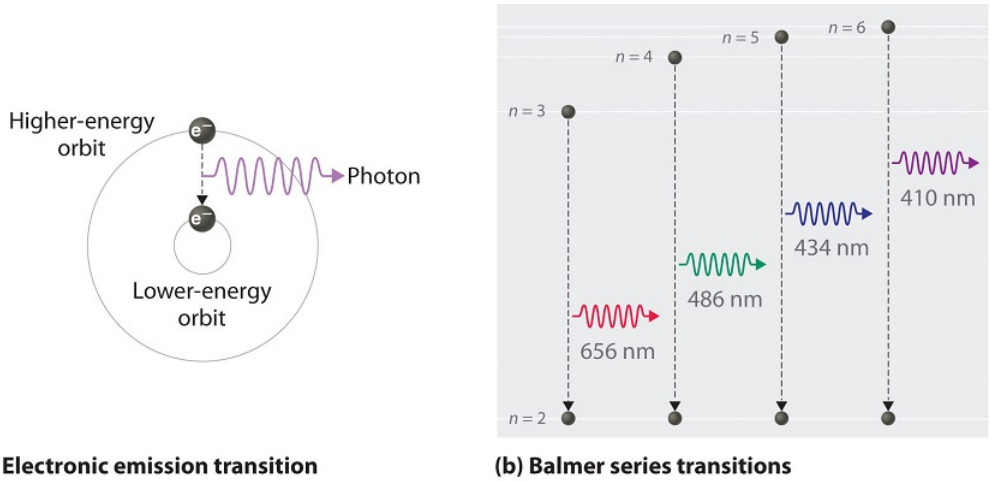
During the Nazi occupation of Denmark in World War II, Bohr escaped to the United States, where he became associated with the Atomic Energy Project.



In his final years, he devoted himself to the peaceful application of atomic physics and to resolving political problems arising from the development of atomic weapons.

As n decreases, the energy holding the electron and the nucleus together becomes increasingly negative, the radius of the orbit shrinks and more energy is needed to ionize the atom. The orbit with n = 1 is the lowest lying and most tightly bound. The negative

sign in Equation ??? indicates that the electron-nucleus pair is more tightly bound (i.e. at a lower potential energy) when they are near each other than when they are far apart. Because a hydrogen atom with its one electron in this orbit has the lowest possible energy, this is the **ground state** (the most stable arrangement of electrons for an element or a compound) for a hydrogen atom. As n increases, the radius of the orbit increases; the electron is farther from the proton, which results in a less stable arrangement with higher potential energy (Figure 2.2.2*a*). A hydrogen atom with an electron in an orbit with n > 1 is therefore in an **excited state**, defined as any arrangement of electrons that is higher in energy than the ground state. When an atom in an excited state undergoes a transition to the ground state in a process called decay, it loses energy by emitting a photon whose energy corresponds to the *difference* in energy between the two states (Figure 2.2.1).



(a) Electronic emission transition **(b) Balmer series transitions**

Figure 2.2.3: The Emission of Light by a Hydrogen Atom in an Excited State. (a) Light is emitted when the electron undergoes a transition from an orbit with a higher value of *n* (at a higher energy) to an orbit with a lower value of *n* (at lower energy). (b) The Balmer series of emission lines is due to transitions from orbits with $n \geq 3$ to the orbit with $n = 2$. The differences in energy between these levels corresponds to light in the visible portion of the electromagnetic spectrum.

This quantum mechanical model for where electrons reside in an atom can be used to look at electronic transitions, the events when an electron moves from one energy level to another. If the transition is to a higher energy level, energy is absorbed, and the energy change has a positive value. To obtain the amount of energy necessary for the transition to a higher energy level, a photon is absorbed by the atom. A transition to a lower energy level involves a release of energy, and the energy change is negative. This process is accompanied by emission of a photon by the atom. So the difference in energy (ΔE) between any two orbits or energy levels is given by $\Delta E = E_{n_f} - E_{n_i}$ where n_f is the final orbit and n_i the initial orbit. Substituting from Bohr's equation (Equation 2.2.1) for each energy value gives the following equation:

$$\begin{aligned}\Delta E &= E_\text{final} - E_\text{initial} \\ &= -2.18 \times 10^{-18} \left(\frac{1}{n_\text{f}^2} - \frac{1}{n_\text{i}^2} \right) \text{ J}\end{aligned}$$

The values n_f and n_i are the final and initial energy states of the electron.

We can now understand the physical basis for the Balmer series of lines in the emission spectrum of hydrogen (2.2.3*b*); the lines in this series correspond to transitions from higher-energy orbits (n > 2) to the second orbit (n = 2). Thus the hydrogen atoms in the sample have absorbed energy from the electrical discharge and decayed from a higher-energy excited state (n > 2) to a lower-energy state (n = 2) by emitting a photon of electromagnetic radiation whose energy corresponds exactly to the difference in energy between the two states (Figure 2.2.3*a*). The n = 3 to n = 2 transition gives rise to the line at 656 nm (red), the n = 4 to n = 2 transition to the line at 486 nm (green), the n = 5 to n = 2 transition to the line at 434 nm (blue), and the n = 6 to n = 2 transition to the line at 410 nm (violet). Because a sample of hydrogen contains a large number of atoms, the intensity of the various lines in a line spectrum depends on the number of atoms in each excited state. At the temperature in the gas discharge tube, more atoms are in the n = 3 than the n ≥ 4 levels. Consequently, the n = 3 to n = 2 transition is the most intense line, producing the characteristic red color of a hydrogen discharge (Figure 2.2.1*a*). Other families of lines are produced by transitions from excited states with n > 1 to the orbit with n = 1 or to orbits with n ≥ 3. These transitions are shown schematically in Figure 2.2.4



The Bohr Atom: The Bohr Atom, YouTube(opens in new window) [youtu.be]

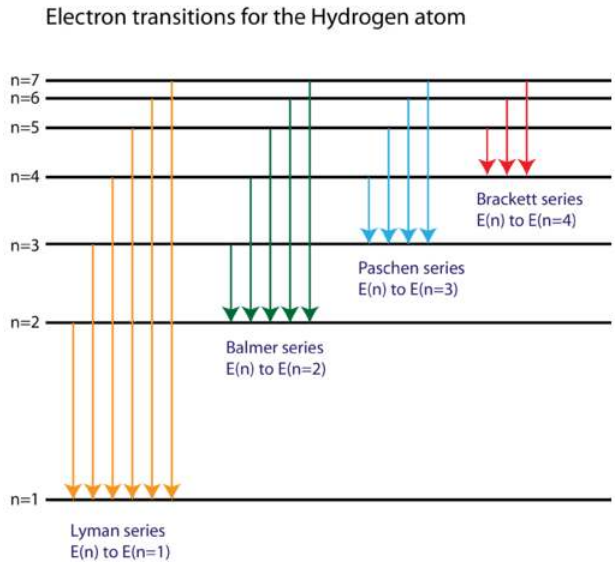


Figure 2.2.4: The electron energy level diagram for the hydrogen atom. Electron Transitions Responsible for the Various Series of Lines Observed in the Emission Spectrum of Hydrogen. The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit (n = 1); these transitions release a great deal of energy, corresponding to radiation in the ultraviolet portion of the electromagnetic spectrum. The Paschen, Brackett, and Pfund series of lines are due to transitions from higher-energy orbits to orbits with n = 3, 4, and 5, respectively; these transitions release substantially less energy, corresponding to infrared radiation. (Orbits are not drawn to scale.) (Credit: Christopher Auyeung; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

Using Atoms to Time

In contemporary applications, electron transitions are used in timekeeping that needs to be exact. Telecommunications systems, such as cell phones, depend on timing signals that are accurate to within a millionth of a second per day, as are the devices that control the US power grid. Global positioning system (GPS) signals must be accurate to within a billionth of a second per day, which is equivalent to gaining or losing no more than one second in 1,400,000 years. Quantifying time requires finding an event with an interval that repeats on a regular basis.

To achieve the accuracy required for modern purposes, physicists have turned to the atom. The current standard used to calibrate clocks is the cesium atom. Supercooled cesium atoms are placed in a vacuum chamber and bombarded with microwaves whose frequencies are carefully controlled. When the frequency is exactly right, the atoms absorb enough energy to undergo an electronic transition to a higher-energy state. Decay to a lower-energy state emits radiation. The microwave frequency is continually adjusted, serving as the clock's pendulum.

In 1967, the second was defined as the duration of 9,192,631,770 oscillations of the resonant frequency of a cesium atom, called the *cesium clock*. Research is currently under way to develop the next generation of atomic clocks that promise to be even more accurate. Such devices would allow scientists to monitor vanishingly faint electromagnetic signals produced by nerve pathways in the brain and geologists to measure variations in gravitational fields, which cause fluctuations in time, that would aid in the discovery of oil or minerals.

Example 2.2.1: The Lyman Series

Calculate the wavelength(nm) of an emitted photon from the transition of a hydrogen electron from n=4 to n=1. In what region of the electromagnetic spectrum does it occur?

Given: initial and final energy levels

Asked for: wavelength of the emitted photon and corresponding region of the spectrum

Strategy:

A. Substitute the appropriate values into Equation ??? (the Rydberg equation) and solve for ΔE.
B. Use ΔE to calculate wavelength and convert wavelength to nanometers
C. Use Figure 2.2.1 to locate the region of the electromagnetic spectrum corresponding to the calculated wavelength.

Solution:

a. We can use the Rydberg equation to calculate the change in energy:

$$\Delta E = -2.18 \times 10^{-18} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \text{ J}$$

$$\Delta E = -2.18 \times 10^{-18} \left(\frac{1}{1^2} - \frac{1}{4^2} \right) \text{ J}$$

$$\Delta E = -2.18 \times 10^{-18} \left(1 - 0.0625\right) \text{ J}$$

$$\Delta E = -2.04 \times 10^{-18} J$$

It makes sense that the change in energy for the hydrogen electron is negative because energy is being lost. Where is the energy? It leaves in the form of an emitted photon of light. Next when determining the wavelength of the emitted photon, we will use the absolute value (positive value) for ΔE

b. use the relationship between frequency, Plank's constant (h), the speed of light (c) and energy to calculate wavelength from ΔE

$$\lambda = \frac{hc}{\Delta E}$$

$$= \frac{(6.626 \times 10^{-34} \text{ J } \cancel{s})(2.998 \times 10^{8} \text{ m } \cancel{s}^{-1})}{\left(2.04 \times 10^{-18} \text{J}\right)}$$

$$= 9.74 \times 10^{-8} \text{ m}$$

$$\lambda = (9.74 \times 10^{-8} \ \cancel{m}) \left(\frac{1nm}{10^{-}9 \ \cancel{m}} \right)$$

$$\lambda = 97.4nm$$

c. This wavelength is in the ultraviolet region of the spectrum.

Exercise 2.2.1: The Pfund Series

The Pfund series of lines in the emission spectrum of hydrogen corresponds to transitions from higher excited states to the *n* = 5 orbit. Calculate the wavelength of the *second* line in the Pfund series to three significant figures. In which region of the spectrum does it lie?

Answer

4.65×10^3 nm; infrared

Bohr's model of the hydrogen atom gave an exact explanation for its observed emission spectrum. The following are his key contributions to our understanding of atomic structure:

Unfortunately, Bohr could not explain *why* the electron should be restricted to particular orbits. Also, despite a great deal of tinkering, such as assuming that orbits could be ellipses rather than circles, his model could not quantitatively explain the emission spectra of any element other than hydrogen (Figure 2.2.5). In fact, Bohr's model worked only for species that contained just one electron: H, He^+, Li^{2+}, and so forth. Scientists needed a fundamental change in their way of thinking about the electronic structure of atoms to advance beyond the Bohr model.

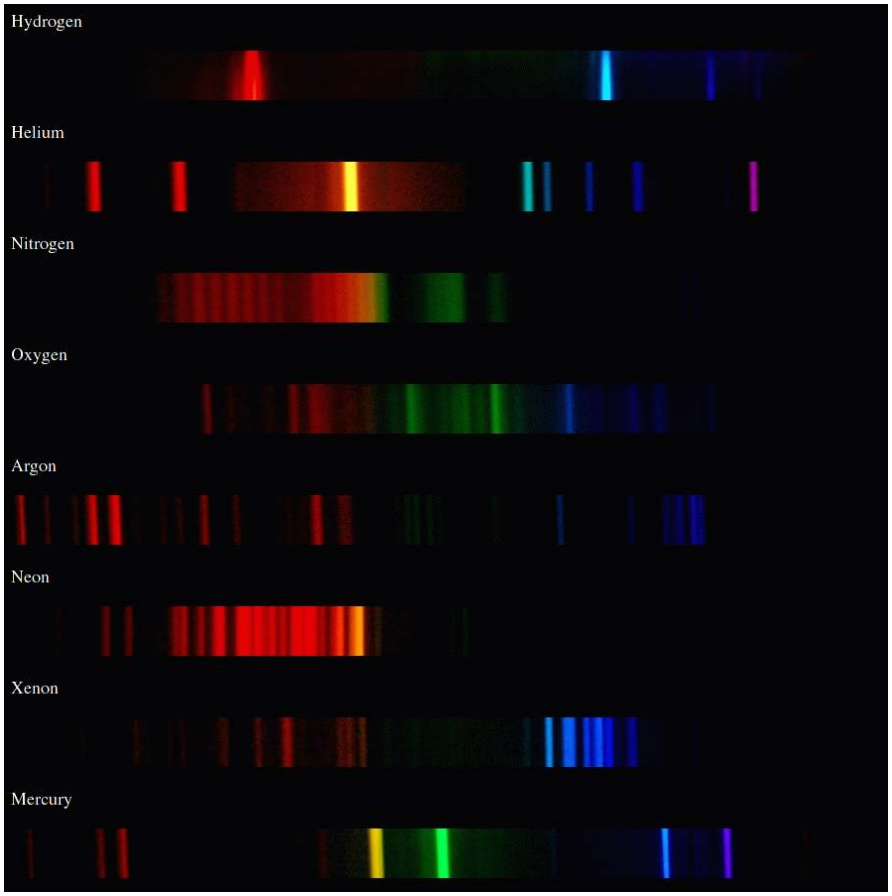


Figure 2.2.5: The atomic emission spectra for various elements. Each thin band in each spectrum corresponds to a single, unique transition between energy levels in an atom. Astronomical spectra image(opens in new window) from the Rochester Institute of Technology, CC BY-NC-SA 2.0(opens in new window).

The Energy States of the Hydrogen Atom

Thus far we have explicitly considered only the emission of light by atoms in excited states, which produces an emission spectrum (a spectrum produced by the emission of light by atoms in excited states). The converse, absorption of light by ground-state atoms to produce an excited state, can also occur, producing an absorption spectrum (a spectrum produced by the absorption of light by ground-state atoms).

> When an atom emits light, it decays to a lower energy state; when an atom absorbs light, it is excited to a higher energy state.

If white light is passed through a sample of hydrogen, hydrogen atoms absorb energy as an electron is excited to higher energy levels (orbits with $n \geq 2$). If the light that emerges is passed through a prism, it forms a continuous spectrum with *black* lines (corresponding to no light passing through the sample) at 656, 468, 434, and 410 nm. These wavelengths correspond to the $n = 2$ to

n = 3, n = 2 to n = 4, n = 2 to n = 5, and n = 2 to n = 6 transitions. Any given element therefore has both a characteristic emission spectrum and a characteristic absorption spectrum, which are essentially complementary images.

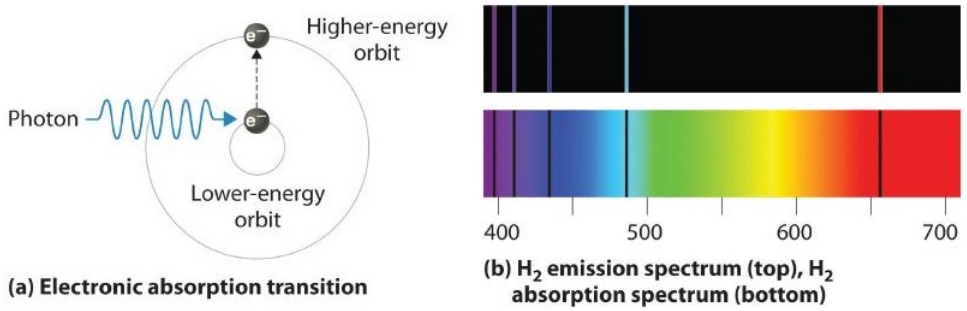


Figure 2.2.6: Absorption and Emission Spectra. Absorption of light by a hydrogen atom. (a) When a hydrogen atom absorbs a photon of light, an electron is excited to an orbit that has a higher energy and larger value of n. (b) Images of the emission and absorption spectra of hydrogen are shown here. (CC BY-NC-SA 3.0; anonymous)

Emission and absorption spectra form the basis of *spectroscopy*, which uses spectra to provide information about the structure and the composition of a substance or an object. In particular, astronomers use emission and absorption spectra to determine the composition of stars and interstellar matter. As an example, consider the spectrum of sunlight shown in Figure 2.2.7 Because the sun is very hot, the light it emits is in the form of a continuous emission spectrum. Superimposed on it, however, is a series of dark lines due primarily to the absorption of specific frequencies of light by cooler atoms in the outer atmosphere of the sun. By comparing these lines with the spectra of elements measured on Earth, we now know that the sun contains large amounts of hydrogen, iron, and carbon, along with smaller amounts of other elements. During the solar eclipse of 1868, the French astronomer Pierre Janssen (1824–1907) observed a set of lines that did not match those of any known element. He suggested that they were due to the presence of a new element, which he named *helium*, from the Greek *helios*, meaning “sun.” Helium was finally discovered in uranium ores on Earth in 1895. Alpha particles are helium nuclei. Alpha particles emitted by the radioactive uranium pick up electrons from the rocks to form helium atoms.

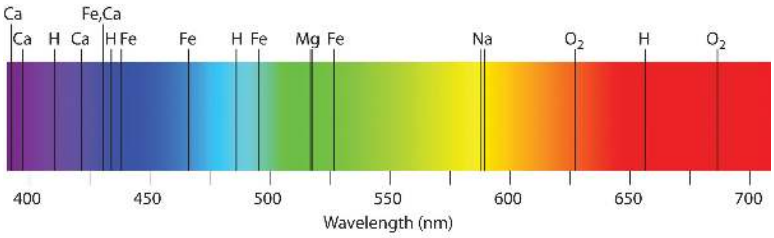


Figure 2.2.7: The Visible Spectrum of Sunlight. The characteristic dark lines are mostly due to the absorption of light by elements that are present in the cooler outer part of the sun’s atmosphere; specific elements are indicated by the labels. The lines at 628 and 687 nm, however, are due to the absorption of light by oxygen molecules in Earth’s atmosphere. (CC BY-NC-SA 3.0; anonymous)

The familiar red color of neon signs used in advertising is due to the emission spectrum of neon shown in part (b) in Figure 2.2.5. Similarly, the blue and yellow colors of certain street lights are caused, respectively, by mercury and sodium discharges. In all these cases, an electrical discharge excites neutral atoms to a higher energy state, and light is emitted when the atoms decay to the ground state. In the case of mercury, most of the emission lines are below 450 nm, which produces a blue light (part (c) in Figure 2.2.5). In the case of sodium, the most intense emission lines are at 589 nm, which produces an intense yellow light.

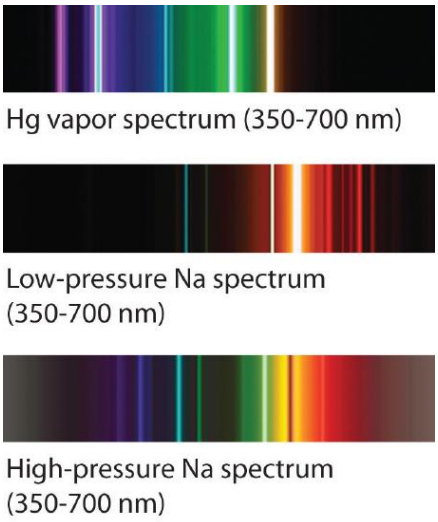


Figure 2.2.8: The emission spectra of sodium and mercury. Sodium and mercury spectra. Many street lights use bulbs that contain sodium or mercury vapor. Due to the very different emission spectra of these elements, they emit light of different colors. The lines in the sodium lamp are broadened by collisions. The dark line in the center of the high pressure sodium lamp where the low pressure lamp is strongest is cause by absorption of light in the cooler outer part of the lamp.

Summary

There is an intimate connection between the atomic structure of an atom and its spectral characteristics. Atoms of individual elements emit light at only specific wavelengths, producing a **line spectrum** rather than the continuous spectrum of all wavelengths produced by a hot object. Niels Bohr explained the line spectrum of the hydrogen atom by assuming that the electron moved in circular orbits and that orbits with only certain radii were allowed. Lines in the spectrum were due to transitions in which an electron moved from a higher-energy orbit with a larger radius to a lower-energy orbit with smaller radius. The orbit closest to the nucleus represented the **ground state** of the atom and was most stable; orbits farther away were higher-energy **excited states**. Transitions from an excited state to a lower-energy state resulted in the emission of light with only a limited number of wavelengths. Atoms can also absorb light of certain energies, resulting in a transition from the ground state or a lower-energy excited state to a higher-energy excited state. This produces an **absorption spectrum**, which has dark lines in the same position as the bright lines in the **emission spectrum** of an element. Bohr's model revolutionized the understanding of the atom but could not explain the spectra of atoms heavier than hydrogen.

Key Concepts

- Electrons can occupy only certain regions of space, called *orbits*.
- Orbits closer to the nucleus are lower in energy.
- Electrons can move from one orbit to another by absorbing or emitting energy, giving rise to characteristic spectra.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

2.2: Atomic Spectroscopy and The Bohr Model is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **6.3: Line Spectra and the Bohr Model** is licensed CC BY-NC-SA 3.0.
- **1.5: The Rydberg Formula and the Hydrogen Atomic Spectrum** by Michael Fowler is licensed CC BY-NC-SA 4.0.
- **6.3: Development of Quantum Theory** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.3: The Wavelength Nature of Matter

Learning Objectives

- To understand the wave–particle duality of matter.

Einstein's photons of light were individual packets of energy having many of the characteristics of particles. Recall that the collision of an electron (a particle) with a sufficiently energetic photon can eject a *photoelectron* from the surface of a metal. Any excess energy is transferred to the electron and is converted to the kinetic energy of the ejected electron. Einstein's hypothesis that energy is concentrated in localized bundles, however, was in sharp contrast to the classical notion that energy is spread out uniformly in a wave. We now describe Einstein's theory of the relationship between energy and mass, a theory that others built on to develop our current model of the atom.

The Wave Character of Matter

Einstein initially assumed that photons had zero mass, which made them a peculiar sort of particle indeed. In 1905, however, he published his special theory of relativity, which related energy and mass according to the famous equation:

$$E = hu = h\frac{c}{\lambda} = mc^2 \tag{2.3.1}$$

According to this theory, a photon of wavelength λ and frequency u has a nonzero mass, which is given as follows:

$$m = \frac{E}{c^2} = \frac{hu}{c^2} = \frac{h}{\lambda c} \tag{2.3.2}$$

That is, light, which had always been regarded as a wave, also has properties typical of particles, a condition known as wave–particle duality (a principle that matter and energy have properties typical of both waves and particles). Depending on conditions, light could be viewed as either a wave or a particle.

In 1922, the American physicist Arthur Compton (1892–1962) reported the results of experiments involving the collision of x-rays and electrons that supported the particle nature of light. At about the same time, a young French physics student, Louis de Broglie (1892–1972), began to wonder whether the converse was true: Could particles exhibit the properties of waves? In his PhD dissertation submitted to the Sorbonne in 1924, de Broglie proposed that a particle such as an electron could be described by a wave whose wavelength is given by

$$\lambda = \frac{h}{mv} \tag{2.3.3}$$

where

- h is Planck's constant,
- m is the mass of the particle, and
- v is the velocity of the particle.

This revolutionary idea was quickly confirmed by American physicists Clinton Davisson (1881–1958) and Lester Germer (1896–1971), who showed that beams of electrons, regarded as particles, were diffracted by a sodium chloride crystal in the same manner as x-rays, which were regarded as waves. It was proven experimentally that electrons do exhibit the properties of waves. For his work, de Broglie received the Nobel Prize in Physics in 1929.

If particles exhibit the properties of waves, why had no one observed them before? The answer lies in the numerator of de Broglie's equation, which is an extremely small number. As you will calculate in Example 2.3.1, Planck's constant (6.63×10^{-34} J•s) is so small that the wavelength of a particle with a large mass is too short (less than the diameter of an atomic nucleus) to be noticeable.



The de Broglie Equation: The de Broglie Equation, YouTube(opens in new window) [youtu.be]

Example 2.3.1: Wavelength of a Baseball in Motion

Calculate the wavelength of a baseball, which has a mass of 149 g and a speed of 100 mi/h.

Given: mass and speed of object

Asked for: wavelength

Strategy:

A. Convert the speed of the baseball to the appropriate SI units: meters per second.

B. Substitute values into Equation 2.3.3 and solve for the wavelength.

Solution:

The wavelength of a particle is given by $\lambda = h/mv$. We know that m = 0.149 kg, so all we need to find is the speed of the baseball:

$$v = \left(\frac{100\ \cancel{mi}}{\cancel{h}}\right)\left(\frac{1\ \cancel{h}}{60\ \cancel{min}}\right)\left(\frac{1.609\ \cancel{km}}{\cancel{mi}}\right)\left(\frac{1000\ m}{\cancel{km}}\right)$$

B Recall that the joule is a derived unit, whose units are (kg•m^2)/s^2. Thus the wavelength of the baseball is

$$\lambda = \frac{6.626 \times 10^{-34}\ J \cdot s}{(0.149\ kg)\,(44.69\ m \cdot s)} = \frac{6.626 \times 10^{-34}\ \cancel{kg} \cdot m^{\cancel{2}} \cdot \cancel{s}^{\cancel{-2}} \cdot \cancel{s}}{\left(0.149\ \cancel{kg}\right)\left(44.69\ \cancel{m} \cdot \cancel{s^{-1}}\right)} = 9.95 \times 10^{-35}\ m$$

(You should verify that the units cancel to give the wavelength in meters.) Given that the diameter of the nucleus of an atom is approximately 10^{-14} m, the wavelength of the baseball is almost unimaginably small.

Exercise 2.3.1: Wavelength of a Neutron in Motion

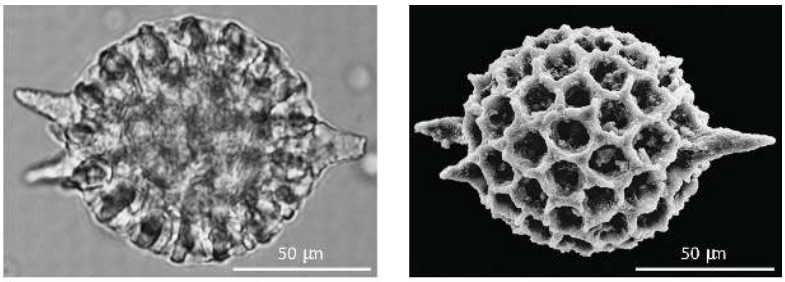
Calculate the wavelength of a neutron that is moving at 3.00 × 10^3 m/s.

Answer

1.32 Å, or 132 pm

As you calculated in Example 2.3.1, objects such as a baseball or a neutron have such short wavelengths that they are best regarded primarily as particles. In contrast, objects with very small masses (such as photons) have large wavelengths and can be viewed primarily as waves. Objects with intermediate masses, however, such as electrons, exhibit the properties of both particles *and* waves. Although we still usually think of electrons as particles, the wave nature of electrons is employed in an *electron microscope*, which has revealed most of what we know about the microscopic structure of living organisms and materials. Because the

wavelength of an electron beam is much shorter than the wavelength of a beam of visible light, this instrument can resolve smaller details than a light microscope can (Figure 2.3.1).



(a) Radiolarian under light microscope (b) Radiolarian under electron microscope

Figure 2.3.1: A Comparison of Images Obtained Using a Light Microscope and an Electron Microscope. Because of their shorter wavelength, high-energy electrons have a higher resolving power than visible light. Consequently, an electron microscope (b) is able to resolve finer details than a light microscope (a). (Radiolaria, which are shown here, are unicellular planktonic organisms.)

An Important Wave Property: Phase And Interference

A wave is a disturbance that travels in space. The magnitude of the wave at any point in space and time varies sinusoidally. While the absolute value of the magnitude of one wave at any point is not very important, the *relative* displacement of two waves, called the phase difference, is vitally important because it determines whether the waves reinforce or interfere with each other. Figure 2.3.2A shows an arbitrary phase difference between two wave and Figure 2.3.2B shows what happens when the two waves are 180 degrees out of phase. The green line is their sum. Figure 2.3.2C shows what happens when the two lines are in phase, exactly superimposed on each other. Again, the green line is the sum of the intensities. A pattern of constructive and destructive interference is obtained when two (or more) diffracting waves interact with each other. This principle of diffraction and interference was used to prove the wave properties of electrons and is the basis for how electron microscopes work.

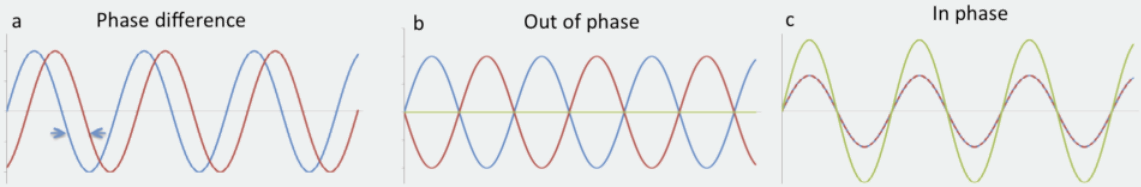
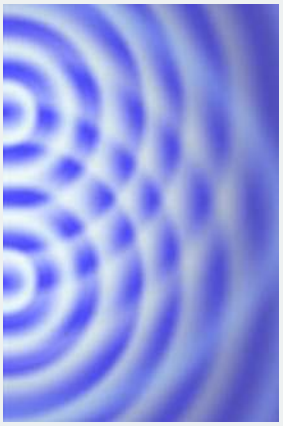


Figure 2.3.2: Phase. Two waves traveling together are displaced by a phase difference. If the phase difference is 0° then they lay on top of each other and reinforce. If the phase difference is 180° they completely cancel each other out.

A shows two waves with a phase difference where the peaks are slightly misaligned. B shows two waves out of phase, the two waves are opposite of each other. C shows two waves in phase, the two waves peak at the same time.



The waves are the white circles that start from the left side. The waves intersect at multiple points.

Photograph of an interference pattern produced by circular water waves in a ripple tank.

For a mathematical analysis of phase aspects in sinusoids, check the math Libretexts library.

Standing Waves

De Broglie also investigated why only certain orbits were allowed in Bohr's model of the hydrogen atom. He hypothesized that the electron behaves like a **standing wave** (a wave that does not travel in space). An example of a standing wave is the motion of a string of a violin or guitar. When the string is plucked, it vibrates at certain fixed frequencies because it is fastened at both ends (Figure 2.3.3). If the length of the string is L, then the lowest-energy vibration (the fundamental) has wavelength

$$\begin{aligned} \frac{\lambda}{2} &= L \\ \lambda &= 2L \end{aligned} \tag{2.3.4}$$

Higher-energy vibrations are called *overtones* (the vibration of a standing wave that is higher in energy than the fundamental vibration) and are produced when the string is plucked more strongly; they have wavelengths given by

$$\lambda = \frac{2L}{n} \tag{2.3.5}$$

where n has any integral value. When plucked, all other frequencies die out immediately. Only the resonant frequencies survive and are heard. Thus, we can think of the resonant frequencies of the string as being quantized. Notice in Figure 2.3.3 that all overtones have one or more nodes, points where the string does not move. The amplitude of the wave at a node is zero.

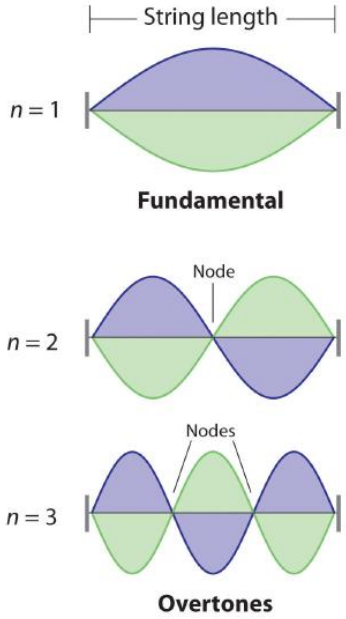


Figure 2.3.3: Standing Waves on a Vibrating String. The vibration with \(*n* = 1\) is the fundamental and contains no nodes. Vibrations with higher values of *n* are called overtones; they contain \(*n* − 1\) nodes.

Quantized vibrations and overtones containing nodes are not restricted to one-dimensional systems, such as strings. A two-dimensional surface, such as a drumhead, also has quantized vibrations. Similarly, when the ends of a string are joined to form a circle, the only allowed vibrations are those with wavelength

$$2\pi r = n\lambda \tag{2.3.6}$$

where r is the radius of the circle. De Broglie argued that Bohr's allowed orbits could be understood if the electron behaved like a *standing circular wave* (Figure 2.3.4). The standing wave could exist only if the circumference of the circle was an integral multiple of the wavelength such that the propagated waves were all in phase, thereby increasing the net amplitudes and causing *constructive interference*. Otherwise, the propagated waves would be out of phase, resulting in a net decrease in amplitude and causing *destructive interference*. The nonresonant waves interfere with themselves! De Broglie's idea explained Bohr's allowed orbits and energy levels nicely: in the lowest energy level, corresponding to $n = 1$ in Equation 2.3.6, one complete wavelength would close the circle. Higher energy levels would have successively higher values of *n* with a corresponding number of nodes.

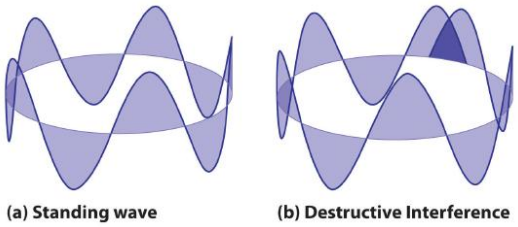


Figure 2.3.4: Standing Circular Wave and Destructive Interference. (a) In a standing circular wave with \(*n* = 5\), the circumference of the circle corresponds to exactly five wavelengths, which results in constructive interference of the wave with itself when overlapping occurs. (b) If the circumference of the circle is not equal to an integral multiple of wavelengths, then the wave does not overlap exactly with itself, and the resulting destructive interference will result in cancellation of the wave. Consequently, a standing wave cannot exist under these conditions.

Like all analogies, although the standing wave model helps us understand much about why Bohr's theory worked, it also, if pushed too far, can mislead. As you will see, some of de Broglie's ideas are retained in the modern theory of the electronic structure of the atom: the wave behavior of the electron and the presence of nodes that increase in number as the energy level increases. Unfortunately, his (and Bohr's) explanation also contains one major feature that we now know to be incorrect: in the currently accepted model, the electron in a given orbit is *not* always at the same distance from the nucleus.

The Heisenberg Uncertainty Principle

Because a wave is a disturbance that travels in space, it has no fixed position. One might therefore expect that it would also be hard to specify the exact position of a *particle* that exhibits wavelike behavior. A characteristic of light is that is can be bent or spread out by passing through a narrow slit. You can literally see this by half closing your eyes and looking through your eye lashes. This reduces the brightness of what you are seeing and somewhat fuzzes out the image, but the light bends around your lashes to provide a complete image rather than a bunch of bars across the image. This is called diffraction.

This behavior of waves is captured in Maxwell's equations (1870 or so) for electromagnetic waves and was and is well understood. An "uncertainty principle" for light is, if you will, merely a conclusion about the nature of electromagnetic waves and nothing new. De Broglie's idea of wave-particle duality means that particles such as electrons which exhibit wavelike characteristics will also undergo diffraction from slits whose size is on the order of the electron wavelength.

This situation was described mathematically by the German physicist Werner Heisenberg (1901–1976; Nobel Prize in Physics, 1932), who related the position of a particle to its momentum. Referring to the electron, Heisenberg stated that "at every moment the electron has only an inaccurate position and an inaccurate velocity, and between these two inaccuracies there is this uncertainty relation." Mathematically, the **Heisenberg uncertainty principle** states that the uncertainty in the position of a particle (Δx) multiplied by the uncertainty in its momentum [$\Delta(mv)$] is greater than or equal to Planck's constant divided by 4π:

$$(\Delta x)\,(\Delta\,[mv]) \geq \frac{h}{4\pi} \tag{2.3.7}$$

Because Planck's constant is a very small number, the Heisenberg uncertainty principle is important only for particles such as electrons that have very low masses. These are the same particles predicted by de Broglie's equation to have measurable wavelengths.

If the precise position x of a particle is known absolutely ($\Delta x = 0$), then the uncertainty in its momentum must be infinite:

$$(\Delta\,[mv]) = \frac{h}{4\pi\,(\Delta x)} = \frac{h}{4\pi\,(0)} = \infty \tag{2.3.8}$$

Because the mass of the electron at rest (m) is both constant and accurately known, the uncertainty in $\Delta(mv)$ must be due to the Δv term, which would have to be infinitely large for $\Delta(mv)$ to equal infinity. That is, according to Equation 2.3.8, the more accurately we know the exact position of the electron (as $\Delta x \to 0$), the less accurately we know the speed and the kinetic energy of the electron (1/2 mv^2) because $\Delta(mv) \to \infty$. Conversely, the more accurately we know the precise momentum (and the energy) of the electron [as $\Delta(mv) \to 0$], then $\Delta x \to \infty$ and we have no idea where the electron is.

Bohr's model of the hydrogen atom violated the Heisenberg uncertainty principle by trying to specify *simultaneously* both the position (an orbit of a particular radius) and the energy (a quantity related to the momentum) of the electron. Moreover, given its mass and wavelike nature, the electron in the hydrogen atom could not possibly orbit the nucleus in a well-defined circular path as

predicted by Bohr. You will see, however, that the *most probable radius* of the electron in the hydrogen atom is exactly the one predicted by Bohr's model.

Example 2.3.1: Quantum Nature of Baseballs

Calculate the minimum uncertainty in the position of the pitched baseball from Example 2.3.1 that has a mass of exactly 149 g and a speed of 100 ± 1 mi/h.

Given: mass and speed of object

Asked for: minimum uncertainty in its position

Strategy:

A. Rearrange the inequality that describes the Heisenberg uncertainty principle (Equation 2.3.7) to solve for the minimum uncertainty in the position of an object (Δ*x*).
B. Find Δ*v* by converting the velocity of the baseball to the appropriate SI units: meters per second.
C. Substitute the appropriate values into the expression for the inequality and solve for Δ*x*.

Solution:

A The Heisenberg uncertainty principle (Equation 2.3.7) tells us that

$$(\Delta x)(\Delta(mv)) = h/4\pi$$

. Rearranging the inequality gives

$$\Delta x \geq \left(\frac{h}{4\pi}\right)\left(\frac{1}{\Delta(mv)}\right)$$

B We know that $h = 6.626 \times 10^{-34}$ J•s and $m = 0.149$ kg. Because there is no uncertainty in the mass of the baseball, $\Delta(mv) = m\Delta v$ and $\Delta v = \pm 1$ mi/h. We have

$$\Delta u = \left(\frac{1\ \cancel{mi}}{\cancel{h}}\right)\left(\frac{1\ \cancel{h}}{60\ \cancel{min}}\right)\left(\frac{1\ \cancel{min}}{60\ s}\right)\left(\frac{1.609\ \cancel{km}}{\cancel{mi}}\right)\left(\frac{1000\ m}{\cancel{km}}\right) = 0.4469\ m/s$$

C Therefore,

$$\Delta x \geq \left(\frac{6.626 \times 10^{-34}\ J \cdot s}{4\,(3.1416)}\right)\left(\frac{1}{(0.149\ kg)\,(0.4469\ m \cdot s^{-1})}\right)$$

Inserting the definition of a joule (1 J = 1 kg•m^2/s^2) gives

$$\Delta x \geq \left(\frac{6.626 \times 10^{-34}\ \cancel{kg} \cdot m^{\cancel{2}} \cdot s}{4\,(3.1416)\left(\cancel{s^2}\right)}\right)\left(\frac{1\ \cancel{s}}{\left(0.149\ \cancel{kg}\right)(0.4469\ \cancel{m})}\right)$$

$$\Delta x \geq 7.92 \pm \times 10^{-34}\ m$$

This is equal to 3.12×10^{-32} inches. We can safely say that if a batter misjudges the speed of a fastball by 1 mi/h (about 1%), he will not be able to blame Heisenberg's uncertainty principle for striking out.

Exercise 2.3.2

Calculate the minimum uncertainty in the position of an electron traveling at one-third the speed of light, if the uncertainty in its speed is ±0.1%. Assume its mass to be equal to its mass at rest.

Answer

6×10^{-10} m, or 0.6 nm (about the diameter of a benzene molecule)

Videos and Examples

- de Broglie Waves - Sixty Symbols - a bit of history and explanation (as well as wave particle duality can be explained)
- Calculating the wavelength of a proton - Josh Samson
- Calculating the wavelength of a small car - Prof. Heath
- What is the Uncertainty Principle? - Minute Physics
- AP Chem Heisenberg Uncertainty Principle - Mind Bite
- deBroglie Example - about education
- Heisenberg uncertainty principle quiz worked out - C Craig
- Quantum Chemistry - Ohio State
- Quantum Chemistry Quizzes - mhe education
- AP Chemistry Chapter 7 Review - Science Geek

Answers for these quizzes are included.

Summary

An electron possesses both particle and wave properties. The modern model for the electronic structure of the atom is based on recognizing that an electron possesses particle and wave properties, the so-called **wave–particle duality**. Louis de Broglie showed that the wavelength of a particle is equal to Planck's constant divided by the mass times the velocity of the particle.

$$\lambda = \frac{h}{mv}$$

The electron in Bohr's circular orbits could thus be described as a **standing wave**, one that does not move through space. Standing waves are familiar from music: the lowest-energy standing wave is the **fundamental** vibration, and higher-energy vibrations are **overtones** and have successively more **nodes**, points where the amplitude of the wave is always zero. Werner Heisenberg's **uncertainty principle** states that it is impossible to precisely describe both the location and the speed of particles that exhibit wavelike behavior.

$$(\Delta x)\,(\Delta\,[mv]) \geqslant \frac{h}{4\pi}$$

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

2.3: The Wavelength Nature of Matter is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **6.4: The Wave Behavior of Matter** is licensed CC BY-NC-SA 3.0.

2.4: Quantum Mechanics and The Atom

Learning Objectives

- To apply the results of quantum mechanics to chemistry.

The paradox described by Heisenberg's uncertainty principle and the wavelike nature of subatomic particles such as the electron made it impossible to use the equations of classical physics to describe the motion of electrons in atoms. Scientists needed a new approach that took the wave behavior of the electron into account. In 1926, an Austrian physicist, Erwin Schrödinger (1887–1961; Nobel Prize in Physics, 1933), developed *wave mechanics*, a mathematical technique that describes the relationship between the motion of a particle that exhibits wavelike properties (such as an electron) and its allowed energies.

Erwin Schrödinger (1887–1961)

Schrödinger's unconventional approach to atomic theory was typical of his unconventional approach to life. He was notorious for his intense dislike of memorizing data and learning from books. When Hitler came to power in Germany, Schrödinger escaped to Italy. He then worked at Princeton University in the United States but eventually moved to the Institute for Advanced Studies in Dublin, Ireland, where he remained until his retirement in 1955.

Although quantum mechanics uses sophisticated mathematics, you do not need to understand the mathematical details to follow our discussion of its general conclusions. We focus on the properties of the *wavefunctions* that are the solutions of Schrödinger's equations.

Wavefunctions

A wavefunction (Ψ) is a mathematical function that relates the location of an electron at a given point in space (identified by x, y, and z coordinates) to the amplitude of its wave, which corresponds to its energy. Thus each wavefunction is associated with a particular energy E. The properties of wavefunctions derived from quantum mechanics are summarized here:

- **A wavefunction uses three variables to describe the position of an electron.** A fourth variable is usually required to fully describe the location of objects in motion. Three specify the position in space (as with the Cartesian coordinates x, y, and z), and one specifies the time at which the object is at the specified location. For example, if you were the captain of a ship trying to intercept an enemy submarine, you would need to know its latitude, longitude, and depth, as well as the time at which it was going to be at this position (Figure 2.4.1). For electrons, we can ignore the time dependence because we will be using standing waves, which by definition do not change with time, to describe the position of an electron.

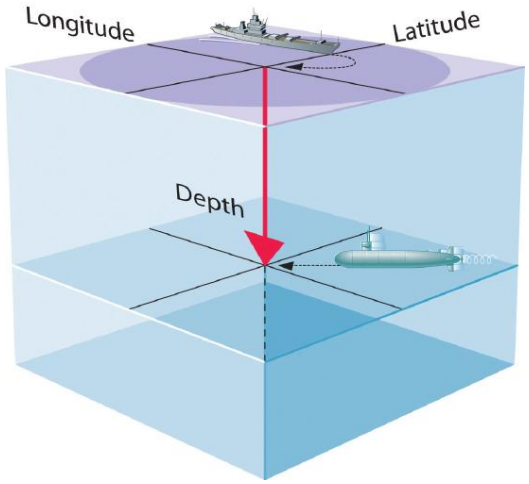


Figure 2.4.1: The Four Variables (Latitude, Longitude, Depth, and Time) required to precisely locate an object

- **The magnitude of the wavefunction at a particular point in space is proportional to the amplitude of the wave at that point.** Many wavefunctions are complex functions, which is a mathematical term indicating that they contain $\sqrt{-1}$, represented as i. Hence the amplitude of the wave has no real physical significance. In contrast, the sign of the wavefunction (either positive

or negative) corresponds to the phase of the wave, which will be important in our discussion of chemical bonding. The sign of the wavefunction should *not* be confused with a positive or negative electrical charge.

- **The square of the wavefunction at a given point is proportional to the probability of finding an electron at that point, which leads to a distribution of probabilities in space.** The square of the wavefunction (Ψ^2) is always a real quantity [recall that that $\sqrt{-1}^2 = -1$] and is proportional to the probability of finding an electron at a given point. More accurately, the probability is given by the product of the wavefunction Ψ and its complex conjugate Ψ*, in which all terms that contain *i* are replaced by $-i$. We use probabilities because, according to Heisenberg's uncertainty principle, we cannot precisely specify the position of an electron. The probability of finding an electron at any point in space depends on several factors, including the distance from the nucleus and, in many cases, the atomic equivalent of latitude and longitude. As one way of graphically representing the probability distribution, the probability of finding an electron is indicated by the density of colored dots, as shown for the ground state of the hydrogen atom in Figure 2.4.2.
- **Describing the electron distribution as a standing wave leads to sets of *quantum numbers* that are characteristic of each wavefunction.** From the patterns of one- and two-dimensional standing waves shown previously, you might expect (correctly) that the patterns of three-dimensional standing waves would be complex. Fortunately, however, in the 18th century, a French mathematician, Adrien Legendre (1752–1783), developed a set of equations to describe the motion of tidal waves on the surface of a flooded planet. Schrödinger incorporated Legendre's equations into his wavefunctions. The requirement that the waves must be in phase with one another to avoid cancellation and produce a standing wave results in a limited number of solutions (wavefunctions), each of which is specified by a set of numbers called quantum numbers.
- **Each wavefunction is associated with a particular energy.** As in Bohr's model, the energy of an electron in an atom is quantized; it can have only certain allowed values. The major difference between Bohr's model and Schrödinger's approach is that Bohr had to impose the idea of quantization arbitrarily, whereas in Schrödinger's approach, quantization is a natural consequence of describing an electron as a standing wave.

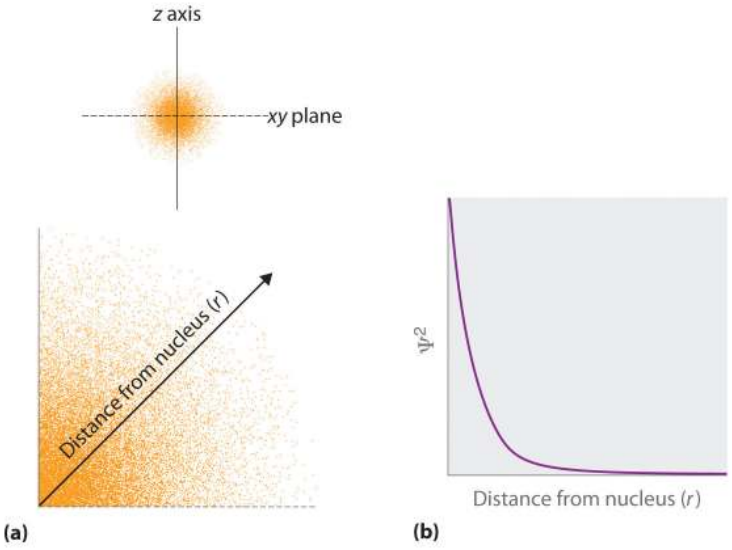


Figure 2.4.2: Probability of Finding the Electron in the Ground State of the Hydrogen Atom at Different Points in Space. (a) The density of the dots shows electron probability. (b) In this plot of Ψ^2 versus *r* for the ground state of the hydrogen atom, the electron probability density is greatest at *r* = 0 (the nucleus) and falls off with increasing *r*. Because the line never actually reaches the horizontal axis, the probability of finding the electron at very large values of *r* is very small but *not* zero.

Quantum Numbers

Schrödinger's approach uses three quantum numbers (*n*, *l*, and m_l) to specify any wavefunction. The quantum numbers provide information about the spatial distribution of an electron. Although *n* can be any positive integer, only certain values of *l* and m_l are allowed for a given value of *n*.

The Principal Quantum Number

The **principal quantum number** (n) tells the average relative distance of an electron from the nucleus:

$$n = 1, 2, 3, 4, \ldots \tag{2.4.1}$$

As n increases for a given atom, so does the average distance of an electron from the nucleus. A negatively charged electron that is, on average, closer to the positively charged nucleus is attracted to the nucleus more strongly than an electron that is farther out in space. This means that electrons with higher values of n are easier to remove from an atom. All wavefunctions that have the same value of n are said to constitute a principal shell because those electrons have similar average distances from the nucleus. As you will see, the principal quantum number n corresponds to the n used by Bohr to describe electron orbits and by Rydberg to describe atomic energy levels.

The Azimuthal Quantum Number

The second quantum number is often called the **azimuthal quantum number (l)**. The value of l describes the *shape* of the region of space occupied by the electron. The allowed values of l depend on the value of n and can range from 0 to n − 1:

$$l = 0, 1, 2, \ldots, n-1 \tag{2.4.2}$$

For example, if n = 1, l can be only 0; if n = 2, l can be 0 or 1; and so forth. For a given atom, all wavefunctions that have the same values of both n and l form a subshell. The regions of space occupied by electrons in the same subshell usually have the same shape, but they are oriented differently in space.



Principal quantum number (n) & Orbital angular momentum (l): The Orbital Subshell:
https://youtu.be/ms7WR149fAY

The Magnetic Quantum Number

The third quantum number is the magnetic quantum number (m_l). The value of m_l describes the *orientation* of the region in space occupied by an electron with respect to an applied magnetic field. The allowed values of m_l depend on the value of l: m_l can range from $-l$ to l in integral steps:

$$m_l = -l, -l+1, \ldots, 0, \ldots, l-1, l \tag{2.4.3}$$

For example, if $l = 0$, m_l can be only 0; if l = 1, m_l can be −1, 0, or +1; and if l = 2, m_l can be −2, −1, 0, +1, or +2.

Each wavefunction with an allowed combination of n, l, and m_l values describes an atomic **orbital**, a particular spatial distribution for an electron. For a given set of quantum numbers, each principal shell has a fixed number of subshells, and each subshell has a fixed number of orbitals.

Example2.4.1: n=4 Shell Structure

How many subshells and orbitals are contained within the principal shell with n = 4?

Given: value of n

Asked for: number of subshells and orbitals in the principal shell

Strategy:

A. Given n = 4, calculate the allowed values of l. From these allowed values, count the number of subshells.

B. For each allowed value of l, calculate the allowed values of m_l. The sum of the number of orbitals in each subshell is the number of orbitals in the principal shell.

Solution:

A We know that l can have all integral values from 0 to $n - 1$. If $n = 4$, then l can equal 0, 1, 2, or 3. Because the shell has four values of l, it has four subshells, each of which will contain a different number of orbitals, depending on the allowed values of m_l.

B For $l = 0$, m_l can be only 0, and thus the $l = 0$ subshell has only one orbital. For $l = 1$, m_l can be 0 or ±1; thus the $l = 1$ subshell has three orbitals. For $l = 2$, m_l can be 0, ±1, or ±2, so there are five orbitals in the $l = 2$ subshell. The last allowed value of l is $l = 3$, for which m_l can be 0, ±1, ±2, or ±3, resulting in seven orbitals in the $l = 3$ subshell. The total number of orbitals in the $n = 4$ principal shell is the sum of the number of orbitals in each subshell and is equal to $n^2 = 16$

? Exercise 2.4.1: n=3 Shell Structure

How many subshells and orbitals are in the principal shell with $n = 3$?

Answer

three subshells; nine orbitals

Rather than specifying all the values of n and l every time we refer to a subshell or an orbital, chemists use an abbreviated system with lowercase letters to denote the value of l for a particular subshell or orbital:

l =	0	1	2	3
Designation	*s*	*p*	*d*	*f*

The principal quantum number is named first, followed by the letter *s*, *p*, *d*, or *f* as appropriate. (These orbital designations are derived from historical terms for corresponding spectroscopic characteristics: *s*harp, *p*rinciple, *d*iffuse, and *f*undamental.) A 1*s* orbital has $n = 1$ and $l = 0$; a 2*p* subshell has $n = 2$ and $l = 1$ (and has three 2*p* orbitals, corresponding to $m_l = -1$, 0, and +1); a 3*d* subshell has $n = 3$ and $l = 2$ (and has five 3*d* orbitals, corresponding to $m_l = -2$, −1, 0, +1, and +2); and so forth.

We can summarize the relationships between the quantum numbers and the number of subshells and orbitals as follows (Table 6.5.1):

- Each principal shell has n subshells. For $n = 1$, only a single subshell is possible (1*s*); for $n = 2$, there are two subshells (2*s* and 2*p*); for $n = 3$, there are three subshells (3*s*, 3*p*, and 3*d*); and so forth. Every shell has an *ns* subshell, any shell with $n \geq 2$ also has an *np* subshell, and any shell with $n \geq 3$ also has an *nd* subshell. Because a 2*d* subshell would require both $n = 2$ and $l = 2$, which is not an allowed value of l for $n = 2$, a 2*d* subshell does not exist.
- Each subshell has $2l + 1$ orbitals. This means that all *ns* subshells contain a single *s* orbital, all *np* subshells contain three *p* orbitals, all *nd* subshells contain five *d* orbitals, and all *nf* subshells contain seven *f* orbitals.

> *Each principal shell has n subshells, and each subshell has 2l + 1 orbitals.*

Table 2.4.1: Values of n, l, and ml through n = 4

n	l	Subshell Designation	m_l	Number of Orbitals in Subshell	Number of Orbitals in Shell
1	0	1*s*	0	1	1
2	0	2*s*	0	1	4
	1	2*p*	−1, 0, 1	3	
3	0	3*s*	0	1	9
	1	3*p*	−1, 0, 1	3	

n	l	Subshell Designation	m_l	Number of Orbitals in Subshell	Number of Orbitals in Shell
	2	3*d*	−2, −1, 0, 1, 2	5	
4	0	4*s*	0	1	16
	1	4*p*	−1, 0, 1	3	
	2	4*d*	−2, −1, 0, 1, 2	5	
	3	4*f*	−3, −2, −1, 0, 1, 2, 3	7	



Magnetic Quantum Number (ml) & Spin Quantum Number (ms): https://youtu.be/gbmGVUXBOBk

Summary

There is a relationship between the motions of electrons in atoms and molecules and their energies that is described by quantum mechanics. Because of wave–particle duality, scientists must deal with the probability of an electron being at a particular point in space. To do so required the development of **quantum mechanics**, which uses **wavefunctions (Ψ)** to describe the mathematical relationship between the motion of electrons in atoms and molecules and their energies. Wavefunctions have five important properties:

1. the wavefunction uses three variables (Cartesian axes *x*, *y*, and *z*) to describe the position of an electron;
2. the magnitude of the wavefunction is proportional to the intensity of the wave;
3. the probability of finding an electron at a given point is proportional to the square of the wavefunction at that point, leading to a distribution of probabilities in space that is often portrayed as an **electron density** plot;
4. describing electron distributions as standing waves leads naturally to the existence of sets of **quantum numbers** characteristic of each wavefunction; and
5. each spatial distribution of the electron described by a wavefunction with a given set of quantum numbers has a particular energy.

Quantum numbers provide important information about the energy and spatial distribution of an electron. The **principal quantum number** *n* can be any positive integer; as *n* increases for an atom, the average distance of the electron from the nucleus also increases. All wavefunctions with the same value of *n* constitute a **principal shell** in which the electrons have similar average distances from the nucleus. The **azimuthal quantum number** *l* can have integral values between 0 and $n - 1$; it describes the shape of the electron distribution. wavefunctions that have the same values of both *n* and *l* constitute a **subshell**, corresponding to electron distributions that usually differ in orientation rather than in shape or average distance from the nucleus. The **magnetic quantum number** m_l can have $2l + 1$ integral values, ranging from $-l$ to $+l$, and describes the orientation of the electron distribution. Each wavefunction with a given set of values of *n*, *l*, and m_l describes a particular spatial distribution of an electron in an atom, an **atomic orbital**.

The Spin Quantum Number

The other three quantum numbers, n, l, and m_l, are properties of specific atomic orbitals that also define in what part of the space an electron is most likely to be located. Orbitals are a result of solving the Schrödinger equation for electrons in atoms. The electron spin is a different kind of property. It is a completely quantum phenomenon with no analogues in the classical realm. In addition, it cannot be derived from solving the Schrödinger equation and is not related to the normal spatial coordinates (such as the Cartesian x, y, and z). Electron spin describes an intrinsic electron "rotation" or "spinning." Each electron acts as a tiny magnet or a tiny rotating object with an angular momentum, even though this rotation cannot be observed in terms of the spatial coordinates.

The magnitude of the overall electron spin can only have one value, and an electron can only "spin" in one of two quantized states. One is termed the α state, with the z component of the spin being in the positive direction of the z axis. This corresponds to the spin quantum number ms=1/2. The other is called the β state, with the z component of the spin being negative and ms=−1/2. Any electron, regardless of the atomic orbital it is located in, can only have one of those two values of the spin quantum number. The energies of electrons having ms=−1/2 and ms=1/2 are different if an external magnetic field is applied.

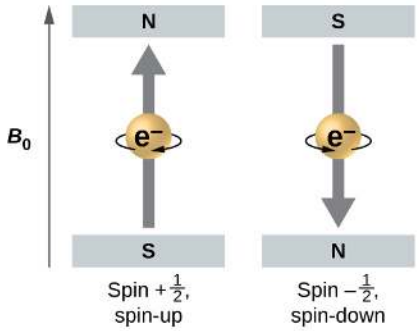


Figure 2.4.3: Electrons with spin values \(±\ce{1/2}\) *in an external magnetic field.*

Figure 2.4.3 illustrates this phenomenon. An electron acts like a tiny magnet. Its moment is directed up (in the positive direction of the z axis) for the 1/2 spin quantum number and down (in the negative z direction) for the spin quantum number of −1/2. A magnet has a lower energy if its magnetic moment is aligned with the external magnetic field (the left electron) and a higher energy for the magnetic moment being opposite to the applied field. This is why an electron with ms=1/2 has a slightly lower energy in an external field in the positive z direction, and an electron with ms=−1/2 has a slightly higher energy in the same field. This is true even for an electron occupying the same orbital in an atom. A spectral line corresponding to a transition for electrons from the same orbital but with different spin quantum numbers has two possible values of energy; thus, the line in the spectrum will show a fine structure splitting.

2.4: Quantum Mechanics and The Atom is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **6.5: Quantum Mechanics and Atomic Orbitals** is licensed CC BY-NC-SA 3.0.

2.5: The Shape of Atomic Orbitals

Learning Objectives

- To understand the 3D representation of electronic orbitals

An orbital is the quantum mechanical refinement of Bohr's orbit. In contrast to his concept of a simple circular orbit with a fixed radius, orbitals are mathematically derived regions of space with different **probabilities** of containing an electron.

One way of representing electron probability distributions was illustrated previously for the 1**s** orbital of hydrogen. Because Ψ^2 gives the probability of finding an electron in a given volume of space (such as a cubic picometer), a plot of Ψ^2 versus distance from the nucleus (**r**) is a plot of the **probability density**. The 1**s** orbital is spherically symmetrical, so the probability of finding a 1**s** electron at any given point depends **only** on its distance from the nucleus. The probability density is greatest at $r = 0$ (at the nucleus) and decreases steadily with increasing distance. At very large values of **r**, the electron probability density is very small but **not** zero.

In contrast, we can calculate the **radial probability** (the probability of finding a 1s electron at a distance r from the nucleus) by adding together the probabilities of an electron being at all points on a series of **x** spherical shells of radius $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$,…, $\mathbf{r}_{x-1}$, $\mathbf{r}_x$. In effect, we are dividing the atom into very thin concentric shells, much like the layers of an onion (Figure $2.5.1a$), and calculating the probability of finding an electron on each spherical shell. Recall that the electron probability density is greatest at r = 0 (Figure $2.5.1b$), so the density of dots is greatest for the smallest spherical shells in part (a) in Figure $2.5.1$. In contrast, the surface area of each spherical shell is equal to $4\pi r^2$, which increases very rapidly with increasing r (Figure $2.5.1c$). Because the surface area of the spherical shells increases more rapidly with increasing r than the electron probability density decreases, the plot of radial probability has a maximum at a particular distance (Figure $2.5.1d$). Most important, when r is very small, the surface area of a spherical shell is so small that the **total** probability of finding an electron close to the nucleus is very low; at the nucleus, the electron probability vanishes (Figure $2.5.1d$).

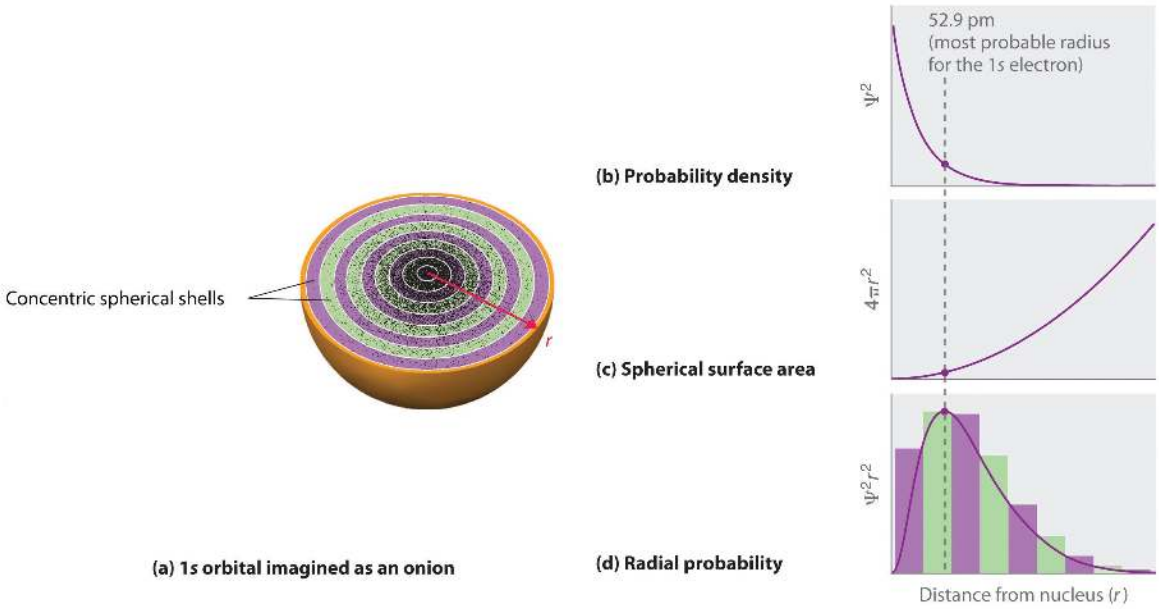


Figure 2.5.1: Most Probable Radius for the Electron in the Ground State of the Hydrogen Atom. (a) Imagine dividing the atom's total volume into very thin concentric shells as shown in the onion drawing. (b) A plot of electron probability density Ψ^2 versus r shows that the electron probability density is greatest at r = 0 and falls off smoothly with increasing r. The density of the dots is therefore greatest in the innermost shells of the onion. (c) The surface area of each shell, given by $4\pi\mathbf{r}^2$, increases rapidly with increasing r. (d) If we count the number of dots in each spherical shell, we obtain the total probability of finding the electron at a given value of r. Because the surface area of each shell increases more rapidly with increasing r than the electron probability density decreases, a plot of electron probability versus r (the **radial probability**) shows a peak. This peak corresponds to the most probable radius for the electron, 52.9 pm, which is exactly the radius predicted by Bohr's model of the hydrogen atom.

For the hydrogen atom, the peak in the radial probability plot occurs at r = 0.529 Å (52.9 pm), which is exactly the radius calculated by Bohr for the **n** = 1 orbit. Thus the **most probable radius** obtained from quantum mechanics is identical to the radius

calculated by classical mechanics. In Bohr's model, however, the electron was assumed to be at this distance 100% of the time, whereas in the Schrödinger model, it is at this distance only some of the time. The difference between the two models is attributable to the wavelike behavior of the electron and the Heisenberg uncertainty principle.

Figure 2.5.2 compares the electron probability densities for the hydrogen 1**s**, 2**s**, and 3**s** orbitals. Note that all three are spherically symmetrical. For the 2**s** and 3**s** orbitals, however (and for all other **s** orbitals as well), the electron probability density does not fall off smoothly with increasing r. Instead, a series of minima and maxima are observed in the radial probability plots (Figure 2.5.2*c*). The minima correspond to spherical **nodes** (regions of zero electron probability), which alternate with spherical regions of nonzero electron probability. The existence of these nodes is a consequence of changes of wave **phase** in the wavefunction Ψ.

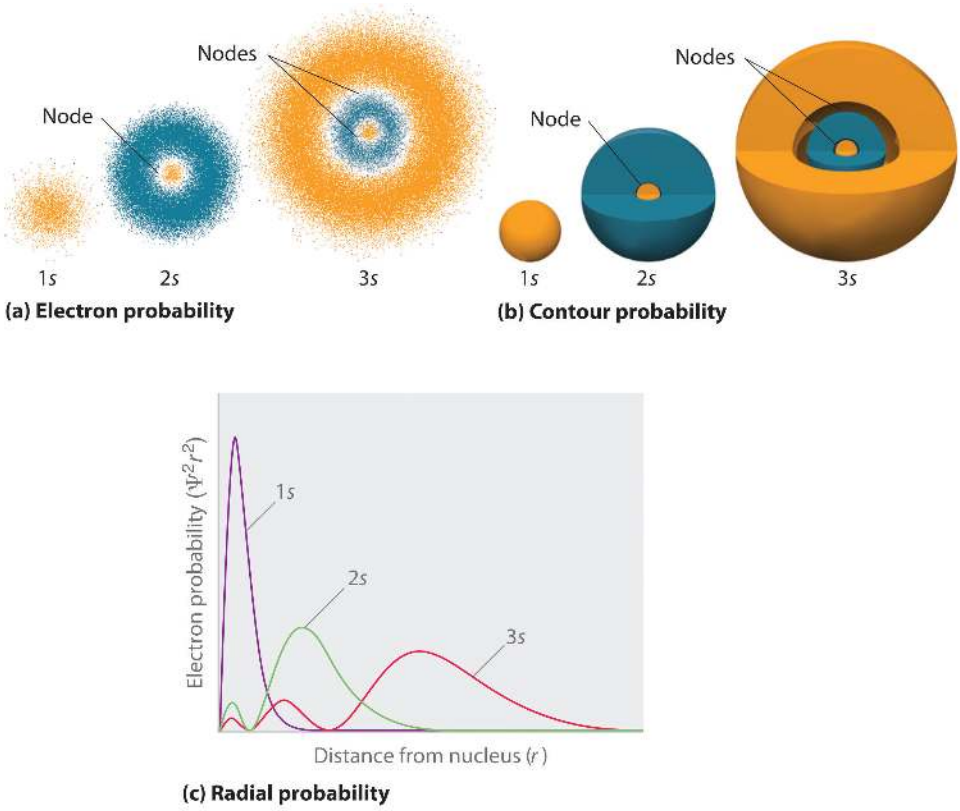


Figure 2.5.2: Probability Densities for the 1**s**, 2**s**, and 3**s** Orbitals of the Hydrogen Atom. (a) The electron probability density in any plane that contains the nucleus is shown. Note the presence of circular regions, or nodes, where the probability density is zero. (b) Contour surfaces enclose 90% of the electron probability, which illustrates the different sizes of the 1**s**, 2**s**, and 3**s** orbitals. The cutaway drawings give partial views of the internal spherical nodes. The orange color corresponds to regions of space where the phase of the wave function is positive, and the blue color corresponds to regions of space where the phase of the wave function is negative. (c) In these plots of electron probability as a function of distance from the nucleus (**r**) in all directions (radial probability), the most probable radius increases as **n** increases, but the 2**s** and 3**s** orbitals have regions of significant electron probability at small values of r.

s Orbitals (l=0)

Three things happen to **s** orbitals as **n** increases (Figure 2.5.2):

1. They become larger, extending farther from the nucleus.
2. They contain more nodes. This is similar to a standing wave that has regions of significant amplitude separated by nodes, points with zero amplitude.
3. For a given atom, the **s** orbitals also become higher in energy as **n** increases because of their increased distance from the nucleus.

Orbitals are generally drawn as three-dimensional surfaces that enclose 90% of the electron density, as was shown for the hydrogen 1**s**, 2**s**, and 3**s** orbitals in part (b) in Figure 2.5.2. Although such drawings show the relative sizes of the orbitals, they do not normally show the spherical nodes in the 2**s** and 3**s** orbitals because the spherical nodes lie inside the 90% surface. Fortunately, the positions of the spherical nodes are not important for chemical bonding.

p Orbitals (l=1)

Only **s** orbitals are spherically symmetrical. As the value of **l** increases, the number of orbitals in a given subshell increases, and the shapes of the orbitals become more complex. Because the 2**p** subshell has **l** = 1, with three values of $\mathbf{m_l}$ (−1, 0, and +1), there are three 2**p** orbitals.

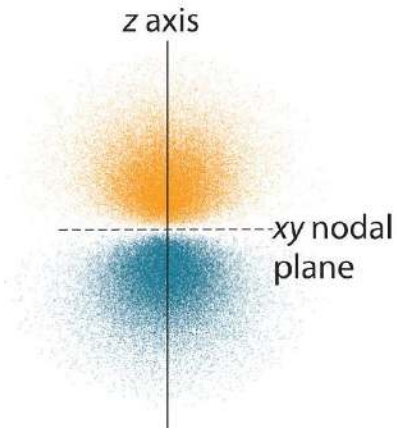


Figure 2.5.3: Electron Probability Distribution for a Hydrogen 2**p** Orbital. The nodal plane of zero electron density separates the two lobes of the 2**p** orbital. As in Figure 2.5.2, the colors correspond to regions of space where the phase of the wave function is positive (orange) and negative (blue).

The electron probability distribution for one of the hydrogen 2**p** orbitals is shown in Figure 2.5.3. Because this orbital has two lobes of electron density arranged along the **z** axis, with an electron density of zero in the **xy** plane (i.e., the **xy** plane is a nodal plane), it is a $2p_z$ orbital. As shown in Figure 2.5.4, the other two 2**p** orbitals have identical shapes, but they lie along the **x** axis ($2p_x$) and y axis ($2p_y$), respectively. Note that each **p** orbital has just one **nodal plane**. In each case, the phase of the wave function for each of the 2**p** orbitals is positive for the lobe that points along the positive axis and negative for the lobe that points along the negative axis. It is important to emphasize that these signs correspond to the **phase** of the wave that describes the electron motion, **not** to positive or negative charges.

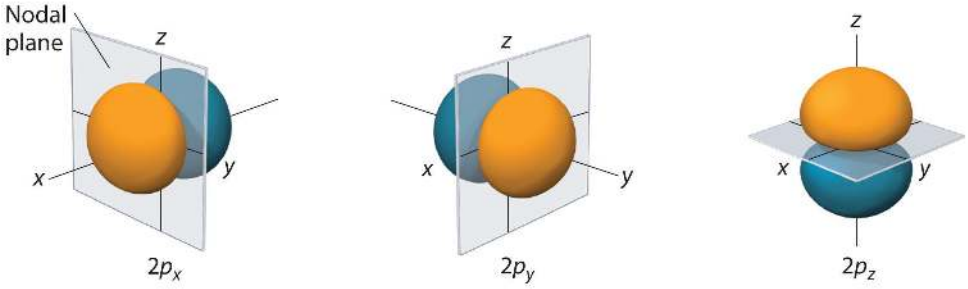


Figure 2.5.4 The Three Equivalent 2**p** Orbitals of the Hydrogen Atom

The surfaces shown enclose 90% of the total electron probability for the $2\mathbf{p_x}$, $2\mathbf{p_y}$, and $2\mathbf{p_z}$ orbitals. Each orbital is oriented along the axis indicated by the subscript and a nodal plane that is perpendicular to that axis bisects each 2**p** orbital. The phase of the wave function is positive (orange) in the region of space where **x**, **y**, or **z** is positive and negative (blue) where **x**, **y**, or **z** is negative. Just as with the **s** orbitals, the size and complexity of the **p** orbitals for any atom increase as the principal quantum number **n** increases. The shapes of the 90% probability surfaces of the 3**p**, 4**p**, and higher-energy **p** orbitals are, however, essentially the same as those shown in Figure 2.5.4.

d Orbitals (l=2)

Subshells with **l** = 2 have five **d** orbitals; the first principal shell to have a **d** subshell corresponds to **n** = 3. The five **d** orbitals have $\mathbf{m_l}$ values of −2, −1, 0, +1, and +2.

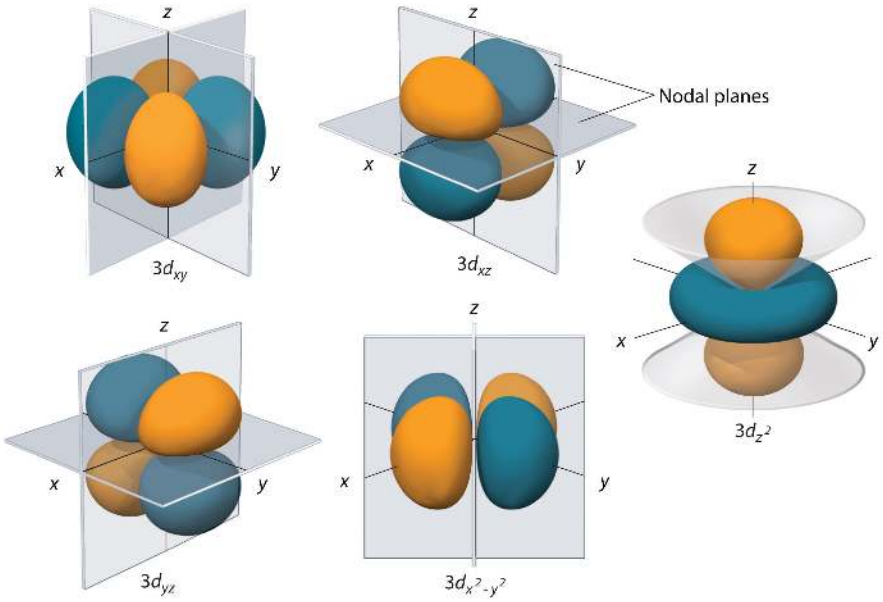


Figure 2.5.5: The Five Equivalent 3d Orbitals of the Hydrogen Atom. The surfaces shown enclose 90% of the total electron probability for the five hydrogen 3d orbitals. Four of the five 3d orbitals consist of four lobes arranged in a plane that is intersected by two perpendicular nodal planes. These four orbitals have the same shape but different orientations. The fifth 3d orbital, $3d_{z^2}$, has a distinct shape even though it is mathematically equivalent to the others. The phase of the wave function for the different lobes is indicated by color: orange for positive and blue for negative.

The hydrogen 3d orbitals, shown in Figure 2.5.5, have more complex shapes than the 2p orbitals. All five 3d orbitals contain two nodal surfaces, as compared to one for each p orbital and zero for each s orbital. In three of the d orbitals, the lobes of electron density are oriented between the x and y, x and z, and y and z planes; these orbitals are referred to as the $3d_{xy}$, \)3d_{xz}\), and $3d_{yz}$ orbitals, respectively. A fourth d orbital has lobes lying along the x and y axes; this is the $3d_{x^2-y^2}$ orbital. The fifth 3d orbital, called the $3d_{z^2}$ orbital, has a unique shape: it looks like a $2p_z$ orbital combined with an additional doughnut of electron probability lying in the xy plane. Despite its peculiar shape, the $3d_{z^2}$ orbital is mathematically equivalent to the other four and has the same energy. In contrast to p orbitals, the phase of the wave function for d orbitals is the same for opposite pairs of lobes. As shown in Figure 2.5.5, the phase of the wave function is positive for the two lobes of the dz^2 orbital that lie along the z axis, whereas the phase of the wave function is negative for the doughnut of electron density in the xy plane. Like the s and p orbitals, as n increases, the size of the d orbitals increases, but the overall shapes remain similar to those depicted in Figure 2.5.5.

f Orbitals (l=3)

Principal shells with **n** = 4 can have subshells with **l** = 3 and $\mathbf{m_l}$ values of −3, −2, −1, 0, +1, +2, and +3. These subshells consist of seven **f** orbitals. Each **f** orbital has three nodal surfaces, so their shapes are complex. Because **f** orbitals are not particularly important for our purposes, we do not discuss them further, and orbitals with higher values of **l** are not discussed at all.

Orbital Energies

Although we have discussed the shapes of orbitals, we have said little about their comparative energies. We begin our discussion of orbital energies by considering atoms or ions with only a single electron (such as H or He^+).

The relative energies of the atomic orbitals with **n** ≤ 4 for a hydrogen atom are plotted in Figure 2.5.6; note that the orbital energies depend on **only** the principal quantum number **n**. Consequently, the energies of the 2**s** and 2**p** orbitals of hydrogen are the same; the energies of the 3**s**, 3**p**, and 3**d** orbitals are the same; and so forth. Quantum mechanics predicts that in the hydrogen atom, all orbitals with the same value of **n** (e.g., the three 2**p** orbitals) are **degenerate**, meaning that they have the same energy. The orbital energies obtained for hydrogen using quantum mechanics are exactly the same as the allowed energies calculated by Bohr. In contrast to Bohr's model, however, which allowed only one orbit for each energy level, quantum mechanics predicts that there are **4** orbitals with different electron density distributions in the **n** = 2 principal shell (one 2**s** and three 2**p** orbitals), **9** in the **n** = 3 principal shell, and **16** in the **n** = 4 principal shell.The different values of **l** and $\mathbf{m_l}$ for the individual orbitals within a given principal shell are not important for understanding the emission or absorption spectra of the hydrogen atom under most conditions, but they do explain the splittings of the main lines that are observed when hydrogen atoms are placed in a magnetic field. Figure

2.5.6 shows that the energy levels become closer and closer together as the value of **n** increases, as expected because of the 1/**n**^{2} dependence of orbital energies.

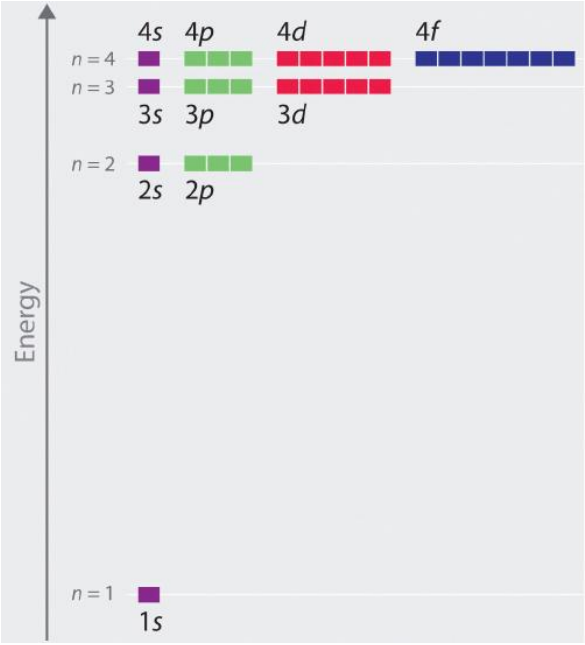


Figure 2.5.6: Orbital Energy Level Diagram for the Hydrogen Atom with a single electron. Each box corresponds to one orbital. Note that the difference in energy between orbitals decreases rapidly with increasing values of **n**.

The energies of the orbitals in any species with only one electron can be calculated by a minor variation of Bohr's equation, which can be extended to other single-electron species by incorporating the nuclear charge Z (the number of protons in the nucleus):

$$E = -\frac{Z^2}{n^2} Rhc \tag{2.5.1}$$

In general, both energy and radius decrease as the nuclear charge increases. Thus the most stable orbitals (those with the lowest energy) are those closest to the nucleus. For example, in the ground state of the hydrogen atom, the single electron is in the 1s orbital, whereas in the first excited state, the atom has absorbed energy and the electron has been promoted to one of the n = 2 orbitals. In ions with only a single electron, the energy of a given orbital depends on only n, and all subshells within a principal shell, such as the p_x, p_y, and p_z orbitals, are degenerate.

Summary

The four chemically important types of atomic orbital correspond to values of $\ell = 0$, 1, 2, and 3. Orbitals with $\ell = 0$ are s orbitals and are spherically symmetrical, with the greatest probability of finding the electron occurring at the nucleus. All orbitals with values of $n > 1$ and $ell = 0$ contain one or more nodes. Orbitals with $\ell = 1$ are p orbitals and contain a nodal plane that includes the nucleus, giving rise to a dumbbell shape. Orbitals with $\ell = 2$ are d orbitals and have more complex shapes with at least two nodal surfaces. Orbitals with $\ell = 3$ are f orbitals, which are still more complex.

Because its average distance from the nucleus determines the energy of an electron, each atomic orbital with a given set of quantum numbers has a particular energy associated with it, the **orbital energy**.

$$E = -\frac{Z^2}{n^2} Rhc$$

In atoms or ions with only a single electron, all orbitals with the same value of n have the same energy (they are degenerate), and the energies of the principal shells increase smoothly as n increases. An atom or ion with the electron(s) in the lowest-energy orbital(s) is said to be in its ground state, whereas an atom or ion in which one or more electrons occupy higher-energy orbitals is said to be in an excited state.

Figure 2.5.7 shows the breakdown for basic orbital shapes, and the number of suborbitals within each orbital type. Each suborbital can hold a maximum of two electrons. You are only required to know s, p, and d orbital shapes for this course, but it is important to

know other orbital shapes exist. Figure 2.5.7 below shows up through the f-orbital.

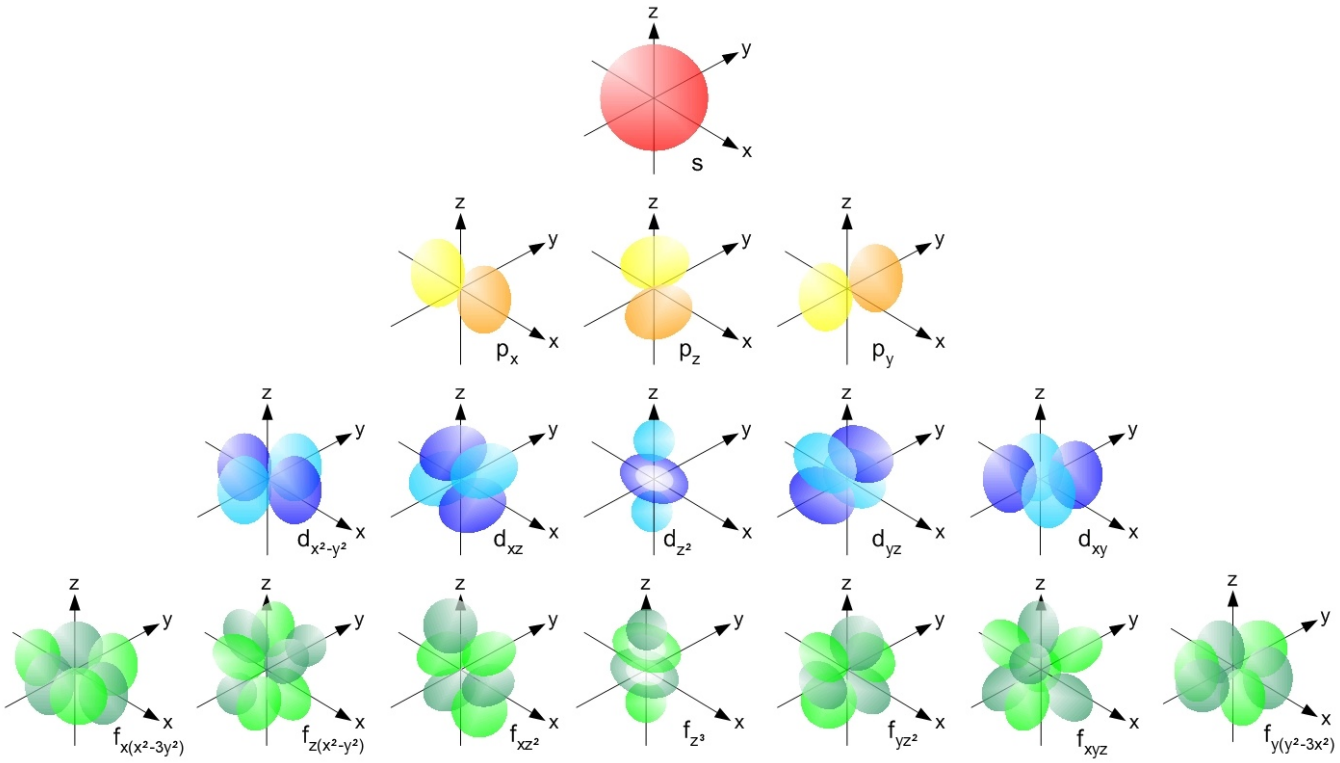


Figure 2.5.7: Orbital shapes and their orientation along various axes.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

2.5: The Shape of Atomic Orbitals is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **6.6: 3D Representation of Orbitals** is licensed CC BY-NC-SA 3.0.

2.6: Electronic Structure of Atoms (Electron Configurations)

Learning Objectives

- Derive the predicted ground-state electron configurations of atoms
- Identify and explain exceptions to predicted electron configurations for atoms and ions
- Relate electron configurations to element classifications in the periodic table

Having introduced the basics of atomic structure and quantum mechanics, we can use our understanding of quantum numbers to determine how atomic orbitals relate to one another. This allows us to determine which orbitals are occupied by electrons in each atom. The specific arrangement of electrons in orbitals of an atom determines many of the chemical properties of that atom.

2.6.1: Orbital Energies and Atomic Structure

The energy of atomic orbitals increases as the principal quantum number, n, increases. In any atom with two or more electrons, the repulsion between the electrons makes energies of subshells with different values of l differ so that the energy of the orbitals increases within a shell in the order $s < p < d < f$. Figure 2.6.1 depicts how these two trends in increasing energy relate. The 1*s* orbital at the bottom of the diagram is the orbital with electrons of lowest energy. The energy increases as we move up to the 2*s* and then 2*p*, 3*s*, and 3*p* orbitals, showing that the increasing *n* value has more influence on energy than the increasing *l* value for small atoms. However, this pattern does not hold for larger atoms. The 3*d* orbital is higher in energy than the 4*s* orbital. Such overlaps continue to occur frequently as we move up the chart.

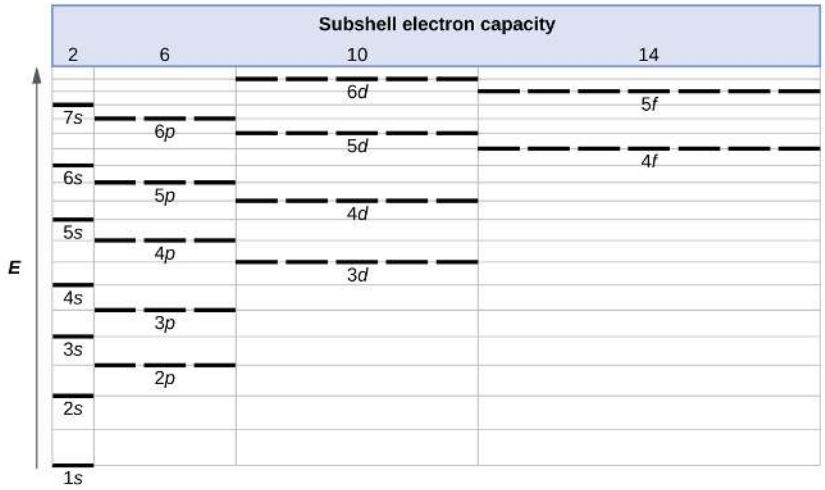


Figure 2.6.1: Generalized energy-level diagram for atomic orbitals in an atom with two or more electrons (not to scale).

Electrons in successive atoms on the periodic table tend to fill low-energy orbitals first. Thus, many students find it confusing that, for example, the 5*p* orbitals fill immediately after the 4*d*, and immediately before the 6*s*. The filling order is based on observed experimental results, and has been confirmed by theoretical calculations. As the principal quantum number, *n*, increases, the size of the orbital increases and the electrons spend more time farther from the nucleus. Thus, the attraction to the nucleus is weaker and the energy associated with the orbital is higher (less stabilized). But this is not the only effect we have to take into account. Within each shell, as the value of *l* increases, the electrons are less penetrating (meaning there is less electron density found close to the nucleus), in the order $s > p > d > f$. Electrons that are closer to the nucleus slightly repel electrons that are farther out, offsetting the more dominant electron–nucleus attractions slightly (recall that all electrons have −1 charges, but nuclei have $+Z$ charges). This phenomenon is called shielding and will be discussed in more detail in the next section. Electrons in orbitals that experience more shielding are less stabilized and thus higher in energy. For small orbitals (1*s* through 3*p*), the increase in energy due to *n* is more significant than the increase due to *l*; however, for larger orbitals the two trends are comparable and cannot be simply predicted. We will discuss methods for remembering the observed order.

The arrangement of electrons in the orbitals of an atom is called the electron configuration of the atom. We describe an electron configuration with a symbol that contains three pieces of information (Figure 2.6.2):

1. The number of the principal quantum shell, *n*,

2. The letter that designates the orbital type (the subshell, *l*), and
3. A superscript number that designates the number of electrons in that particular subshell.

For example, the notation $2p^4$ (read "two–p–four") indicates four electrons in a *p* subshell ($l = 1$) with a principal quantum number (n) of 2. The notation $3d^8$ (read "three–d–eight") indicates eight electrons in the *d* subshell (i.e., $l = 2$) of the principal shell for which $n = 3$.

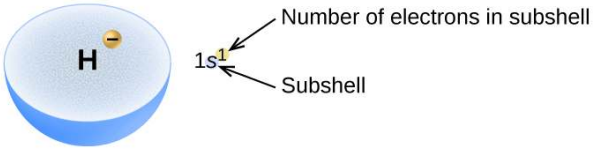


Figure 2.6.2: The diagram of an electron configuration specifies the subshell (n and l value, with letter symbol) and superscript number of electrons.

2.6.2: The Aufbau Principle

To determine the electron configuration for any particular atom, we can “build” the structures in the order of atomic numbers. Beginning with hydrogen, and continuing across the periods of the periodic table, we add one proton at a time to the nucleus and one electron to the proper subshell until we have described the electron configurations of all the elements. This procedure is called the Aufbau principle, from the German word *Aufbau* (“to build up”). Each added electron occupies the subshell of lowest energy available (in the order shown in Figure 2.6.3), subject to the limitations imposed by the allowed quantum numbers according to the Pauli exclusion principle. Electrons enter higher-energy subshells only after lower-energy subshells have been filled to capacity. Figure 2.6.3 illustrates the traditional way to remember the filling order for atomic orbitals.

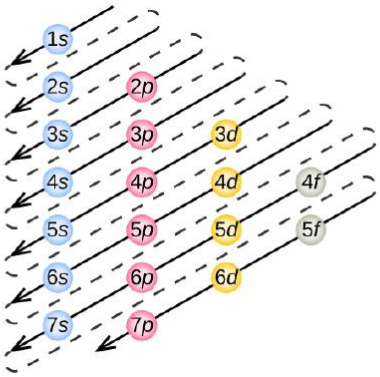


Figure 2.6.3: The arrow leads through each subshell in the appropriate filling order for electron configurations. This chart is straightforward to construct. Simply make a column for all the s orbitals with each n shell on a separate row. Repeat for p, d, and f. Be sure to only include orbitals allowed by the quantum numbers (no 1p or 2d, and so forth). Finally, draw diagonal lines from top to bottom as shown.

Since the arrangement of the periodic table is based on the electron configurations, Figure 2.6.4 provides an alternative method for determining the electron configuration. The filling order simply begins at hydrogen and includes each subshell as you proceed in increasing *Z* order. For example, after filling the 3*p* block up to Ar, we see the orbital will be 4s (K, Ca), followed by the 3*d* orbitals.

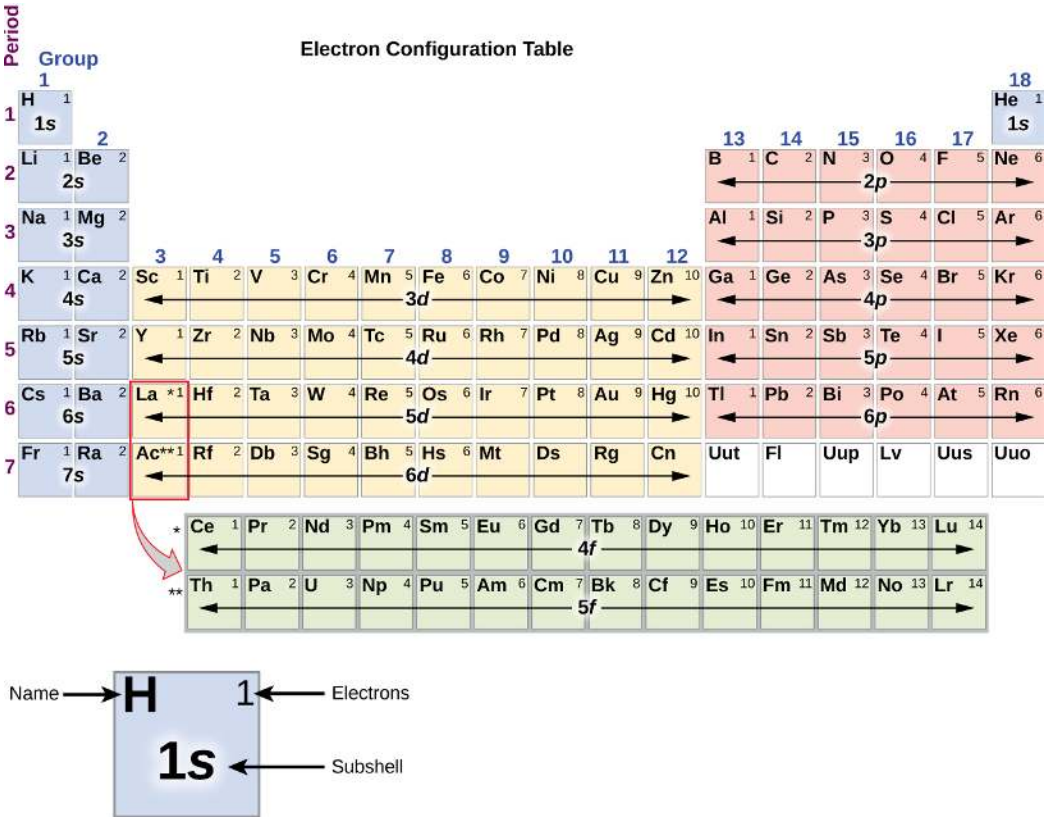
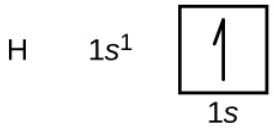
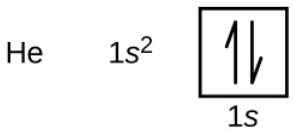


Figure 2.6.4: This periodic table shows the electron configuration for each subshell. By "building up" from hydrogen, this table can be used to determine the electron configuration for any atom on the periodic table.

We will now construct the ground-state electron configuration and orbital diagram for a selection of atoms in the first and second periods of the periodic table. Orbital diagrams are pictorial representations of the electron configuration, showing the individual orbitals and the pairing arrangement of electrons. We start with a single hydrogen atom (atomic number 1), which consists of one proton and one electron. Referring to either Figure 2.6.3 or 2.6.4, we would expect to find the electron in the 1*s* orbital. By convention, the $m_s = +\frac{1}{2}$ value is usually filled first. The electron configuration and the orbital diagram are:



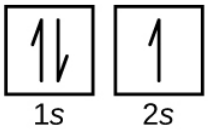
Following hydrogen is the noble gas helium, which has an atomic number of 2. The helium atom contains two protons and two electrons. The first electron has the same four quantum numbers as the hydrogen atom electron (n = 1, l = 0, m_l = 0, $m_s = +\frac{1}{2}$). The second electron also goes into the 1*s* orbital and fills that orbital. The second electron has the same n, l, and m_l quantum numbers, but must have the opposite spin quantum number, $m_s = -\frac{1}{2}$. This is in accord with the Pauli exclusion principle: No two electrons in the same atom can have the same set of four quantum numbers. For orbital diagrams, this means two arrows go in each box (representing two electrons in each orbital) and the arrows must point in opposite directions (representing paired spins). The electron configuration and orbital diagram of helium are:



The n = 1 shell is completely filled in a helium atom.

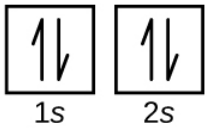
The next atom is the alkali metal lithium with an atomic number of 3. The first two electrons in lithium fill the 1*s* orbital and have the same sets of four quantum numbers as the two electrons in helium. The remaining electron must occupy the orbital of next lowest energy, the 2*s* orbital (Figure 2.6.3 or 2.6.4). Thus, the electron configuration and orbital diagram of lithium are:

Li $1s^2 2s^1$



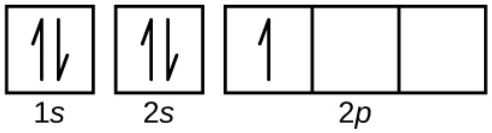
An atom of the alkaline earth metal beryllium, with an atomic number of 4, contains four protons in the nucleus and four electrons surrounding the nucleus. The fourth electron fills the remaining space in the 2*s* orbital.

Be $1s^2 2s^2$



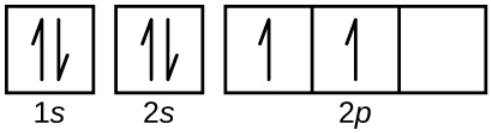
An atom of boron (atomic number 5) contains five electrons. The $n = 1$ shell is filled with two electrons and three electrons will occupy the $n = 2$ shell. Because any *s* subshell can contain only two electrons, the fifth electron must occupy the next energy level, which will be a 2*p* orbital. There are three degenerate 2*p* orbitals ($m_l = -1, 0, +1$) and the electron can occupy any one of these *p* orbitals. When drawing orbital diagrams, we include empty boxes to depict any empty orbitals in the same subshell that we are filling.

B $1s^2 2s^2 2p^1$



Carbon (atomic number 6) has six electrons. Four of them fill the 1*s* and 2*s* orbitals. The remaining two electrons occupy the 2*p* subshell. We now have a choice of filling one of the 2*p* orbitals and pairing the electrons or of leaving the electrons unpaired in two different, but degenerate, *p* orbitals. The orbitals are filled as described by Hund's rule: the lowest-energy configuration for an atom with electrons within a set of degenerate orbitals is that having the maximum number of unpaired electrons. Thus, the two electrons in the carbon 2*p* orbitals have identical *n*, *l*, and m_s quantum numbers and differ in their m_l quantum number (in accord with the Pauli exclusion principle). The electron configuration and orbital diagram for carbon are:

C $1s^2 2s^2 2p^2$



Nitrogen (atomic number 7) fills the 1*s* and 2*s* subshells and has one electron in each of the three 2*p* orbitals, in accordance with Hund's rule. These three electrons have unpaired spins. Oxygen (atomic number 8) has a pair of electrons in any one of the 2*p* orbitals (the electrons have opposite spins) and a single electron in each of the other two. Fluorine (atomic number 9) has only one 2*p* orbital containing an unpaired electron. All of the electrons in the noble gas neon (atomic number 10) are paired, and all of the orbitals in the $n = 1$ and the $n = 2$ shells are filled. The electron configurations and orbital diagrams of these four elements are:

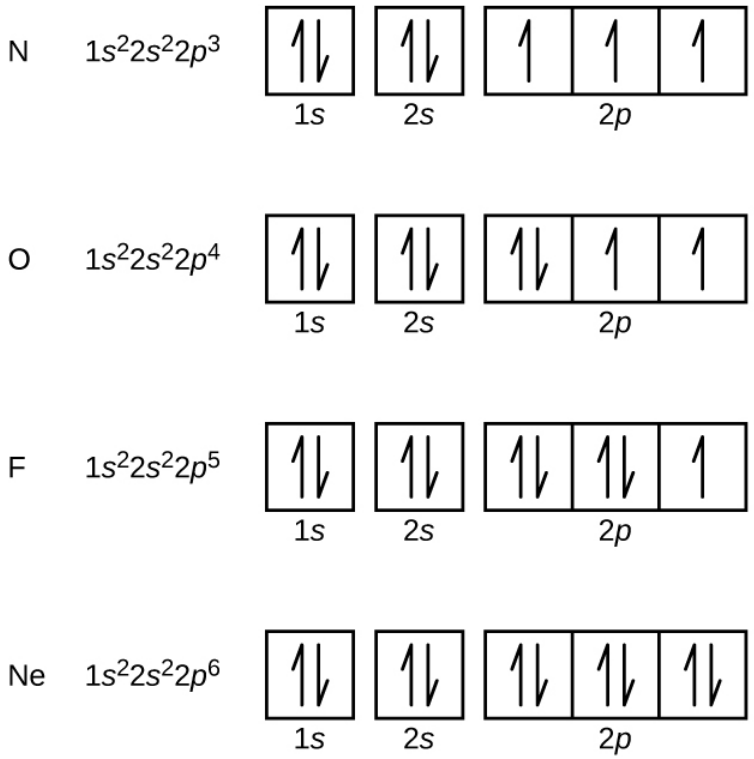


Figure 2.6.5: Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, ($1s^2 2s^2 2p^6$) and our abbreviated or condensed configuration is [Ne]$3s^1$.

The alkali metal sodium (atomic number 11) has one more electron than the neon atom. This electron must go into the lowest-energy subshell available, the 3*s* orbital, giving a $1s^2 2s^2 2p^6 3s^1$ configuration. The electrons occupying the outermost shell orbital(s) (highest value of *n*) are called valence electrons, and those occupying the inner shell orbitals are called core electrons (Figure \PageIndex5\PageIndex5). Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, ($1s^2 2s^2 2p^6$) and our abbreviated or condensed configuration is [Ne]$3s^1$.

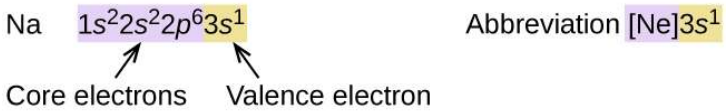


Figure 2.6.5: A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

Similarly, the abbreviated configuration of lithium can be represented as [He]$2s^1$, where [He] represents the configuration of the helium atom, which is identical to that of the filled inner shell of lithium. Writing the configurations in this way emphasizes the similarity of the configurations of lithium and sodium. Both atoms, which are in the alkali metal family, have only one electron in a valence *s* subshell outside a filled set of inner shells.

$$\text{Li} : [\text{He}]\, 2s^1$$
$$\text{Na} : [\text{Ne}]\, 3s^1$$

The alkaline earth metal magnesium (atomic number 12), with its 12 electrons in a [Ne]$3s^2$ configuration, is analogous to its family member beryllium, [He]$2s^2$. Both atoms have a filled *s* subshell outside their filled inner shells. Aluminum (atomic number 13), with 13 electrons and the electron configuration [Ne]$3s^2 3p^1$, is analogous to its family member boron, [He]$2s^2 2p^1$.

The electron configurations of silicon (14 electrons), phosphorus (15 electrons), sulfur (16 electrons), chlorine (17 electrons), and argon (18 electrons) are analogous in the electron configurations of their outer shells to their corresponding family members carbon, nitrogen, oxygen, fluorine, and neon, respectively, except that the principal quantum number of the outer shell of the heavier elements has increased by one to $n = 3$. Figure 2.6.6 shows the lowest energy, or ground-state, electron configuration for these elements as well as that for atoms of each of the known elements.

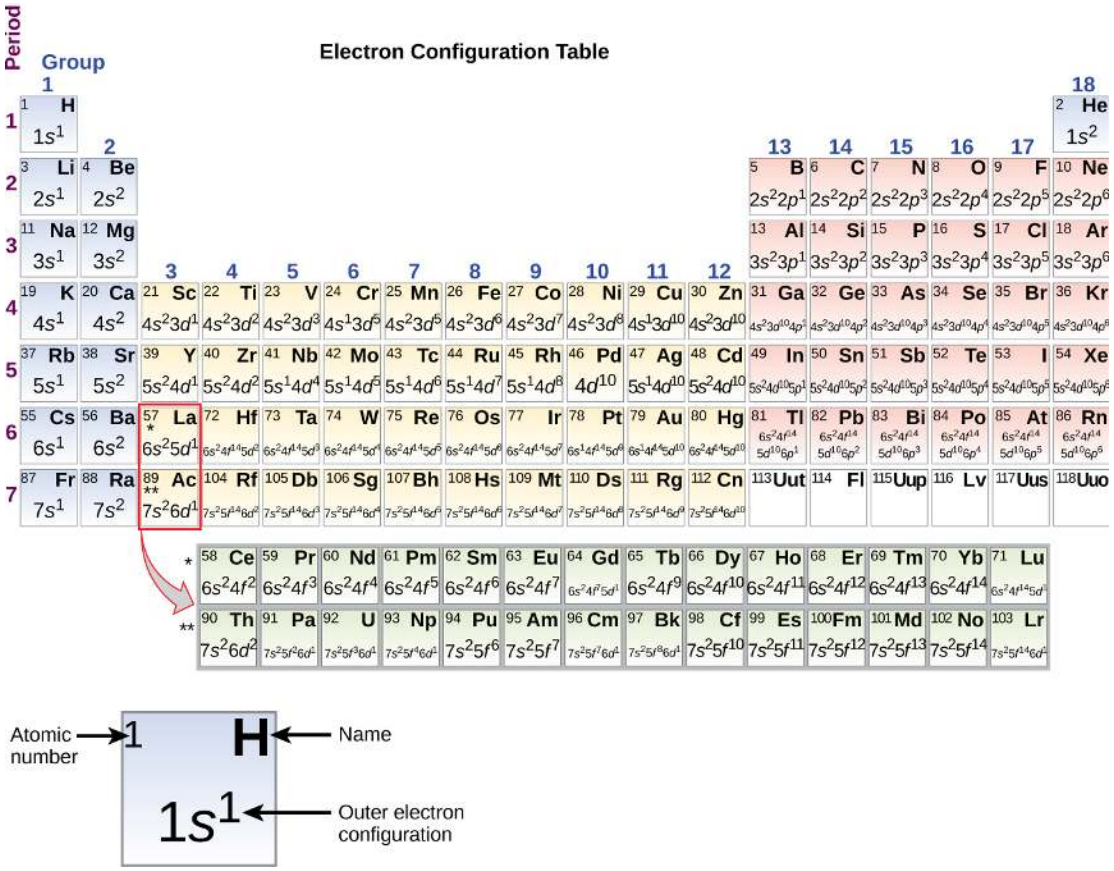


Figure 2.6.6: This version of the periodic table shows the outer-shell electron configuration of each element. Note that down each group, the configuration is often similar.

When we come to the next element in the periodic table, the alkali metal potassium (atomic number 19), we might expect that we would begin to add electrons to the 3*d* subshell. However, all available chemical and physical evidence indicates that potassium is like lithium and sodium, and that the next electron is not added to the 3*d* level but is, instead, added to the 4*s* level (Figure 2.6.3 or 2.6.4). As discussed previously, the 3*d* orbital with no radial nodes is higher in energy because it is less penetrating and more shielded from the nucleus than the 4*s*, which has three radial nodes. Thus, potassium has an electron configuration of $[Ar]4s^1$. Hence, potassium corresponds to Li and Na in its valence shell configuration. The next electron is added to complete the 4*s* subshell and calcium has an electron configuration of $[Ar]4s^2$. This gives calcium an outer-shell electron configuration corresponding to that of beryllium and magnesium.

Beginning with the transition metal scandium (atomic number 21), additional electrons are added successively to the 3*d* subshell. This subshell is filled to its capacity with 10 electrons (remember that for $l = 2$ [*d* orbitals], there are $2l + 1 = 5$ values of m_l, meaning that there are five *d* orbitals that have a combined capacity of 10 electrons). The 4*p* subshell fills next. Note that for three series of elements, scandium (Sc) through copper (Cu), yttrium (Y) through silver (Ag), and lutetium (Lu) through gold (Au), a total of 10 *d* electrons are successively added to the $(n - 1)$ shell next to the *n* shell to bring that $(n - 1)$ shell from 8 to 18 electrons. For two series, lanthanum (La) through lutetium (Lu) and actinium (Ac) through lawrencium (Lr), 14 *f* electrons ($l = 3$, $2l + 1 = 7$ m_l values; thus, seven orbitals with a combined capacity of 14 electrons) are successively added to the $(n - 2)$ shell to bring that shell from 18 electrons to a total of 32 electrons.

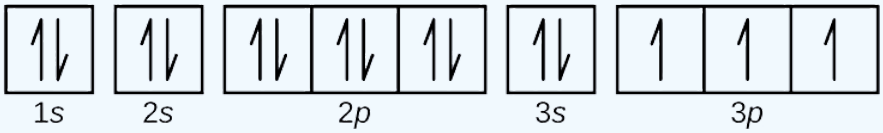
Example 2.6.1: Quantum Numbers and Electron Configurations

What is the electron configuration and orbital diagram for a phosphorus atom? What are the four quantum numbers for the last electron added?

Solution

The atomic number of phosphorus is 15. Thus, a phosphorus atom contains 15 electrons. The order of filling of the energy levels is 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, . . . The 15 electrons of the phosphorus atom will fill up to the 3*p* orbital, which will contain three electrons:

P $1s^2 2s^2 2p^6 3s^2 3p^3$



The last electron added is a 3*p* electron. Therefore, $n = 3$ and, for a *p*-type orbital, $l = 1$. The m_l value could be –1, 0, or +1. The three *p* orbitals are degenerate, so any of these m_l values is correct. For unpaired electrons, convention assigns the value of $+\frac{1}{2}$ for the spin quantum number; thus, $m_s = +\frac{1}{2}$.

Exercise 2.6.1

Identify the atoms from the electron configurations given:

a. $[Ar]4s^2 3d^5$
b. $[Kr]5s^2 4d^{10} 5p^6$

Answer a

Mn

Answer b

Xe

The periodic table can be a powerful tool in predicting the electron configuration of an element. However, we do find exceptions to the order of filling of orbitals that are shown in Figure 2.6.3 or 2.6.4. For instance, the electron configurations of the transition metals chromium (Cr; atomic number 24) and copper (Cu; atomic number 29), among others, are not those we would expect. In general, such exceptions involve subshells with very similar energy, and small effects can lead to changes in the order of filling.

In the case of Cr and Cu, we find that half-filled and completely filled subshells apparently represent conditions of preferred stability. This stability is such that an electron shifts from the 4*s* into the 3*d* orbital to gain the extra stability of a half-filled 3*d* subshell (in Cr) or a filled 3*d* subshell (in Cu). Other exceptions also occur. For example, niobium (Nb, atomic number 41) is predicted to have the electron configuration $[Kr]5s^2 4d^3$. Experimentally, we observe that its ground-state electron configuration is actually $[Kr]5s^1 4d^4$. We can rationalize this observation by saying that the electron–electron repulsions experienced by pairing the electrons in the 5*s* orbital are larger than the gap in energy between the 5*s* and 4*d* orbitals. There is no simple method to predict the exceptions for atoms where the magnitude of the repulsions between electrons is greater than the small differences in energy between subshells.

2.6.3: Electron Configurations and the Periodic Table

As described earlier, the periodic table arranges atoms based on increasing atomic number so that elements with the same chemical properties recur periodically. When their electron configurations are added to the table (Figure 2.6.6), we also see a periodic recurrence of similar electron configurations in the outer shells of these elements. Because they are in the outer shells of an atom, valence electrons play the most important role in chemical reactions. The outer electrons have the highest energy of the electrons in

an atom and are more easily lost or shared than the core electrons. Valence electrons are also the determining factor in some physical properties of the elements.

Elements in any one group (or column) have the same number of valence electrons; the alkali metals lithium and sodium each have only one valence electron, the alkaline earth metals beryllium and magnesium each have two, and the halogens fluorine and chlorine each have seven valence electrons. The similarity in chemical properties among elements of the same group occurs because they have the same number of valence electrons. It is the loss, gain, or sharing of valence electrons that defines how elements react.

It is important to remember that the periodic table was developed on the basis of the chemical behavior of the elements, well before any idea of their atomic structure was available. Now we can understand why the periodic table has the arrangement it has—the arrangement puts elements whose atoms have the same number of valence electrons in the same group. This arrangement is emphasized in Figure 2.6.6, which shows in periodic-table form the electron configuration of the last subshell to be filled by the Aufbau principle. The colored sections of Figure 2.6.6 show the three categories of elements classified by the orbitals being filled: main group, transition, and inner transition elements. These classifications determine which orbitals are counted in the valence shell, or highest energy level orbitals of an atom.

1. **Main group elements** (sometimes called **representative elements**) are those in which the last electron added enters an *s* or a *p* orbital in the outermost shell, shown in blue and red in Figure 2.6.6. This category includes all the nonmetallic elements, as well as many metals and the intermediate semimetallic elements. The valence electrons for main group elements are those with the highest *n* level. For example, gallium (Ga, atomic number 31) has the electron configuration [Ar]$\underline{4s}^2 3d^{10} \underline{4p}^1$, which contains three valence electrons (underlined). The completely filled *d* orbitals count as core, not valence, electrons.
2. **Transition elements or transition metals**. These are metallic elements in which the last electron added enters a *d* orbital. The valence electrons (those added after the last noble gas configuration) in these elements include the *ns* and $(n - 1)$ *d* electrons. The official IUPAC definition of transition elements specifies those with partially filled *d* orbitals. Thus, the elements with completely filled orbitals (Zn, Cd, Hg, as well as Cu, Ag, and Au in Figure 2.6.6) are not technically transition elements. However, the term is frequently used to refer to the entire *d* block (colored yellow in Figure 2.6.6), and we will adopt this usage in this textbook.
3. **Inner transition elements** are metallic elements in which the last electron added occupies an *f* orbital. They are shown in green in Figure 2.6.6. The valence shells of the inner transition elements consist of the $(n - 2)f$, the $(n - 1)d$, and the *ns* subshells. There are two inner transition series:
    1. The lanthanide series: lanthanide (La) through lutetium (Lu)
    2. The actinide series: actinide (Ac) through lawrencium (Lr)

Lanthanum and actinium, because of their similarities to the other members of the series, are included and used to name the series, even though they are transition metals with no *f* electrons.

2.6.4: Electron Configurations of Ions

We have seen that ions are formed when atoms gain or lose electrons. A cation (positively charged ion) forms when one or more electrons are removed from a parent atom. For main group elements, the electrons that were added last are the first electrons removed. For transition metals and inner transition metals, however, electrons in the *s* orbital are easier to remove than the *d* or *f* electrons, and so the highest *ns* electrons are lost, and then the $(n - 1)d$ or $(n - 2)f$ electrons are removed. An anion (negatively charged ion) forms when one or more electrons are added to a parent atom. The added electrons fill in the order predicted by the Aufbau principle.

Example 2.6.2: Predicting Electron Configurations of Ions

What is the electron configuration and orbital diagram of:

a. Na^+
b. P^{3-}
c. Al^{2+}
d. Fe^{2+}
e. Sm^{3+}

Solution

First, write out the electron configuration for each parent atom. We have chosen to show the full, unabbreviated configurations to provide more practice for students who want it, but listing the core-abbreviated electron configurations is also acceptable.

Next, determine whether an electron is gained or lost. Remember electrons are negatively charged, so ions with a positive charge have *lost* an electron. For main group elements, the last orbital gains or loses the electron. For transition metals, the last *s* orbital loses an electron before the *d* orbitals.

a. Na: $1s^2 2s^2 2p^6 3s^1$. Sodium cation loses one electron, so Na^+: $1s^2 2s^2 2p^6 3s^1 = Na^+$: $1s^2 2s^2 2p^6$.
b. P: $1s^2 2s^2 2p^6 3s^2 3p^3$. Phosphorus trianion gains three electrons, so P^{3-}: $1s^2 2s^2 2p^6 3s^2 3p^6$.
c. Al: $1s^2 2s^2 2p^6 3s^2 3p^1$. Aluminum dication loses two electrons Al^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^1 = Al^{2+}$: $1s^2 2s^2 2p^6 3s^1$.
d. Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$. Iron(II) loses two electrons and, since it is a transition metal, they are removed from the 4*s* orbital Fe^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6 = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$.
e. Sm: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6$. Samarium trication loses three electrons. The first two will be lost from the 6*s* orbital, and the final one is removed from the 4*f* orbital. Sm^{3+}: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6 = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 4f^5$.

? Exercise 2.6.2

a. Which ion with a +2 charge has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^5$?
b. Which ion with a +3 charge has this configuration?

Answer a

Tc^{2+}

Answer b

Ru^{3+}

Summary

The relative energy of the subshells determine the order in which atomic orbitals are filled (1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, and so on). Electron configurations and orbital diagrams can be determined by applying the Pauli exclusion principle (no two electrons can have the same set of four quantum numbers) and Hund's rule (whenever possible, electrons retain unpaired spins in degenerate orbitals).

Electrons in the outermost orbitals, called valence electrons, are responsible for most of the chemical behavior of elements. In the periodic table, elements with analogous valence electron configurations usually occur within the same group. There are some exceptions to the predicted filling order, particularly when half-filled or completely filled orbitals can be formed. The periodic table can be divided into three categories based on the orbital in which the last electron to be added is placed: main group elements (*s* and *p* orbitals), transition elements (*d* orbitals), and inner transition elements (*f* orbitals).

Glossary

Aufbau principle
procedure in which the electron configuration of the elements is determined by "building" them in order of atomic numbers, adding one proton to the nucleus and one electron to the proper subshell at a time

core electron
electron in an atom that occupies the orbitals of the inner shells

electron configuration
electronic structure of an atom in its ground state given as a listing of the orbitals occupied by the electrons

Hund's rule

every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin

orbital diagram

pictorial representation of the electron configuration showing each orbital as a box and each electron as an arrow

valence electrons

electrons in the outermost or valence shell (highest value of *n*) of a ground-state atom; determine how an element reacts

valence shell

outermost shell of electrons in a ground-state atom; for main group elements, the orbitals with the highest *n* level (*s* and *p* subshells) are in the valence shell, while for transition metals, the highest energy *s* and *d* subshells make up the valence shell and for inner transition elements, the highest *s*, *d*, and *f* subshells are included

---

This page titled 2.6: Electronic Structure of Atoms (Electron Configurations) is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **6.4: Electronic Structure of Atoms (Electron Configurations)** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.E: Quantum Theory and Electronic Structure (Exercises)

2.E.1: Electromagnetic Energy

Exercise 2.E.1

The light produced by a red neon sign is due to the emission of light by excited neon atoms. Qualitatively describe the spectrum produced by passing light from a neon lamp through a prism.

Answer

The spectrum consists of colored lines, at least one of which (probably the brightest) is red.

Exercise 2.E.2

An FM radio station found at 103.1 on the FM dial broadcasts at a frequency of 1.031×10^8 s^{-1} (103.1 MHz). What is the wavelength of these radio waves in meters?

Answer

$$\lambda = \frac{c}{\nu}$$

$$\lambda = \frac{2.998 \times 10^8 \ \frac{m}{s}}{1.031 \times 10^8 \ \frac{1}{s}} = 2.908 \ m$$

Exercise 2.E.3

FM-95, an FM radio station, broadcasts at a frequency of 9.51×10^7 s^{-1} (95.1 MHz). What is the wavelength of these radio waves in meters?

Answer

$$\lambda = \frac{c}{\nu}$$

$$\lambda = \frac{2.998 \times 10^8 \ \frac{m}{s}}{9.51 \times 10^7 \ \frac{1}{s}} = 3.15 \ m$$

Exercise 2.E.4

A bright violet line occurs at 435.8 nm in the emission spectrum of mercury vapor. What amount of energy, in joules, must be released by an electron in a mercury atom to produce a photon of this light?

Answer

$$E = \frac{hc}{\lambda}$$

$$E = \frac{(2.998 \times 10^8 \frac{m}{s}) \ (6.6262 \times 10^{-34} Js)}{4.358 \times 10^{-7} m}$$

$$= 4.56 \times 10^{-19} J$$

Exercise 2.E.5

Light with a wavelength of 614.5 nm looks orange. What is the energy, in joules, per photon of this orange light? What is the energy in eV (1 eV = 1.602×10^{-19} J)?

Answer

First convert 614.5 nm into meters

$6.145nm = 6.145 \times 10^{-7} m$

Then calculate the amount of energy this wavelength of light contains using the equations:

$E = h\nu$ and $\nu = \frac{c}{\lambda}$ which can be manipulated algebraically into: $E = \frac{hc}{\lambda}$

h = Plancks constant → $6.6262 \times 10^{-34} Js$ c = Speed of light → $2.998 \times 10^{8} \frac{m}{s}$ λ = wavelength of photon → $6.145 \times 10^{-7} m$

Then convert Joules into eV:

$$= (3.233 \times 10^{-19} J) \times \frac{1eV}{1.602 \times 10^{-19} J} \tag{2.E.1}$$

$$= 2.018eV \tag{2.E.2}$$

$$= \frac{(6.6262 \times 10^{-34}\ Js)\ (2.998 \times 10^{8}\ \frac{m}{s})}{6.145 \times 10^{-7} m} = 3.233 \times 10^{-19} J \tag{2.E.3}$$

Exercise 2.E.6

Heated lithium atoms emit photons of light with an energy of 2.961×10^{-19} J. Calculate the frequency and wavelength of one of these photons. What is the total energy in 1 mole of these photons? What is the color of the emitted light?

Answer

$E = h\nu$ and $\nu = \frac{E}{h}$

h = Plancks constant → $6.6262 \times 10^{-34} Js$

Frequency: $\nu = \frac{2.961 \times 10^{-19} J}{6.6262 \times 10^{-34} Js} = 4.469 \times 10^{14} Hz$

$\lambda = \frac{c}{\nu}$

c = Speed of light → $2.998 \times 10^{8}\ \frac{m}{s}$

Wavelength: $\lambda = \frac{2.998 \times 10^{8} \frac{m}{s}}{4.469 \times 10^{14} \frac{1}{s}} = 6.709 \times 10^{-7} m$ = **Red Light**

Total energy:

$E = \frac{2.961 \times 10^{-19} J}{1\ photon} \times \frac{6.022 \times 10^{23}\ photons}{1\ mole} = 1.783 \times 10^{5} J$

Exercise 2.E.7

A photon of light produced by a surgical laser has an energy of 3.027×10^{-19} J. Calculate the frequency and wavelength of the photon. What is the total energy in 1 mole of photons? What is the color of the emitted light?

Answer

$\nu = 4.568 \times 10^{14}$ s; $\lambda = 656.3$ nm; Energy $mol^{-1} = 1.823 \times 10^{5}$ J mol^{-1}; red

Exercise 2.E.8

When rubidium ions are heated to a high temperature, two lines are observed in its line spectrum at wavelengths (a) 7.9×10^{-7} m and (b) 4.2×10^{-7} m. What are the frequencies of the two lines? What color do we see when we heat a rubidium compound?

Answer

Add texts here. Do not delete this text first.

Exercise 2.E.9

The emission spectrum of cesium contains two lines whose frequencies are (a) 3.45×10^{14} Hz and (b) 6.53×10^{14} Hz. What are the wavelengths and energies per photon of the two lines? What color are the lines?

Answer

(a) $\lambda = 8.69 \times 10^{-7}$ m; $E = 2.29 \times 10^{-19}$ J; (b) $\lambda = 4.59 \times 10^{-7}$ m; $E = 4.33 \times 10^{-19}$ J; The color of (a) is red; (b) is blue.

Exercise 2.E.10

Photons of infrared radiation are responsible for much of the warmth we feel when holding our hands before a fire. These photons will also warm other objects. How many infrared photons with a wavelength of 1.5×10^{-6} m must be absorbed by the water to warm a cup of water (175 g) from 25.0 °C to 40 °

Answer

First we must use the equation: $q=mC\Delta T^{\circ}$ to calculate the amount of Energy in Joules (J) to warm 175g of H_2O a total of 15° Celsius

m = mass in grams(g) → 175g C = Specific heat of $H_2O_{(l)}$ → $\frac{4.184J}{g^{\circ}C}$ ΔT° = Difference in temperature → 40 - 25 =15°

$$= \frac{(6.6262 \times 10^{-34}\ Js)\ (2.998 \times 10^{8}\ \frac{m}{s})}{1.5 \times 10^{-6} m} = 1.3 \times 10^{-19} J \tag{2.E.4}$$

This is the energy in one photon, so now we have to see how many times 1.3×10^{-19} J fits into the 11,000 J from our first calculation:

$$= \frac{11,000\ J}{1.3 \times 10^{-19}\ \frac{J}{photon}} = 8.3 \times 10^{22} photons \tag{2.E.5}$$

$$= 8.3 \times 10^{22} photons \tag{2.E.6}$$

$$q = 175g \times \frac{4.184J}{g^{\circ}C} \times 15^{\circ}C \tag{2.E.7}$$

q= 11,000 J

Now we need to calculate the amount of energy in Joules (J) that one Photon with a wavelength of 1.5x10^{-6} m contains. We will use the equations:

$E = h\nu$ and $\nu = \frac{c}{\lambda}$ which can be manipulated algebraically into: $E = \frac{hc}{\lambda}$

h = Plancks constant → $6.6262 \times 10^{-34} Js$ c = Speed of light → $2.998 \times 10^{8}\ \frac{m}{s}$ λ = wavelength of photon → $1.5 \times 10^{-6} m$

Exercise 2.E.11

One of the radiographic devices used in a dentist's office emits an X-ray of wavelength 2.090 × 10^{-11} m. What is the energy, in joules, and frequency of this X-ray?

Answer

E = 9.502 × 10^{-15} J; ν = 1.434 × 10^{19} s^{-1}

Exercise 2.E.12

The eyes of certain reptiles pass a single visual signal to the brain when the visual receptors are struck by photons of a wavelength of 850 nm. If a total energy of 3.15 × 10^{-14} J is required to trip the signal, what is the minimum number of photons that must strike the receptor?

Answer

First we need to convert nanometers to meters

850nm = 8.5 x 10^{-7} m

Then calculate Energy in Joules a photon of this wavelength (λ) produces:

$$(E = \frac{hc}{\lambda}) = \frac{(6.6262 \times 10^{-34}\ Js)\ (2.998 \times 10^{8}\ \frac{m}{s})}{8.5 \times 10^{-7} m} = 2.3 \times 10^{-19} \frac{J}{photon} \tag{2.E.8}$$

Then we need to find out how many of these photons it will take to trip the visual signal to the brain:

$$= \frac{3.15 \times 10^{-14}\ \cancel{J}}{2.3 \times 10^{-19}\ \frac{\cancel{J}}{photon}} \tag{2.E.9}$$

$$= 1.3 \times 10^{5}\ photons \tag{2.E.10}$$

Exercise 2.E.13

RGB color television and computer displays use cathode ray tubes that produce colors by mixing red, green, and blue light. If we look at the screen with a magnifying glass, we can see individual dots turn on and off as the colors change. Using a spectrum of visible light, determine the approximate wavelength of each of these colors. What is the frequency and energy of a photon of each of these colors?

Answer

Red: 660 nm; 4.54 × 10^{14} Hz; 3.01 × 10^{-19} J.

Green: 520 nm; 5.77 × 10^{14} Hz; 3.82 × 10^{-19} J.

Blue: 440 nm; 6.81 × 10^{14} Hz; 4.51 × 10^{-19} J.

Somewhat different numbers are also possible.

Exercise 2.E.14

Answer the following questions about a Blu-ray laser:

a. The laser on a Blu-ray player has a wavelength of 405 nm. In what region of the electromagnetic spectrum is this radiation? What is its frequency?
b. A Blu-ray laser has a power of 5 milliwatts (1 watt = 1 J s^{-1}). How many photons of light are produced by the laser in 1 hour?
c. The ideal resolution of a player using a laser (such as a Blu-ray player), which determines how close together data can be stored on a compact disk, is determined using the following formula: Resolution = 0.60(λ/NA), where λ is the wavelength of the laser and NA is the numerical aperture. Numerical aperture is a measure of the size of the spot of light on the disk; the larger the NA, the smaller the spot. In a typical Blu-ray system, NA = 0.95. If the 405-nm laser is used in a Blu-ray player, what is the closest that information can be stored on a Blu-ray disk?
d. The data density of a Blu-ray disk using a 405-nm laser is 1.5×10^7 bits mm^{-2}. Disks have an outside diameter of 120 mm and a hole of 15-mm diameter. How many data bits can be contained on the disk? If a Blu-ray disk can hold 9,400,000 pages of text, how many data bits are needed for a typed page? (Hint: Determine the area of the disk that is available to hold data. The area inside a circle is given by $A = \pi r^2$, where the radius r is one-half of the diameter.)

Answer

Add texts here. Do not delete this text first.

Exercise 2.E.15

What is the threshold frequency for sodium metal if a photon with frequency 6.66×10^{14} s^{-1} ejects a photon with 7.74×10^{-20} J kinetic energy? Will the photoelectric effect be observed if sodium is exposed to orange light?

Answer

5.49×10^{14} s^{-1}; no

2.E.2: The Bohr Model

Exercise 2.E.16

Why is the electron in a Bohr hydrogen atom bound less tightly when it has a quantum number of 3 than when it has a quantum number of 1?

Answer

Add texts here. Do not delete this text first.

Exercise 2.E.17

What does it mean to say that the energy of the electrons in an atom is quantized?

Answer

Quantized energy means that the electrons can possess only certain discrete energy values; values between those quantized values are not permitted.

Exercise 2.E.18

Using the Bohr model, determine the energy, in joules, necessary to ionize a ground-state hydrogen atom. Show your calculations.

Answer

Add texts here. Do not delete this text first.

Exercise 2.E.19

The electron volt (eV) is a convenient unit of energy for expressing atomic-scale energies. It is the amount of energy that an electron gains when subjected to a potential of 1 volt; $1\ eV = 1.602 \times 10^{-19}\ J$. Using the Bohr model, determine the energy, in electron volts, of the photon produced when an electron in a hydrogen atom moves from the orbit with $n = 5$ to the orbit with $n = 2$. Show your calculations.

Answer

$$E = E_2 - E_5 = 2.179 \times 10^{-18} \left(\frac{1}{n_2^2} - \frac{1}{n_5^2} \right)\ J \tag{2.E.11}$$

$$= 2.179 \times 10^{-18} \left(\frac{1}{2^2} - \frac{1}{5^2} \right) = 4.576 \times 10^{-19}\ J \tag{2.E.12}$$

$$= \frac{4.576 \times 10^{-19}\ J}{1.602 \times 10^{-19}\ J\ eV^{-1}} = 2.856\ eV \tag{2.E.13}$$

Exercise 2.E.20

Using the Bohr model, determine the lowest possible energy for the electron in the He^+ ion.

Answer

Add texts here. Do not delete this text first.

Exercise 2.E.21

Using the Bohr model, determine the energy of an electron with $n = 6$ in a hydrogen atom.

Answer

−8.716 × 10−18 J

Exercise 2.E.22

Using the Bohr model, determine the energy of an electron with $n = 8$ in a hydrogen atom.

Answer

Add texts here. Do not delete this text first.

Exercise 2.E.23

How far from the nucleus in angstroms (1 angstrom = 1×10^{-10} m) is the electron in a hydrogen atom if it has an energy of -8.72×10^{-20} J?

Answer

$-3.405 \times 10^{-20} J$

Exercise 2.E.24

What is the radius, in angstroms, of the orbital of an electron with n = 8 in a hydrogen atom?

Answer

Add texts here. Do not delete this text first.

Exercise 2.E.25

Using the Bohr model, determine the energy in joules of the photon produced when an electron in a He^{+} ion moves from the orbit with n = 5 to the orbit with n = 2.

Answer

Add texts here. Do not delete this text first.

Exercise 2.E.26

Using the Bohr model, determine the energy in joules of the photon produced when an electron in a Li2+ ion moves from the orbit with n = 2 to the orbit with n = 1.

Answer

1.471 × 10−17 J

Exercise 2.E.27

Consider a large number of hydrogen atoms with electrons randomly distributed in the n = 1, 2, 3, and 4 orbits

a. How many different wavelengths of light are emitted by these atoms as the electrons fall into lower-energy orbitals?
b. Calculate the lowest and highest energies of light produced by the transitions described in part (a).
c. Calculate the frequencies and wavelengths of the light produced by the transitions described in part (b).

Answer

Add texts here. Do not delete this text first.

Exercise 2.E.28

How are the Bohr model and the Rutherford model of the atom similar? How are they different?

Answer

Add texts here. Do not delete this text first.

Exercise 2.E.29

The spectra of hydrogen and of calcium are shown in [link]. What causes the lines in these spectra? Why are the colors of the lines different? Suggest a reason for the observation that the spectrum of calcium is more complicated than the spectrum of hydrogen

Answer

Both involve a relatively heavy nucleus with electrons moving around it, although strictly speaking, the Bohr model works only for one-electron atoms or ions. According to classical mechanics, the Rutherford model predicts a miniature "solar system" with electrons moving about the nucleus in circular or elliptical orbits that are confined to planes. If the requirements of classical electromagnetic theory that electrons in such orbits would emit electromagnetic radiation are ignored, such atoms would be stable, having constant energy and angular momentum, but would not emit any visible light (contrary to observation). If classical electromagnetic theory is applied, then the Rutherford atom would emit electromagnetic radiation of continually increasing frequency (contrary to the observed discrete spectra), thereby losing energy until the atom collapsed in an absurdly short time (contrary to the observed long-term stability of atoms). The Bohr model retains the classical mechanics view of circular orbits confined to planes having constant energy and angular momentum, but restricts these to quantized values dependent on a single quantum number, n. The orbiting electron in Bohr's model is assumed not to emit any electromagnetic radiation while moving about the nucleus in its stationary orbits, but the atom can emit or absorb electromagnetic radiation when the electron changes from one orbit to another. Because of the quantized orbits, such "quantum jumps" will produce discrete spectra, in agreement with observations.

2.E.3: Development of Quantum Theory

? Exercise 2.E.30

How are the Bohr model and the quantum mechanical model of the hydrogen atom similar? How are they different?

Answer

Both models have a central positively charged nucleus with electrons moving about the nucleus in accordance with the Coulomb electrostatic potential. The Bohr model *assumes* that the electrons move in circular orbits that have quantized energies, angular momentum, and radii that are specified by a single quantum number, n = 1, 2, 3, …, but this quantization is an ad hoc assumption made by Bohr to incorporate quantization into an essentially classical mechanics description of the atom. Bohr also assumed that electrons orbiting the nucleus normally do not emit or absorb electromagnetic radiation, but do so when the electron switches to a different orbit. In the quantum mechanical model, the electrons do not move in precise orbits (such orbits violate the Heisenberg uncertainty principle) and, instead, a probabilistic interpretation of the electron's position at any given instant is used, with a mathematical function ψ called a wavefunction that can be used to determine the electron's spatial probability distribution. These wavefunctions, or orbitals, are three-dimensional stationary waves that can be specified by three quantum numbers that arise naturally from their underlying mathematics (no ad hoc assumptions required): the principal quantum number, n (the same one used by Bohr), which specifies shells such that orbitals having the same n all have the same energy and approximately the same spatial extent; the angular momentum quantum number l, which is a measure of the orbital's angular momentum and corresponds to the orbitals' general shapes, as well as specifying subshells such that orbitals having the same l (and n) all have the same energy; and the orientation quantum number m, which is a measure of the z component of the angular momentum and corresponds to the orientations of the orbitals. The Bohr model gives the same expression for the energy as the quantum mechanical expression and, hence, both properly account for hydrogen's discrete spectrum (an example of getting the right answers for the wrong reasons, something that many chemistry students can sympathize with), but gives the wrong expression for the angular momentum (Bohr orbits necessarily all have non-zero angular momentum, but some quantum orbitals [s orbitals] can have zero angular momentum).

? Exercise 2.E.31

What are the allowed values for each of the four quantum numbers: n, l, m_l, and m_s?

Answer

Add texts here. Do not delete this text first.

https://chem.libretexts.org/@go/page/393218

Exercise 2.E.32

Describe the properties of an electron associated with each of the following four quantum numbers: n, l, m_l, and m_s.

Answer

n determines the general range for the value of energy and the probable distances that the electron can be from the nucleus. l determines the shape of the orbital. m_l determines the orientation of the orbitals of the same l value with respect to one another. m_s determines the spin of an electron.

Exercise 2.E.33

Answer the following questions:

a. Without using quantum numbers, describe the differences between the shells and subshells of an atom.
b. How do the quantum numbers of the shells and subshells of an atom differ?

Answer

Add texts here. Do not delete this text first.

Exercise 2.E.34

Identify the subshell in which electrons with the following quantum numbers are found:

a. $n = 2$, $l = 1$
b. $n = 4$, $l = 2$
c. $n = 6$, $l = 0$

Answer

(a) 2*p*; (b) 4*d*; (c) 6*s*

Exercise 2.E.35

Which of the subshells described in the previous question contain degenerate orbitals? How many degenerate orbitals are in each?

Answer

2p has three degenerate orbitals. 4d has five degenerate orbitals.

Exercise 2.E.36

Identify the subshell in which electrons with the following quantum numbers are found:

a. $n = 3$, $l = 2$
b. $n = 1$, $l = 0$
c. $n = 4$, $l = 3$

Answer

(a) 3*d;* (b) 1*s;* (c) 4*f*

Exercise 2.E.37

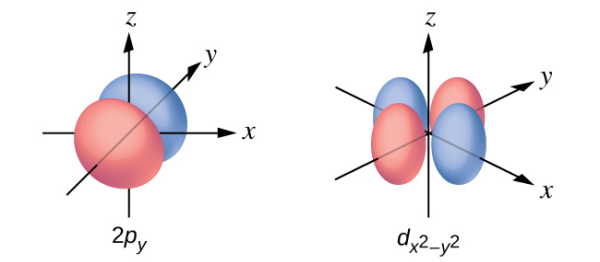
Which of the subshells described in the previous question contain degenerate orbitals? How many degenerate orbitals are in each?

Answer

3d has five degenerate orbitals. 4f has seven degenerate orbitals.

Exercise 2.E.38

Sketch the boundary surface of a $d_{x^2-y^2}$ and a p_y orbital. Be sure to show and label the axes.



Answer

Add texts here. Do not delete this text first.

Exercise 2.E.39

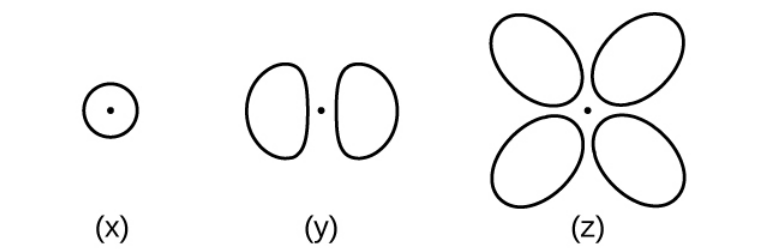
Sketch the p_x and d_{xz} orbitals. Be sure to show and label the coordinates.

Answer

Add texts here. Do not delete this text first.

Exercise 2.E.40

Consider the orbitals shown here in outline.



a. What is the maximum number of electrons contained in an orbital of type (x)? Of type (y)? Of type (z)?
b. How many orbitals of type (x) are found in a shell with $n = 2$? How many of type (y)? How many of type (z)?
c. Write a set of quantum numbers for an electron in an orbital of type (x) in a shell with $n = 4$. Of an orbital of type (y) in a shell with $n = 2$. Of an orbital of type (z) in a shell with $n = 3$.
d. What is the smallest possible n value for an orbital of type (x)? Of type (y)? Of type (z)?
e. What are the possible l and m_l values for an orbital of type (x)? Of type (y)? Of type (z)?

Answer

(a) x. 2, y. 2, z. 2;

https://chem.libretexts.org/@go/page/393218

(b) x. 1, y. 3, z. 0;

(c) x. 4 0 0 $\frac{1}{2}$, y. 2 1 0 $\frac{1}{2}$, z. 3 2 0 $\frac{1}{2}$;

(d) x. 1, y. 2, z. 3;

(e) x. $l = 0$, $m_l = 0$, y. $l = 1$, $m_l = -1$, 0, or +1, z. $l = 2$, $m_l = -2, -1, 0, +1, +2$

Exercise 2.E.41

State the Heisenberg uncertainty principle. Describe briefly what the principle implies.

Answer

Add texts here. Do not delete this text first.

Exercise 2.E.42

How many electrons could be held in the second shell of an atom if the spin quantum number m_s could have three values instead of just two? (Hint: Consider the Pauli exclusion principle.)

Answer

12

Exercise 2.E.43

Which of the following equations describe particle-like behavior? Which describe wavelike behavior? Do any involve both types of behavior? Describe the reasons for your choices.

a. $c = \lambda\nu$

b. $E = \frac{m\nu^2}{2}$

c. $r = \frac{n^2 a_0}{Z}$

d. $E = h\nu$

e. $\lambda = \frac{h}{m\nu}$

Answer

Add texts here. Do not delete this text first.

Exercise 2.E.44

Write a set of quantum numbers for each of the electrons with an n of 4 in a Se atom.

Answer

n	l	m_l	s
4	0	0	$+\frac{1}{2}$
4	0	0	$-\frac{1}{2}$
4	1	−1	$+\frac{1}{2}$
4	1	0	$+\frac{1}{2}$

n	l	m_l	s
4	1	+1	$+\frac{1}{2}$
4	1	−1	$-\frac{1}{2}$

2.E.4: Electronic Structure of Atoms (Electron Configurations)

Exercise 2.E. 45

Read the labels of several commercial products and identify monatomic ions of at least four transition elements contained in the products. Write the complete electron configurations of these cations.

Answer

Add texts here. Do not delete this text first.

Exercise 2.E. 46

Read the labels of several commercial products and identify monatomic ions of at least six main group elements contained in the products. Write the complete electron configurations of these cations and anions.

Answer

For example, Na^+: $1s^22s^22p^6$; Ca^{2+}: $1s^22s^22p^6$; Sn^{2+}: $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^2$; F^-: $1s^22s^22p^6$; O^{2-}: $1s^22s^22p^6$; Cl^-: $1s^22s^22p^63s^23p^6$.

Exercise 2.E. 47

Predict the full electron configuration of each of the following atoms:

a. C
b. P
c. V
d. Sb
e. Sm

Answer

a.) $1s^22s^22p^2$

b.) $1s^22s^22p^63s^23p^3$

c.) $1s^22s^22p^63s^23p^63d^34s^2$

d.) $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^3$

e.) $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}4f^65s^25p^66s^2$

Exercise 2.E. 48

Predict the full electron configuration of each of the following atoms:

a. N
b. Si
c. Fe
d. Te

e. Tb

Answer

$1s^22s^22p^3$;

$1s^22s^22p^63s^23p^2$;

$1s^22s^22p^63s^23p^64s^23d^6$;

$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^4$;

$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^9$

Exercise 2.E.49

Is $1s^22s^22p^6$ the symbol for a macroscopic property or a microscopic property of an element? Explain your answer.

Answer

Add texts here. Do not delete this text first.

Exercise 2.E.50

What additional information do we need to answer the question "Which ion has the electron configuration $1s^22s^22p^63s^23p^6$"?

Answer

The charge on the ion.

Exercise 2.E.51

Draw the orbital diagram for the valence shell of each of the following atoms:

a. C
b. P
c. V
d. Sb
e. Ru

Answer

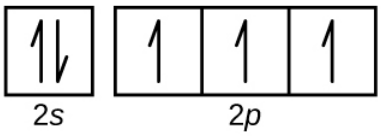
Add texts here. Do not delete this text first.

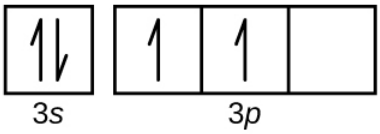
Exercise 2.E.52

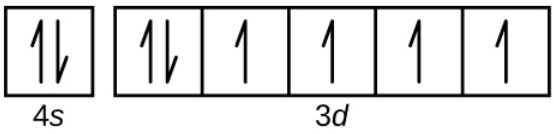
Use an orbital diagram to describe the electron configuration of the valence shell of each of the following atoms:

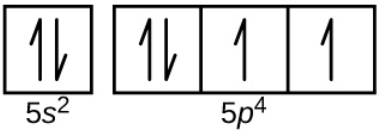
a. N
b. Si
c. Fe
d. Te
e. Mo

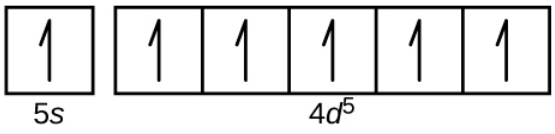
Answer

a) 

b) 

c) 

d) 

e) 

Exercise 2.E.53

Using complete subshell notation ($1s^2 2s^2 2p^6$, and so forth), predict the electron configurations of the following ions.

a. N^{3-}
b. Ca^{2+}
c. S^{-}
d. Cs^{2+}
e. Cr^{2+}
f. Gd^{3+}

Answer

Add texts here. Do not delete this text first.

Exercise 2.E.54

Which atom has the electron configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^2$?

Answer

Zr

Exercise 2.E.55

Which atom has the electron configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$?

Answer

Co ; Cobalt

Exercise 2.E.56

Which ion with a +1 charge has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$? Which ion with a –2 charge has this configuration?

Answer

Rb^+, Se^{2-}

Exercise 2.E.57

Which of the following atoms contains only three valence electrons: Li, B, N, F, Ne?

Answer

B ; Boron

Exercise 2.E.58

Which of the following has two unpaired electrons?

a. Mg
b. Si
c. S
d. Both Mg and S
e. Both Si and S.

Answer

Although both (b) and (c) are correct, (e) encompasses both and is the best answer.

Exercise 2.E.59

Which atom would be expected to have a half-filled 6*p* subshell?

Answer

Bi ; Bismuth

Exercise 2.E.60

Which atom would be expected to have a half-filled 4*s* subshell?

Answer

K

Exercise 2.E.61

In one area of Australia, the cattle did not thrive despite the presence of suitable forage. An investigation showed the cause to be the absence of sufficient cobalt in the soil. Cobalt forms cations in two oxidation states, Co^{2+} and Co^{3+}. Write the electron structure of the two cations.

Answer

Add texts here. Do not delete this text first.

Exercise 2.E.62

Thallium was used as a poison in the Agatha Christie mystery story “The Pale Horse.” Thallium has two possible cationic forms, +1 and +3. The +1 compounds are the more stable. Write the electron structure of the +1 cation of thallium..

Answer

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2 4f^{14} 5d^{10}$

Exercise 2.E.63

Write the electron configurations for the following atoms or ions:

a. B^{3+}
b. O^{-}
c. Cl^{3+}
d. Ca^{2+}
e. Ti

Answer

Add texts here. Do not delete this text first.

Exercise 2.E.64

Cobalt–60 and iodine–131 are radioactive isotopes commonly used in nuclear medicine. How many protons, neutrons, and electrons are in atoms of these isotopes? Write the complete electron configuration for each isotope.

Answer

Co has 27 protons, 27 electrons, and 33 neutrons: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$.

I has 53 protons, 53 electrons, and 78 neutrons: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^5$.

Exercise 2.E.65

Write a set of quantum numbers for each of the electrons with an n of 3 in a Sc atom.

Answer

Add texts here. Do not delete this text first.

This page titled 2.E: Quantum Theory and Electronic Structure (Exercises) is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

2.S: Study Guide

2: Quantum Theory and Electronic Structure of Atoms

Key Topics for TRU students taking CHEM1500

- classical to quantum theory
- the photoelectric effect
- Bohr’s model of the atom
- dual nature of the electron
- quantum mechanics
- quantum numbers
- atomic orbitals
- electron configuration
- the building up (Aufbau) principle

Key Learning Outcomes (Examples)

- describe the major historical developments that led up to the modern periodic table and the quantum physical understanding of the atom
- calculate wavelength, frequency and energy of a photon and the energy changes of an electron within a H atom
- explain Bohr’s theory of the hydrogen atom structure and its relationship to the atomic spectrum of hydrogen
- relate energy changes of an electron within a H atom to specific regions in the electromagnetic spectrum
- describe and explain the electronic structure of the atom based on the concept of atomic orbitals
- perform calculations using the De Broglie relationship and explain the significance of the answers
- use the quantum number rules to determine the allowable values of quantum numbers and hence relate these to the arrangement of electrons in atoms

2.S: Study Guide is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

3: Periodic Relationships Among the Elements

Topic hierarchy

3.1: The Periodic Table
3.2: Periodic Variations in Element Properties
3.E: Periodic Properties (Exercises)
3.S: Study Guide

3: Periodic Relationships Among the Elements is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

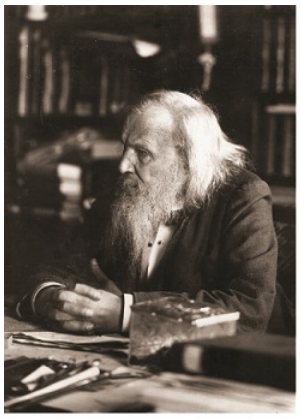
3.1: The Periodic Table

Learning Objectives

- State the periodic law and explain the organization of elements in the periodic table
- Predict the general properties of elements based on their location within the periodic table
- Identify metals, nonmetals, and metalloids by their properties and/or location on the periodic table

As early chemists worked to purify ores and discovered more elements, they realized that various elements could be grouped together by their similar chemical behaviors. One such grouping includes lithium (Li), sodium (Na), and potassium (K): These elements all are shiny, conduct heat and electricity well, and have similar chemical properties. A second grouping includes calcium (Ca), strontium (Sr), and barium (Ba), which also are shiny, good conductors of heat and electricity, and have chemical properties in common. However, the specific properties of these two groupings are notably different from each other. For example: Li, Na, and K are much more reactive than are Ca, Sr, and Ba; Li, Na, and K form compounds with oxygen in a ratio of two of their atoms to one oxygen atom, whereas Ca, Sr, and Ba form compounds with one of their atoms to one oxygen atom. Fluorine (F), chlorine (Cl), bromine (Br), and iodine (I) also exhibit similar properties to each other, but these properties are drastically different from those of any of the elements above.

Dimitri Mendeleev in Russia (1869) and Lothar Meyer in Germany (1870) independently recognized that there was a periodic relationship among the properties of the elements known at that time. Both published tables with the elements arranged according to increasing atomic mass. But Mendeleev went one step further than Meyer: He used his table to predict the existence of elements that would have the properties similar to aluminum and silicon, but were yet unknown. The discoveries of gallium (1875) and germanium (1886) provided great support for Mendeleev's work. Although Mendeleev and Meyer had a long dispute over priority, Mendeleev's contributions to the development of the periodic table are now more widely recognized (Figure 3.1.1).



Reihen	Gruppo I. — R²O	Gruppo II. — RO	Gruppo III. — R²O³	Gruppo IV. RH⁴ RO²	Gruppo V. RH³ R²O⁵	Gruppo VI. RH² RO³	Gruppo VII. RH R²O⁷	Gruppo VIII. — RO⁴
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=86	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

(a) (b)

Figure 3.1.1: (a) Dimitri Mendeleev is widely credited with creating (b) the first periodic table of the elements. (credit a: modification of work by Serge Lachinov; credit b: modification of work by “Den fjättrade ankan”/Wikimedia Commons)

Figure A shows a photograph of Dimitri Mendeleev. Figure B shows the first periodic table developed by Mendeleev, which had eight groups and twelve periods. In the first group (—, R superscript plus sign 0) is the following information: H = 1, L i = 7, N a = 23, K = 39, (C u = 63), R b = 85, (A g = 108), C a = 183, (—),—, (A u = 199) —. Note that each of these entries corresponds to one of the twelve periods respectively. The second group (—, R 0) contains the following information: (not entry for period 1) B o = 9, 4, M g = 24, C a = 40, Z n = 65, S r = 87, C d = 112, B a = 187, —, —, H g = 200, —. Note the ach of these entries corresponds to one of the twelve periods respectively. Group three (—, R superscript one 0 superscript nine) contains the information: (no entry for period 1), B = 11, A l = 27, 8. — = 44, — = 68, ? Y t = 88, I n = 113, ? D I = 138, —, ? E r = 178, T l = 204, —. Note that each of these entries corresponds to one of the twelve periods respectively. Group four (RH superscript four, R0 superscript eight) contains the following information: (no entry for period 1), C = 12, B i = 28, T i = 48, — = 72, Z r = 90, S n = 118, ? C o = 140, ? L a = 180, P b = 207, T h = 231. Note that each of these entries corresponds to one of the twelve periods respectively. Group five (R H superscript two, R superscript two 0 superscript five) contains the following information: (no entry for period 1), N = 14, P = 31, V = 51, A s = 75, N b = 94, S b = 122, —, —, T a = 182, B l = 208, —. Note that each of these entries corresponds to one of the twelve periods respectively. Group six (R H superscript two, R 0 superscript three) contains the following information: (no entry for period 1), O = 16, S = 32, C r = 52, S o = 78, M o = 96, T o = 125, —, —, W = 184, —, U = 240. Note that each of these entries corresponds to one of the twelve periods respectively. Group seven (R H , R superscript plus sing, 0 superscript 7) contains the following information: (no entry for period 1), F = 19, C l = 35, 5, M n = 55, B r = 80, — = 100, J = 127, —, —, —, —, —. Note that each of these entries corresponds to one of the twelve periods respectively. Group 8 (—, R 0 superscript four) contains the following information: (no entry for periods 1, 2, 3), in period 4: F o = 56, C o = 59, N i = 59, C u = 63, no entry for period five, in period 6: R u = 104, R h = 104, P d = 106, A g = 108, no entries for periods 7, 8 , or 9, in period 10: O s = 195, I r = 197, P t = 198, A u = 199, no entries for periods 11 or 12.

By the twentieth century, it became apparent that the periodic relationship involved atomic numbers rather than atomic masses. The modern statement of this relationship, the periodic law, is as follows: *the properties of the elements are periodic functions of their atomic numbers*. A modern periodic table arranges the elements in increasing order of their atomic numbers and groups atoms with similar properties in the same vertical column (Figure 3.1.2). Each box represents an element and contains its atomic number, symbol, average atomic mass, and (sometimes) name. The elements are arranged in seven horizontal rows, called periods or series, and 18 vertical columns, called groups. Groups are labeled at the top of each column. In the United States, the labels traditionally were numerals with capital letters. However, IUPAC recommends that the numbers 1 through 18 be used, and these labels are more common. For the table to fit on a single page, parts of two of the rows, a total of 14 columns, are usually written below the main body of the table.

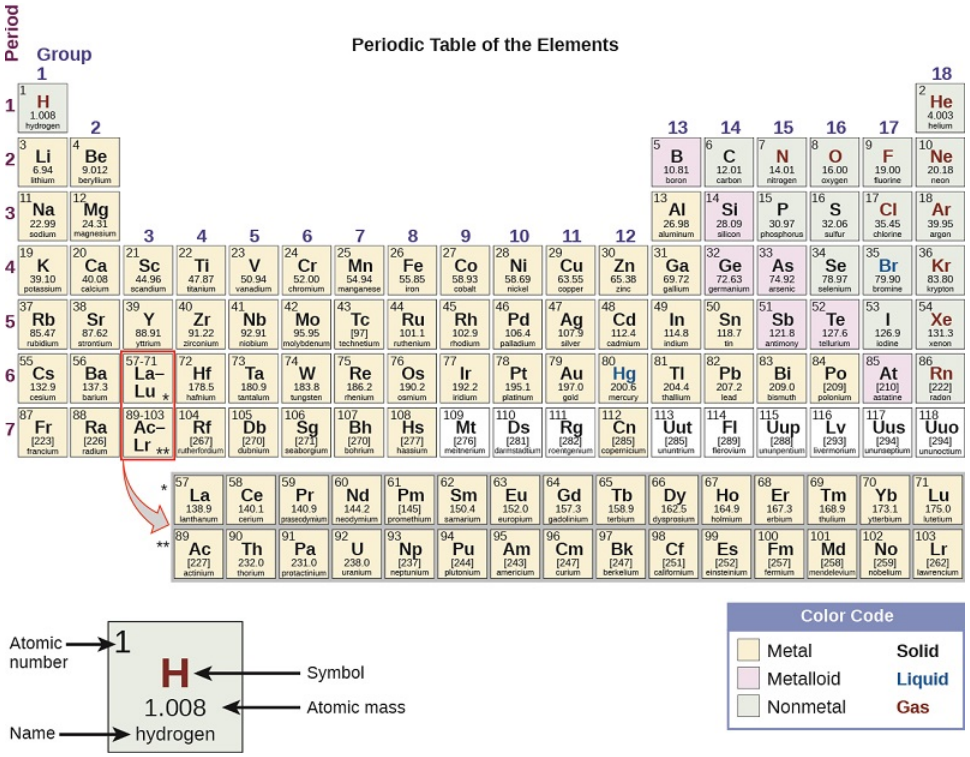


Figure 3.1.2: Elements in the periodic table are organized according to their properties.

The Periodic Table of Elements is shown. The 18 columns are labeled “Group” and the 7 rows are labeled “Period.” Below the table to the right is a box labeled “Color Code” with different colors for metals, metalloids, and nonmetals, as well as solids, liquids, and gases. To the left of this box is an enlarged picture of the upper-left most box on the table. The number 1 is in its upper-left hand corner and is labeled “Atomic number.” The letter “H” is in the middle in red indicating that it is a gas. It is labeled “Symbol.” Below that is the number 1.008 which is labeled “Atomic Mass.” Below that is the word hydrogen which is labeled “name.” The color of the box indicates that it is a nonmetal. Each element will be described in this order: atomic number; name; symbol; whether it is a metal, metalloid, or nonmetal; whether it is a solid, liquid, or gas; and atomic mass. Beginning at the top left of the table, or period 1, group 1, is a box containing “1; hydrogen; H; nonmetal; gas; and 1.008.” There is only one other element box in period 1, group 18, which contains “2; helium; H e; nonmetal; gas; and 4.003.” Period 2, group 1 contains “3; lithium; L i; metal; solid; and 6.94” Group 2 contains “4; beryllium; B e; metal; solid; and 9.012.” Groups 3 through 12 are skipped and group 13 contains “5; boron; B; metalloid; solid; 10.81.” Group 14 contains “6; carbon; C; nonmetal; solid; and 12.01.” Group 15 contains “7; nitrogen; N; nonmetal; gas; and 14.01.” Group 16 contains “8; oxygen; O; nonmetal; gas; and 16.00.” Group 17 contains “9; fluorine; F; nonmetal; gas; and 19.00.” Group 18 contains “10; neon; N e; nonmetal; gas; and 20.18.” Period 3, group 1 contains “11; sodium; N a; metal; solid; and 22.99.” Group 2 contains “12; magnesium; M g; metal; solid; and 24.31.” Groups 3 through 12 are skipped again in period 3 and group 13 contains “13; aluminum; A l; metal; solid; and 26.98.” Group 14 contains “14; silicon; S i; metalloid; solid; and 28.09.” Group 15 contains “15; phosphorous; P; nonmetal; solid; and 30.97.” Group 16 contains “16; sulfur; S; nonmetal; solid; and 32.06.” Group 17 contains “17; chlorine; C l; nonmetal; gas; and 35.45.” Group 18 contains “18; argon; A r; nonmetal; gas; and 39.95.” Period 4, group 1 contains “19; potassium; K; metal; solid; and 39.10.” Group 2 contains “20; calcium; C a; metal; solid; and 40.08.” Group 3 contains “21; scandium; S c; metal; solid; and 44.96.” Group 4 contains “22; titanium; T i; metal; solid; and 47.87.” Group 5 contains “23; vanadium; V; metal; solid; and 50.94.” Group 6 contains “24; chromium; C r; metal; solid; and 52.00.” Group 7 contains “25; manganese; M n; metal; solid; and 54.94.” Group 8 contains “26; iron; F e; metal; solid; and 55.85.” Group 9 contains “27; cobalt; C o; metal; solid; and 58.93.” Group 10 contains “28; nickel; N i; metal; solid; and 58.69.” Group 11 contains “29; copper; C u; metal; solid; and 63.55.” Group 12 contains “30; zinc; Z n; metal; solid; and 65.38.” Group 13 contains “31; gallium; G a; metal; solid; and 69.72.” Group 14 contains “32; germanium; G e; metalloid; solid; and 72.63.” Group 15 contains “33; arsenic; A s; metalloid; solid; and 74.92.” Group 16 contains “34; selenium; S e; nonmetal; solid; and 78.97.” Group 17 contains “35; bromine; B r; nonmetal; liquid; and 79.90.” Group 18 contains “36; krypton; K r; nonmetal; gas; and 83.80.” Period 5, group 1 contains “37; rubidium; R b; metal; solid; and 85.47.” Group 2 contains “38; strontium; S r; metal; solid; and 87.62.” Group 3 contains “39; yttrium; Y; metal; solid; and 88.91.” Group 4 contains “40; zirconium; Z r; metal; solid; and 91.22.” Group 5 contains “41; niobium; N b; metal; solid; and 92.91.” Group 6 contains “42; molybdenum; M o; metal; solid; and 95.95.” Group 7 contains “43; technetium; T c; metal; solid; and 97.” Group 8 contains “44; ruthenium; R u; metal; solid; and 101.1.” Group 9 contains “45; rhodium; R h; metal; solid; and 102.9.” Group 10 contains “46; palladium; P d; metal; solid; and 106.4.” Group 11 contains “47; silver; A g; metal; solid; and 107.9.” Group 12 contains “48; cadmium; C d; metal; solid; and 112.4.” Group 13 contains “49; indium; I n; metal; solid; and 114.8.” Group 14 contains “50; tin; S n; metal; solid; and 118.7.” Group 15 contains “51; antimony; S b; metalloid; solid; and 121.8.” Group 16 contains “52; tellurium; T e; metalloid; solid; and 127.6.” Group 17 contains “53; iodine; I; nonmetal; solid; and 126.9.” Group 18 contains “54; xenon; X e; nonmetal; gas; and 131.3.” Period 6, group 1 contains “55; cesium; C s; metal; solid; and 132.9.” Group 2 contains “56; barium; B a; metal; solid; and 137.3.” Group 3 breaks the pattern. The box has a large arrow pointing to a row of elements below the table with atomic numbers ranging from 57-71. In sequential order by atomic number, the first box in this row

https://chem.libretexts.org/@go/page/393220

contains “57; lanthanum; L a; metal; solid; and 138.9.” To its right, the next is “58; cerium; C e; metal; solid; and 140.1.” Next is “59; praseodymium; P r; metal; solid; and 140.9.” Next is “60; neodymium; N d; metal; solid; and 144.2.” Next is “61; promethium; P m; metal; solid; and 145.” Next is “62; samarium; S m; metal; solid; and 150.4.” Next is “63; europium; E u; metal; solid; and 152.0.” Next is “64; gadolinium; G d; metal; solid; and 157.3.” Next is “65; terbium; T b; metal; solid; and 158.9.” Next is “66; dysprosium; D y; metal; solid; and 162.5.” Next is “67; holmium; H o; metal; solid; and 164.9.” Next is “68; erbium; E r; metal; solid; and 167.3.” Next is “69; thulium; T m; metal; solid; and 168.9.” Next is “70; ytterbium; Y b; metal; solid; and 173.1.” The last in this special row is “71; lutetium; L u; metal; solid; and 175.0.” Continuing in period 6, group 4 contains “72; hafnium; H f; metal; solid; and 178.5.” Group 5 contains “73; tantalum; T a; metal; solid; and 180.9.” Group 6 contains “74; tungsten; W; metal; solid; and 183.8.” Group 7 contains “75; rhenium; R e; metal; solid; and 186.2.” Group 8 contains “76; osmium; O s; metal; solid; and 190.2.” Group 9 contains “77; iridium; I r; metal; solid; and 192.2.” Group 10 contains “78; platinum; P t; metal; solid; and 195.1.” Group 11 contains “79; gold; A u; metal; solid; and 197.0.” Group 12 contains “80; mercury; H g; metal; liquid; and 200.6.” Group 13 contains “81; thallium; T l; metal; solid; and 204.4.” Group 14 contains “82; lead; P b; metal; solid; and 207.2.” Group 15 contains “83; bismuth; B i; metal; solid; and 209.0.” Group 16 contains “84; polonium; P o; metal; solid; and 209.” Group 17 contains “85; astatine; A t; metalloid; solid; and 210.” Group 18 contains “86; radon; R n; nonmetal; gas; and 222.” Period 7, group 1 contains “87; francium; F r; metal; solid; and 223.” Group 2 contains “88; radium; R a; metal; solid; and 226.” Group 3 breaks the pattern much like what occurs in period 6. A large arrow points from the box in period 7, group 3 to a special row containing the elements with atomic numbers ranging from 89-103, just below the row which contains atomic numbers 57-71. In sequential order by atomic number, the first box in this row contains “89; actinium; A c; metal; solid; and 227.” To its right, the next is “90; thorium; T h; metal; solid; and 232.0.” Next is “91; protactinium; P a; metal; solid; and 231.0.” Next is “92; uranium; U; metal; solid; and 238.0.” Next is “93; neptunium; N p; metal; solid; and N p.” Next is “94; plutonium; P u; metal; solid; and 244.” Next is “95; americium; A m; metal; solid; and 243.” Next is “96; curium; C m; metal; solid; and 247.” Next is “97; berkelium; B k; metal; solid; and 247.” Next is “98; californium; C f; metal; solid; and 251.” Next is “99; einsteinium; E s; metal; solid; and 252.” Next is “100; fermium; F m; metal; solid; and 257.” Next is “101; mendelevium; M d; metal; solid; and 258.” Next is “102; nobelium; N o; metal; solid; and 259.” The last in this special row is “103; lawrencium; L r; metal; solid; and 262.” Continuing in period 7, group 4 contains “104; rutherfordium; R f; metal; solid; and 267.” Group 5 contains “105; dubnium; D b; metal; solid; and 270.” Group 6 contains “106; seaborgium; S g; metal; solid; and 271.” Group 7 contains “107; bohrium; B h; metal; solid; and 270.” Group 8 contains “108; hassium; H s; metal; solid; and 277.” Group 9 contains “109; meitnerium; M t; not indicated; solid; and 276.” Group 10 contains “110; darmstadtium; D s; not indicated; solid; and 281.” Group 11 contains “111; roentgenium; R g; not indicated; solid; and 282.” Group 12 contains “112; copernicium; C n; metal; liquid; and 285.” Group 13 contains “113; ununtrium; U u t; not indicated; solid; and 285.” Group 14 contains “114; flerovium; F l; not indicated; solid; and 289.” Group 15 contains “115; ununpentium; U u p; not indicated; solid; and 288.” Group 16 contains “116; livermorium; L v; not indicated; solid; and 293.” Group 17 contains “117; ununseptium; U u s; not indicated; solid; and 294.” Group 18 contains “118; ununoctium; U u o; not indicated; solid; and 294.”

Many elements differ dramatically in their chemical and physical properties, but some elements are similar in their behaviors. For example, many elements appear shiny, are malleable (able to be deformed without breaking) and ductile (can be drawn into wires), and conduct heat and electricity well. Other elements are not shiny, malleable, or ductile, and are poor conductors of heat and electricity. We can sort the elements into large classes with common properties: metals (elements that are shiny, malleable, good conductors of heat and electricity—shaded yellow); nonmetals (elements that appear dull, poor conductors of heat and electricity—shaded green); and metalloids (elements that conduct heat and electricity moderately well, and possess some properties of metals and some properties of nonmetals—shaded purple).

The elements can also be classified into the main-group elements (or representative elements) in the columns labeled 1, 2, and 13–18; the transition metals in the columns labeled 3–12; and inner transition metals in the two rows at the bottom of the table (the top-row elements are called lanthanides and the bottom-row elements are actinides; Figure 3.1.3). The elements can be subdivided further by more specific properties, such as the composition of the compounds they form. For example, the elements in group 1 (the first column) form compounds that consist of one atom of the element and one atom of hydrogen. These elements (except hydrogen) are known as alkali metals, and they all have similar chemical properties. The elements in group 2 (the second column) form compounds consisting of one atom of the element and two atoms of hydrogen: These are called alkaline earth metals, with similar properties among members of that group. Other groups with specific names are the pnictogens (group 15), chalcogens (group 16), halogens (group 17), and the noble gases (group 18, also known as inert gases). The groups can also be referred to by the first element of the group: For example, the chalcogens can be called the oxygen group or oxygen family. Hydrogen is a unique, nonmetallic element with properties similar to both group 1 and group 17 elements. For that reason, hydrogen may be shown at the top of both groups, or by itself.

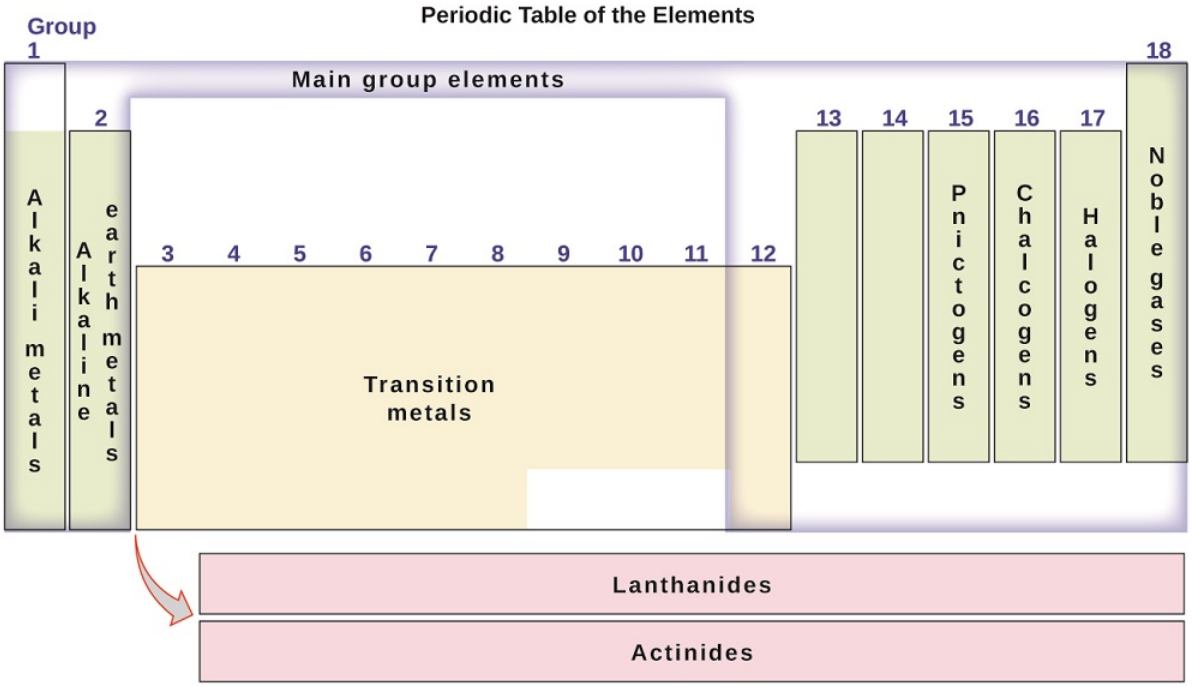


Figure 3.1.3: The periodic table organizes elements with similar properties into groups.

This diagram combines the groups and periods of the periodic table based on their similar properties. Group 1 contains the alkali metals, group 2 contains the earth alkaline metals, group 15 contains the pnictogens, group 16 contains the chalcogens, group 17 contains the halogens and group 18 contains the noble gases. The main group elements consist of groups 1, 2, and 12 through 18. Therefore, most of the transition metals, which are contained in groups 3 through 11, are not main group elements. The lanthanides and actinides are called out at the bottom of the periodic table.

✔ Example 3.1.1: Naming Groups of Elements

Atoms of each of the following elements are essential for life. Give the group name for the following elements:

a. chlorine
b. calcium
c. sodium
d. sulfur

Solution

The family names are as follows:

a. halogen
b. alkaline earth metal
c. alkali metal
d. chalcogen

? Exercise 3.1.1

Give the group name for each of the following elements:

a. krypton
b. selenium
c. barium
d. lithium

Answer a

noble gas

Answer b

chalcogen

Answer c

alkaline earth metal

Answer d

alkali metal

In studying the periodic table, you might have noticed something about the atomic masses of some of the elements. Element 43 (technetium), element 61 (promethium), and most of the elements with atomic number 84 (polonium) and higher have their atomic mass given in square brackets. This is done for elements that consist entirely of unstable, radioactive isotopes (you will learn more about radioactivity in the nuclear chemistry chapter). An average atomic weight cannot be determined for these elements because their radioisotopes may vary significantly in relative abundance, depending on the source, or may not even exist in nature. The number in square brackets is the atomic mass number (and approximate atomic mass) of the most stable isotope of that element.

Summary

The discovery of the periodic recurrence of similar properties among the elements led to the formulation of the periodic table, in which the elements are arranged in order of increasing atomic number in rows known as periods and columns known as groups. Elements in the same group of the periodic table have similar chemical properties. Elements can be classified as metals, metalloids, and nonmetals, or as a main-group elements, transition metals, and inner transition metals. Groups are numbered 1–18 from left to right. The elements in group 1 are known as the alkali metals; those in group 2 are the alkaline earth metals; those in 15 are the pnictogens; those in 16 are the chalcogens; those in 17 are the halogens; and those in 18 are the noble gases.

Glossary

actinide
inner transition metal in the bottom of the bottom two rows of the periodic table

alkali metal
element in group 1

alkaline earth metal
element in group 2

chalcogen
element in group 16

group
vertical column of the periodic table

halogen
element in group 17

inert gas
(also, noble gas) element in group 18

inner transition metal
(also, lanthanide or actinide) element in the bottom two rows; if in the first row, also called lanthanide, or if in the second row, also called actinide

lanthanide
inner transition metal in the top of the bottom two rows of the periodic table

main-group element
(also, representative element) element in columns 1, 2, and 12–18

metal
element that is shiny, malleable, good conductor of heat and electricity

metalloid
element that conducts heat and electricity moderately well, and possesses some properties of metals and some properties of nonmetals

noble gas
(also, inert gas) element in group 18

nonmetal
element that appears dull, poor conductor of heat and electricity

period
(also, series) horizontal row of the periodic table

periodic law
properties of the elements are periodic function of their atomic numbers.

periodic table
table of the elements that places elements with similar chemical properties close together

pnictogen
element in group 15

representative element
(also, main-group element) element in columns 1, 2, and 12–18

transition metal
element in columns 3–11

series
(also, period) horizontal row of the period table

This page titled 3.1: The Periodic Table is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **2.6: The Periodic Table** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

3.2: Periodic Variations in Element Properties

Learning Objectives

- Describe and explain the observed trends in atomic size, ionization energy, and electron affinity of the elements

The elements in groups (vertical columns) of the periodic table exhibit similar chemical behavior. This similarity occurs because the members of a group have the same number and distribution of electrons in their valence shells. However, there are also other patterns in chemical properties on the periodic table. For example, as we move down a group, the metallic character of the atoms increases. Oxygen, at the top of Group 16 (6A), is a colorless gas; in the middle of the group, selenium is a semiconducting solid; and, toward the bottom, polonium is a silver-grey solid that conducts electricity.

As we go across a period from left to right, we add a proton to the nucleus and an electron to the valence shell with each successive element. As we go down the elements in a group, the number of electrons in the valence shell remains constant, but the principal quantum number increases by one each time. An understanding of the electronic structure of the elements allows us to examine some of the properties that govern their chemical behavior. These properties vary periodically as the electronic structure of the elements changes. They are (1) size (radius) of atoms and ions, (2) ionization energies, and (3) electron affinities.

3.2.1: Effective Nuclear Charge: Penetration and Shielding

Electrons are negatively charged and are pulled pretty close to each other by their attraction to the positive charge of a nucleus. The electrons are attracted to the nucleus at the same time as electrons repel each other. The balance between attractive and repulsive forces results in *shielding*. The orbital (n) and subshell (m_l) define how close an electron can approach the nucleus. The ability of an electron to get close to the nucleus is *penetration*.

The force that an electron feels is dependent on the distance from the nearest charge (i.e., an electron, usually with bigger atoms and on the outer shells) and the amount of charge. More distance between the charges will result in less force, and more charge will have more force of attraction or repulsion.

In the simplest case, every electron in an atom would feel the same amount of "pull" from the nucleus. For example, in Li, all three electrons might "feel" the +3 charge from the nucleus. However, this is not the case when observing atomic behavior. When considering the core electrons (or the electrons closest to the nucleus), the nuclear charge "felt" by the electrons (*Effective Nuclear Charge* (Zeff) is close to the actual nuclear charge. As you proceed from the core electrons to the outer valence electrons, Zeff falls significantly. This is because of *shielding*, or simply the electrons closest to the nucleus decrease the amount of nuclear charge affecting the outer electrons. Shielding is caused by the combination of partial neutralization of nuclear charge by core electrons, and by electron-electron repulsion.

The amount of charge felt by an electron depends on its distance from the nucleus. The closer an electron comes to the nucleus, or the more it *penetrates*, the stronger its attraction to the nucleus. Core electrons *penetrate* more and feel more of the nucleus than the other electrons.

3.2.1.1: **Orbital Penetration**

Penetration describes the proximity to which an electron can approach to the nucleus. In a multi-electron system, electron penetration is defined by an electron's relative electron density (probability density) near the nucleus of an atom. Electrons in different orbitals have different wavefunctions and therefore different radial distributions and probabilities (defined by quantum numbers n and m_l around the nucleus). In other words, penetration depends on the shell (n) and subshell (m_l). For example, we see that since a 2s electron has more electron density near the nucleus than a 2p electron, it is penetrating the nucleus of the atom more than the 2p electron. The penetration power of an electron, in a multi-electron atom, is dependent on the values of both the shell and subshell.

Within the same shell value (n), the penetrating power of an electron follows this trend in subshells (m_l):

s>p>d>f

And for different values of shell (n) and subshell (l), penetrating power of an electron follows this trend:

1s>2s>2p>3s>3p>4s>3d>4p>5s>4d>5p>6s>4f....

and the energy of an electron for each shell and subshell goes as follows...

1s<2s<2p<3s<3p<4s<3d<4p....

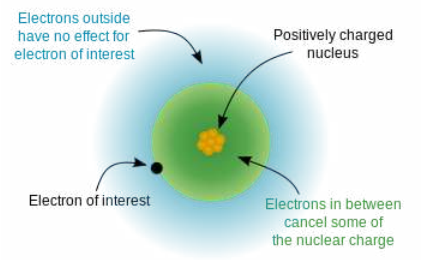
The electron probability density for s-orbitals is highest in the center of the orbital, or at the nucleus. If we imagine a dartboard that represents the circular shape of the s-orbital and if the darts landed in correlation to the probability to where and electron would be found, the greatest dart density would be at the 50 points region but most of the darts would be at the 30 point region. When considering the 1s-orbital, the spherical shell of 53 pm is represented by the 30 point ring.

Electrons which experience greater penetration experience stronger attraction to the nucleus, less shielding, and therefore experience a larger *Effective Nuclear Charge* (Zeff), but shield other electrons more effectively.

3.2.1.2: **Shielding**

An atom (assuming its atomic number is greater than 2) has core electrons that are extremely attracted to the nucleus in the middle of the atom. However the number of protons in the nucleus are never equal to the number of core electrons (relatively) adjacent to the nucleus. The number of protons increase by one across the periodic table, but the number of core electrons change by periods. The first period has no core electrons, the second has 2, the third has 10, and etc. This number is not equal to the number of protons. So that means that the core electrons feel a stronger pull towards the nucleus than any other electron within the system. The valence electrons are farther out from the nucleus, so they experience a smaller force of attraction.

Shielding refers to the core electrons repelling the outer rings and thus lowering the 1:1 ratio. Hence, the nucleus has "less grip" on the outer electrons and are shielded from them. Electrons that have greater penetration can get closer to the nucleus and effectively block out the charge from electrons that have less proximity. For example, Zeff is calculated by subtracting the magnitude of shielding from the total nuclear charge. The value of Zeff will provide information on how much of a charge an electron actually experiences.



3.2.1: This image shows how inner electrons can shield outer electrons from the nuclear charge. (CC BY-SA 3.0; from Wikipedia).

Because the order of electron penetration from greatest to least is s, p, d, f; the order of the amount of shielding done is also in the order s, p, d, f.

Since the 2s electron has more density near the nucleus of an atom than a 2p electron, it is said to shield the 2p electron from the full effective charge of the nucleus. Therefore the 2p electron feels a lesser effect of the positively charged nucleus of the atom due to the shielding ability of the electrons closer to the nucleus than itself, (i.e. 2s electron).

These electrons that are shielded from the full charge of the nucleus are said to experience an *effective nuclear charge* (Zeff) of the nucleus, which is some degree less than the full nuclear charge an electron would feel in a hydrogen atom or hydrogenlike ions. The effective nuclear charge of an atom is given by the equation:

$$Zeff=Z-S$$

where

- Z is the atomic number (number of protons in nucleus) and
- S is the shielding constant

We can see from this equation that the effective nuclear charge of an atom increases as the number of protons in an atom increases. Therefore as we go from left to right on the periodic table the effective nuclear charge of an atom increases in strength and holds the outer electrons closer and tighter to the nucleus. This phenomena can explain the decrease in atomic radii we see as we go across the periodic table as electrons are held closer to the nucleus due to increase in number of protons and increase in effective nuclear charge.

Example 1: *Fluorine, Neon, and Sodium*

What is the effective attraction Zeff experienced by the valence electrons in the three isoelectronic species: the fluorine anion, the neutral neon atom, and sodium cation?

Solution

Each species has 10 electrons, and the number of nonvalence electrons is 2 (10 total electrons - 8 valence) but the effective nuclear charge varies because each has a different atomic number A.

The charge Z of the nucleus of a fluorine atom is 9, but the valence electrons are screened appreciably by the core electrons (four electrons from the 1s and 2s orbitals) and partially by the 7 electrons in the 2p orbitals.

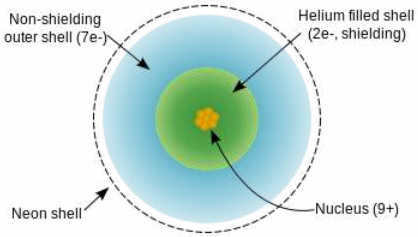


Diagram of a fluorine atom showing the extent of effective nuclear charge. (CC BY-SA- 3.0; Wikipedia).

- Zeff(F−)=9−2=7+
- Zeff(Ne)=10−2=8+
- Zeff(Na+)=11−2=9+

So the sodium cation has the greatest effective nuclear charge, and thus the smallest radius.

3.2.1.3: Radial Distribution Graphs

A radial distribution function graph describes the distribution of orbitals with the effects of shielding (Figure 3.2.2). The small peak of the 2s orbital shows that he electrons in the 2s orbital are closest to the nucleus. Therefore, it is the electrons in the 2p orbital of Be that are being shielded from the nucleus, by the electrons in the 2s orbital. The following is the radial distribution of the 1s and 2s orbitals. Notice the 1s orbital is shifted to the right, while the 2s orbital has a node.

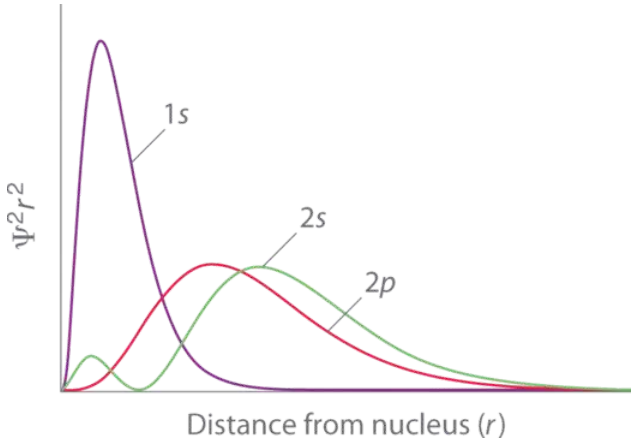


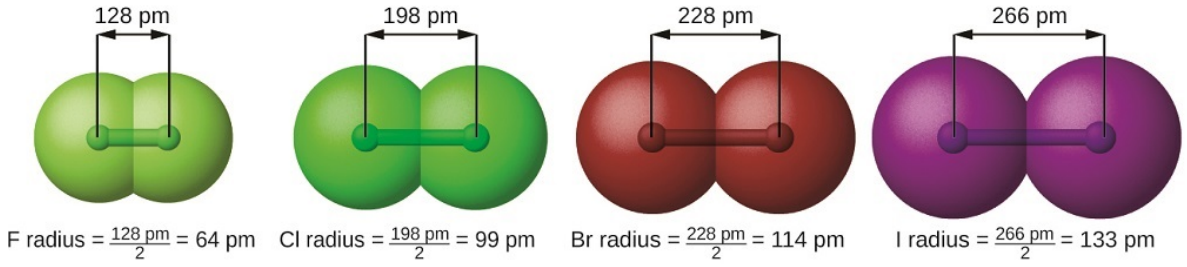
Figure 3.2.2 : Orbital Penetration. A comparison of the radial probability distribution of the 2*s* and 2*p* orbitals for various states of the hydrogen atom shows that the 2*s* orbital penetrates inside the 1*s* orbital more than the 2*p* orbital does. Consequently, when an electron is in the small inner lobe of the 2*s* orbital, it experiences a relatively large value of *Zeff*, which causes the energy of the 2*s* orbital to be lower than the energy of the 2*p* orbital.

3.2.1.4: Periodic Trends Due to Penetration and Shielding

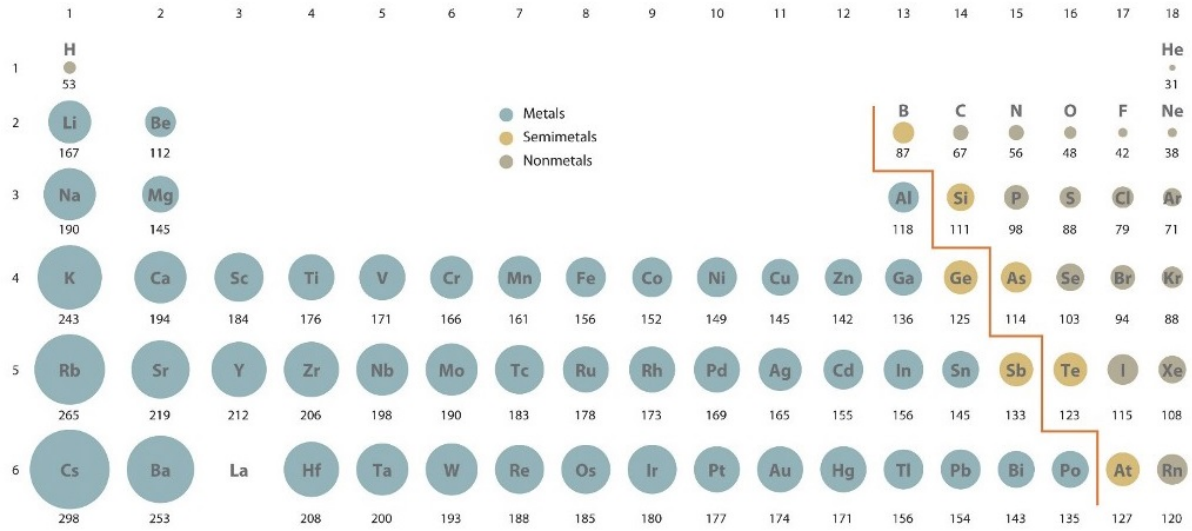
- **Effective Nuclear Charge (ZeffZeff):** The effective nuclear charge increases from left to right and increases from top to bottom on the periodic table.
- **Atomic Radius:** The atomic radius decreases from left to right, and increases from top to bottom.
- **Ionization Energies:** The ionization energies increase from left to right, and decrease from top to bottom.
- **Electronegativity:** The electronegativity of the elements is highest near flourine. In general, it increases from left to right and decreases from top to bottom.

3.2.2: Variation in Covalent Radius

The quantum mechanical picture makes it difficult to establish a definite size of an atom. However, there are several practical ways to define the radius of atoms and, thus, to determine their relative sizes that give roughly similar values. We will use the covalent radius (Figure 3.2.3), which is defined as one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond (this measurement is possible because atoms within molecules still retain much of their atomic identity).



(a)



(b)

Figure 3.2.3: (a) The radius of an atom is defined as one-half the distance between the nuclei in a molecule consisting of two identical atoms joined by a covalent bond. The atomic radius for the halogens increases down the group as n increases. (b) Covalent radii of the elements. The general trend is that radii increase down a group and decrease across a period.

We know that as we scan down a group, the principal quantum number, *n*, increases by one for each element. Thus, the electrons are being added to a region of space that is increasingly distant from the nucleus. Consequently, the size of the atom (and its covalent radius) must increase as we increase the distance of the outermost electrons from the nucleus. This trend is illustrated for the covalent radii of the halogens in Table 3.2.1 and Figure 3.2.3. The trends for the entire periodic table can be seen in Figure 3.2.4.

Table 3.2.1: Covalent Radii of the Halogen Group Elements

Atom	Covalent radius (pm)	Nuclear charge
F	64	+9
Cl	99	+17
Br	114	+35
I	133	+53
At	148	+85

As shown in Figure 3.2.4, as we move across a period from left to right, we generally find that each element has a smaller covalent radius than the element preceding it. This might seem counterintuitive because it implies that atoms with more electrons have a smaller atomic radius. This can be explained with the concept of effective nuclear charge, Z_{eff}. This is the pull exerted on a specific electron by the nucleus, taking into account any electron–electron repulsions. For hydrogen, there is only one electron and so the nuclear charge (Z) and the effective nuclear charge (Z_{eff}) are equal. For all other atoms, the inner electrons partially *shield* the outer electrons from the pull of the nucleus, and thus:

$$Z_{\text{eff}} = Z - shielding$$

Shielding is determined by the probability of another electron being between the electron of interest and the nucleus, as well as by the electron–electron repulsions the electron of interest encounters. Core electrons are adept at shielding, while electrons in the same valence shell do not block the nuclear attraction experienced by each other as efficiently. Thus, each time we move from one element to the next across a period, Z increases by one, but the shielding increases only slightly. Thus, Z_{eff} increases as we move from left to right across a period. The stronger pull (higher effective nuclear charge) experienced by electrons on the right side of the periodic table draws them closer to the nucleus, making the covalent radii smaller.

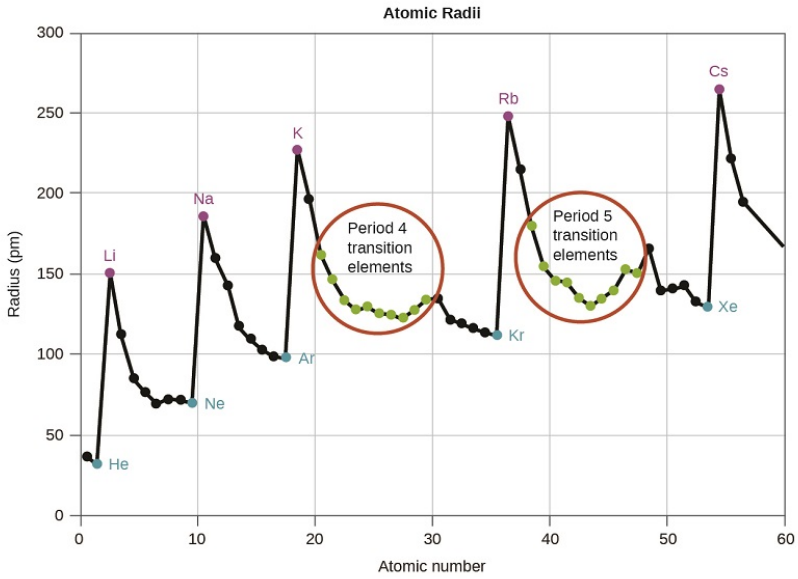


Figure 3.2.4: Within each period, the trend in atomic radius decreases as Z increases; for example, from K to Kr. Within each group (e.g., the alkali metals shown in purple), the trend is that atomic radius increases as Z increases.

Thus, as we would expect, the outermost or valence electrons are easiest to remove because they have the highest energies, are shielded more, and are farthest from the nucleus. As a general rule, when the representative elements form cations, they do so by the loss of the *ns* or *np* electrons that were added last in the Aufbau process. The transition elements, on the other hand, lose the *ns* electrons before they begin to lose the $(n - 1)d$ electrons, even though the *ns* electrons are added first, according to the Aufbau principle.

Example 3.2.1: Sorting Atomic Radii

Predict the order of increasing covalent radius for Ge, Fl, Br, Kr.

Solution

Radius increases as we move down a group, so Ge < Fl (Note: Fl is the symbol for flerovium, element 114, NOT fluorine). Radius decreases as we move across a period, so Kr < Br < Ge. Putting the trends together, we obtain Kr < Br < Ge < Fl.

Exercise 3.2.1

Give an example of an atom whose size is smaller than fluorine.

Answer

Ne or He

3.2.3: Variation in Ionic Radii

Ionic radius is the measure used to describe the size of an ion. A cation always has fewer electrons and the same number of protons as the parent atom; it is smaller than the atom from which it is derived (Figure 3.2.5). For example, the covalent radius of an aluminum atom ($1s^2 2s^2 2p^6 3s^2 3p^1$) is 118 pm, whereas the ionic radius of an Al^{3+} ($1s^2 2s^2 2p^6$) is 68 pm. As electrons are removed from the outer valence shell, the remaining core electrons occupying smaller shells experience a greater effective nuclear charge Z_{eff} (as discussed) and are drawn even closer to the nucleus.



Figure 3.2.5: The radius for a cation is smaller than the parent atom (Al), due to the lost electrons; the radius for an anion is larger than the parent (S), due to the gained electrons.

Cations with larger charges are smaller than cations with smaller charges (e.g., V^{2+} has an ionic radius of 79 pm, while that of V^{3+} is 64 pm). Proceeding down the groups of the periodic table, we find that cations of successive elements with the same charge generally have larger radii, corresponding to an increase in the principal quantum number, n.

An anion (negative ion) is formed by the addition of one or more electrons to the valence shell of an atom. This results in a greater repulsion among the electrons and a decrease in Z_{eff} per electron. Both effects (the increased number of electrons and the decreased Z_{eff}) cause the radius of an anion to be larger than that of the parent atom (Figure 3.2.3). For example, a sulfur atom ($[Ne]3s^2 3p^4$) has a covalent radius of 104 pm, whereas the ionic radius of the sulfide anion ($[Ne]3s^2 3p^6$) is 170 pm. For consecutive elements proceeding down any group, anions have larger principal quantum numbers and, thus, larger radii.

Atoms and ions that have the same electron configuration are said to be isoelectronic. Examples of isoelectronic species are N^{3-}, O^{2-}, F^-, Ne, Na^+, Mg^{2+}, and Al^{3+} ($1s^2 2s^2 2p^6$). Another isoelectronic series is P^{3-}, S^{2-}, Cl^-, Ar, K^+, Ca^{2+}, and Sc^{3+} ($[Ne]3s^2 3p^6$). For atoms or ions that are isoelectronic, the number of protons determines the size. The greater the nuclear charge, the smaller the radius in a series of isoelectronic ions and atoms.

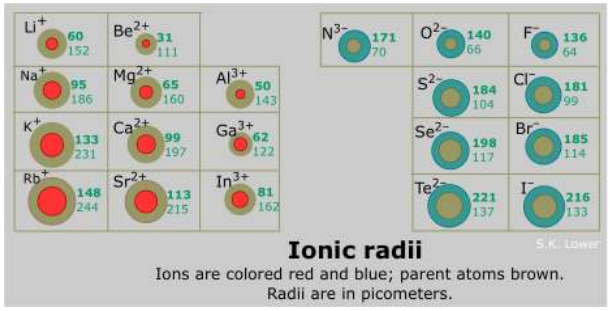


Figure 3.2.6: All non-metals (except for the noble gases which do not form ions) form anions which become larger down a group. For non-metals, a subtle trend of decreasing ionic radii is found across a pegroup theoryriod (Shannon 1976). Anions are almost always larger than cations, although there are some exceptions (i.e. fluorides of some alkali metals).

3.2.4: Variation in Ionization Energies

The amount of energy required to remove the most loosely bound electron from a gaseous atom in its ground state is called its first ionization energy (IE_1). The first ionization energy for an element, X, is the energy required to form a cation with +1 charge:

$$X(g) \longrightarrow X^+(g) + e^- \quad IE_1$$

The energy required to remove the second most loosely bound electron is called the second ionization energy (IE_2).

$$X^+(g) \longrightarrow X^{2+}(g) + e^- \quad IE_2$$

The energy required to remove the third electron is the third ionization energy, and so on. Energy is always required to remove electrons from atoms or ions, so ionization processes are endothermic and IE values are always positive. For larger atoms, the most

loosely bound electron is located farther from the nucleus and so is easier to remove. Thus, as size (atomic radius) increases, the ionization energy should decrease. Relating this logic to what we have just learned about radii, we would expect first ionization energies to decrease down a group and to increase across a period.

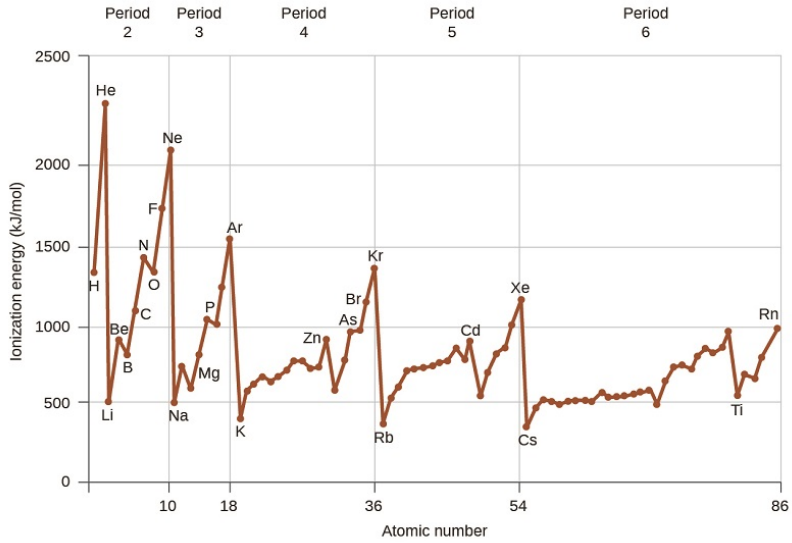


Figure 3.2.7: The first ionization energy of the elements in the first five periods are plotted against their atomic number.

Figure 3.2.7 graphs the relationship between the first ionization energy and the atomic number of several elements. Within a period, the values of first ionization energy for the elements (IE_1) generally increases with increasing *Z*. Down a group, the IE_1 value generally decreases with increasing *Z*. There are some systematic deviations from this trend, however. Note that the ionization energy of boron (atomic number 5) is less than that of beryllium (atomic number 4) even though the nuclear charge of boron is greater by one proton. This can be explained because the energy of the subshells increases as *l* increases, due to penetration and shielding (as discussed previously in this chapter). Within any one shell, the *s* electrons are lower in energy than the *p* electrons. This means that an *s* electron is harder to remove from an atom than a *p* electron in the same shell. The electron removed during the ionization of beryllium ($[He]2s^2$) is an *s* electron, whereas the electron removed during the ionization of boron ($[He]2s^2 2p^1$) is a *p* electron; this results in a lower first ionization energy for boron, even though its nuclear charge is greater by one proton. Thus, we see a small deviation from the predicted trend occurring each time a new subshell begins.

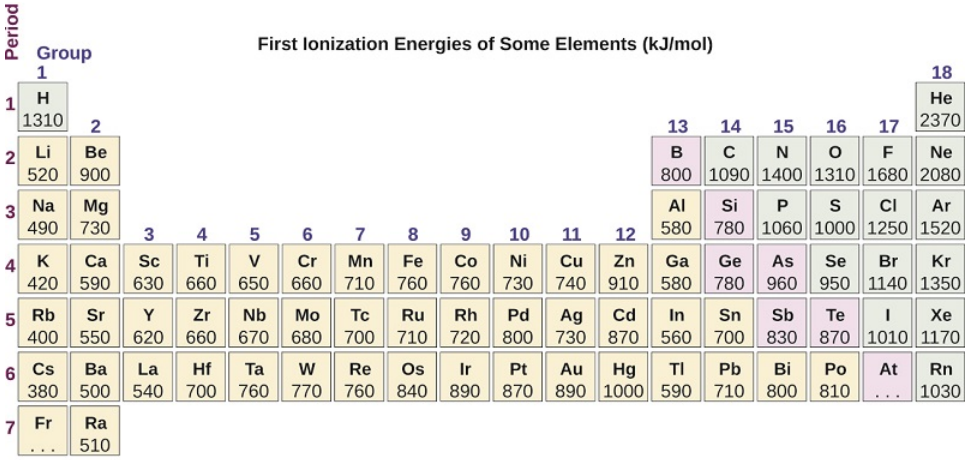
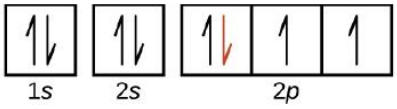


Figure 3.2.8: This version of the periodic table shows the first ionization energy of (IE: $_1$), in kJ/mol, of selected elements.

Another deviation occurs as orbitals become more than one-half filled. The first ionization energy for oxygen is slightly less than that for nitrogen, despite the trend in increasing IE_1 values across a period. Looking at the orbital diagram of oxygen, we can see that removing one electron will eliminate the electron–electron repulsion caused by pairing the electrons in the 2*p* orbital and will result in a half-filled orbital (which is energetically favorable). Analogous changes occur in succeeding periods (note the dip for sulfur after phosphorus in Figure 3.2.7.

O $1s^2 2s^2 2p^4$



Removing an electron from a cation is more difficult than removing an electron from a neutral atom because of the greater electrostatic attraction to the cation. Likewise, removing an electron from a cation with a higher positive charge is more difficult than removing an electron from an ion with a lower charge. Thus, successive ionization energies for one element always increase. As seen in Table 3.2.2, there is a large increase in the ionization energies (color change) for each element. This jump corresponds to removal of the core electrons, which are harder to remove than the valence electrons. For example, Sc and Ga both have three valence electrons, so the rapid increase in ionization energy occurs after the third ionization.

Table 3.2.2: Successive Ionization Energies for Selected Elements (kJ/mol)

Element	IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7
K	418.8	3051.8	4419.6	5876.9	7975.5	9590.6	11343
Ca	589.8	1145.4	4912.4	6490.6	8153.0	10495.7	12272.9
Sc	633.1	1235.0	2388.7	7090.6	8842.9	10679.0	13315.0
Ga	578.8	1979.4	2964.6	6180	8298.7	10873.9	13594.8
Ge	762.2	1537.5	3302.1	4410.6	9021.4	Not available	Not available
As	944.5	1793.6	2735.5	4836.8	6042.9	12311.5	Not available

Example 3.2.2: Ranking Ionization Energies

Predict the order of increasing energy for the following processes: IE_1 for Al, IE_1 for Tl, IE_2 for Na, IE_3 for Al.

Solution

Removing the $6p^1$ electron from Tl is easier than removing the $3p^1$ electron from Al because the higher n orbital is farther from the nucleus, so $IE_1(Tl) < IE_1(Al)$. Ionizing the third electron from

$$\text{Al} \quad (\text{Al}^{2+} \longrightarrow \text{Al}^{3+} + \text{e}^-)$$

requires more energy because the cation Al^{2+} exerts a stronger pull on the electron than the neutral Al atom, so $IE_1(Al) < IE_3(Al)$. The second ionization energy for sodium removes a core electron, which is a much higher energy process than removing valence electrons. Putting this all together, we obtain:

$$IE_1(Tl) < IE_1(Al) < IE_3(Al) < IE_2(Na).$$

Exercise 3.2.2

Which has the lowest value for IE_1: O, Po, Pb, or Ba?

Answer

Ba

3.2.5: Variation in Electron Affinities

The electron affinity [EA] is the energy change for the process of adding an electron to a gaseous atom to form an anion (negative ion).

$$\text{X}(g) + \text{e}^- \longrightarrow \text{X}^-(g) \quad \text{EA}_1$$

This process can be either endothermic or exothermic, depending on the element. The EA of some of the elements is given in Figure 3.2.9. You can see that many of these elements have negative values of EA, which means that energy is released when the gaseous atom accepts an electron. However, for some elements, energy is required for the atom to become negatively charged and

the value of their EA is positive. Just as with ionization energy, subsequent EA values are associated with forming ions with more charge. The second EA is the energy associated with adding an electron to an anion to form a –2 ion, and so on.

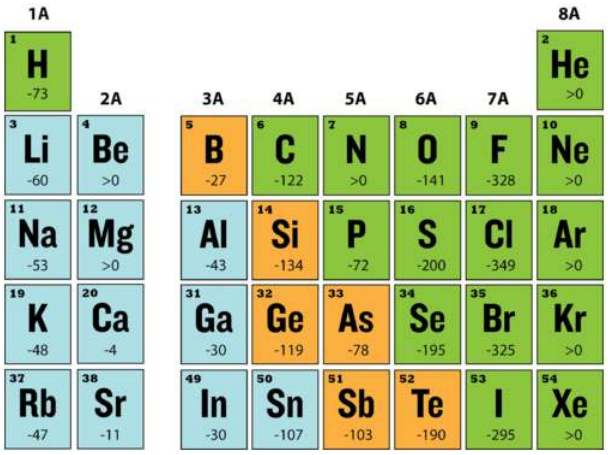


Figure 3.2.9: This version of the periodic table displays the electron affinity values (in kJ/mol) for selected elements.:

As we might predict, it becomes easier to add an electron across a series of atoms as the effective nuclear charge of the atoms increases. We find, as we go from left to right across a period, EAs tend to become more negative. The exceptions found among the elements of group 2 (2A), group 15 (5A), and group 18 (8A) can be understood based on the electronic structure of these groups. The noble gases, group 18 (8A), have a completely filled shell and the incoming electron must be added to a higher *n* level, which is more difficult to do. Group 2 (2A) has a filled *ns* subshell, and so the next electron added goes into the higher energy *np*, so, again, the observed EA value is not as the trend would predict. Finally, group 15 (5A) has a half-filled *np* subshell and the next electron must be paired with an existing *np* electron. In all of these cases, the initial relative stability of the electron configuration disrupts the trend in EA.

We also might expect the atom at the top of each group to have the largest EA; their first ionization potentials suggest that these atoms have the largest effective nuclear charges. However, as we move down a group, we see that the second element in the group most often has the greatest EA. The reduction of the EA of the first member can be attributed to the small size of the $n = 2$ shell and the resulting large electron–electron repulsions. For example, chlorine, with an EA value of –348 kJ/mol, has the highest value of any element in the periodic table. The EA of fluorine is –322 kJ/mol. When we add an electron to a fluorine atom to form a fluoride anion (F^-), we add an electron to the $n = 2$ shell. The electron is attracted to the nucleus, but there is also significant repulsion from the other electrons already present in this small valence shell. The chlorine atom has the same electron configuration in the valence shell, but because the entering electron is going into the $n = 3$ shell, it occupies a considerably larger region of space and the electron–electron repulsions are reduced. The entering electron does not experience as much repulsion and the chlorine atom accepts an additional electron more readily.

The properties discussed in this section (size of atoms and ions, effective nuclear charge, ionization energies, and electron affinities) are central to understanding chemical reactivity. For example, because fluorine has an energetically favorable EA and a large energy barrier to ionization (IE), it is much easier to form fluorine anions than cations. Metallic properties including conductivity and malleability (the ability to be formed into sheets) depend on having electrons that can be removed easily. Thus, metallic character increases as we move down a group and decreases across a period in the same trend observed for atomic size because it is easier to remove an electron that is farther away from the nucleus.

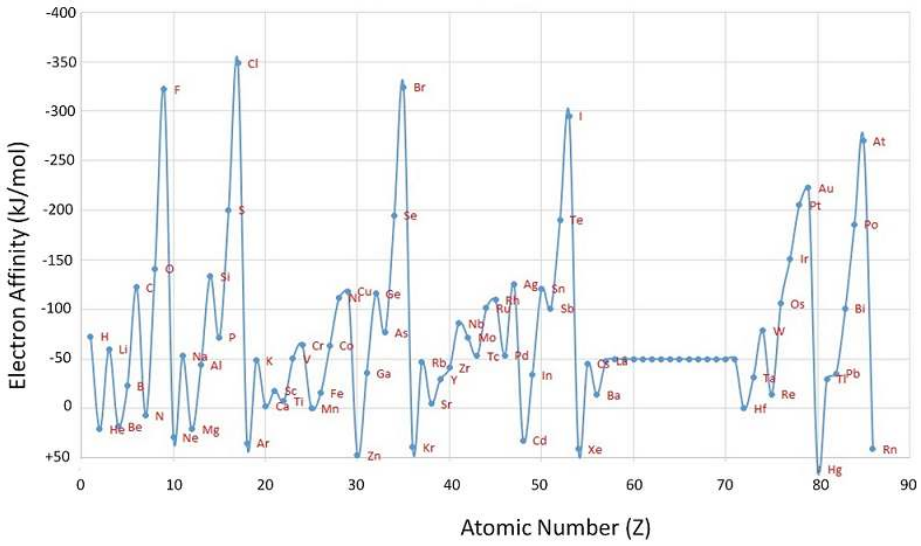


Figure 3.2.10: A Plot of Periodic Variation of Electron Affinity with Atomic Number for the First Six Rows of the Periodic Table. Notice that electron affinities can be both negative and positive. from Robert J. Lancashire (University of the West Indies).

Summary

Electron configurations allow us to understand many periodic trends. Covalent radius increases as we move down a group because the *n* level (orbital size) increases. Covalent radius mostly decreases as we move left to right across a period because the effective nuclear charge experienced by the electrons increases, and the electrons are pulled in tighter to the nucleus. Anionic radii are larger than the parent atom, while cationic radii are smaller, because the number of valence electrons has changed while the nuclear charge has remained constant. Ionization energy (the energy associated with forming a cation) decreases down a group and mostly increases across a period because it is easier to remove an electron from a larger, higher energy orbital. Electron affinity (the energy associated with forming an anion) is more favorable (exothermic) when electrons are placed into lower energy orbitals, closer to the nucleus. Therefore, electron affinity becomes increasingly negative as we move left to right across the periodic table and decreases as we move down a group. For both IE and electron affinity data, there are exceptions to the trends when dealing with completely filled or half-filled subshells.

Glossary

covalent radius

one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond

effective nuclear charge

charge that leads to the Coulomb force exerted by the nucleus on an electron, calculated as the nuclear charge minus shielding

electron affinity

energy required to add an electron to a gaseous atom to form an anion

ionization energy

energy required to remove an electron from a gaseous atom or ion. The associated number (e.g., second ionization energy) corresponds to the charge of the ion produced (X^{2+})

isoelectronic

group of ions or atoms that have identical electron configurations

This page titled 3.2: Periodic Variations in Element Properties is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **6.5: Periodic Variations in Element Properties** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

3.E: Periodic Properties (Exercises)

3.E.1: Periodic Variations in Element Properties

Exercise 3.E.1

Based on their positions in the periodic table, predict which has the smallest atomic radius: Mg, Sr, Si, Cl, I.

Answer

Cl

Exercise 3.E.2

Based on their positions in the periodic table, predict which has the largest atomic radius: Li, Rb, N, F, I.

Answer

Rb

Exercise 3.E.3

Based on their positions in the periodic table, predict which has the largest first ionization energy: Mg, Ba, B, O, Te.

Answer

O

Exercise 3.E.4

Based on their positions in the periodic table, predict which has the smallest first ionization energy: Li, Cs, N, F, I.

Answer

Cs

Exercise 3.E.5

Based on their positions in the periodic table, rank the following atoms in order of increasing first ionization energy: F, Li, N, Rb

Answer

Rb < Li < N < F

Exercise 3.E.6

Based on their positions in the periodic table, rank the following atoms or compounds in order of increasing first ionization energy: Mg, O, S, Si

Answer

Mg < Si < S < O

Exercise 3.E.7

Atoms of which group in the periodic table have a valence shell electron configuration of ns^2np^3?

Answer

15 (5A)

Exercise 3.E.8

Atoms of which group in the periodic table have a valence shell electron configuration of ns^2?

Answer

2

Exercise 3.E.9

Based on their positions in the periodic table, list the following atoms in order of increasing radius: Mg, Ca, Rb, Cs.

Answer

Mg < Ca < Rb < Cs

Exercise 3.E.10

Based on their positions in the periodic table, list the following atoms in order of increasing radius: Sr, Ca, Si, Cl.

Answer

Cl < Si < Ca < Sr

Exercise 3.E.11

Based on their positions in the periodic table, list the following ions in order of increasing radius: K^+, Ca^{2+}, Al^{3+}, Si^{4+}.

Answer

$Si^{4+} < Al^{3+} < Ca^{2+} < K^+$

Exercise 3.E.12

List the following ions in order of increasing radius: Br^-, Li^+, Te^{2-}, Mg^{2+}.

Answer

$Li^+ < Mg^{2+} < Br^- < Te^{2-}$

Exercise 3.E.13

Which atom and/or ion is (are) isoelectronic with Br^+: Se^{2+}, Se, As^-, Kr, Ga^{3+}, Cl^-?

Answer

Se, As^-

Exercise 3.E.14

Which of the following atoms and ions is (are) isoelectronic with S^{2+}: Si^{4+}, Cl^{3+}, Ar, As^{3+}, Si, Al^{3+}?

Answer

Si, Cl^{3+}

Exercise 3.E.15

Compare both the numbers of protons and electrons present in each to rank the following ions in order of increasing radius: As^{3-}, Br^{-}, K^{+}, Mg^{2+}.

Answer

$Mg^{2+} < K^{+} < Br^{-} < As^{3-}$

Exercise 3.E.16

Of the five elements Al, Cl, I, Na, Rb, which has the most exothermic reaction? (E represents an atom.) What name is given to the energy for the reaction? *Hint: note the process depicted does not correspond to electron affinity*

$E^{+}(g) + e^{-} \longrightarrow E(g)$

Answer

Add texts here. Do not delete this text first.

Exercise 3.E.17

Of the five elements Sn, Si, Sb, O, Te, which has the most endothermic reaction? (E represents an atom.) What name is given to the energy for the reaction?

$$E(g) \longrightarrow E^{+}(g) + e^{-} \tag{3.E.1}$$

Answer

O, IE_1

Exercise 3.E.18

The ionic radii of the ions S^{2-}, Cl^{-}, and K^{+} are 184, 181, 138 pm respectively. Explain why these ions have different sizes even though they contain the same number of electrons.

Answer

Add texts here. Do not delete this text first.

Exercise 3.E.19

Which main group atom would be expected to have the lowest second ionization energy?

Answer

Ra

Exercise 3.E. 20

Explain why Al is a member of group 13 rather than group 3?

Answer

Add texts here. Do not delete this text first.? Exercise \(\PageIndex{1

This page titled 3.E: Periodic Properties (Exercises) is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

3.S: Study Guide

3: Periodic Relationships Among the Elements

Key Topics for TRU students taking CHEM1500

- Periodic Table
- periodic classification of the elements
- periodic variation in physical properties
- ionization energy
- electron affinity
- variations in properties of representative elements

Key Learning Outcomes (Examples)

- predict, rank and explain the periodic properties of the elements as related to electronic configuration

3.S: Study Guide is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

4: Chemical Bonding I- Basic Concepts

Topic hierarchy

4.1: Ionic Bonding
4.2: Lattice Enthalpies and Born Haber Cycles
4.3: Covalent Bonding
4.4: Lewis Symbols and Structures
4.5: Formal Charges and Resonance
4.6: Strengths of Ionic and Covalent Bonds
4.E: Chemical Bonding and Molecular Geometry (Exercises)
4.S: Study Guide

4: Chemical Bonding I- Basic Concepts is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

4.1: Ionic Bonding

Learning Objectives

- Explain the formation of cations, anions, and ionic compounds
- Predict the charge of common metallic and nonmetallic elements, and write their electron configurations

As you have learned, ions are atoms or molecules bearing an electrical charge. A cation (a positive ion) forms when a neutral atom loses one or more electrons from its valence shell, and an anion (a negative ion) forms when a neutral atom gains one or more electrons in its valence shell.

Compounds composed of ions are called ionic compounds (or salts), and their constituent ions are held together by ionic bonds: electrostatic forces of attraction between oppositely charged cations and anions. The properties of ionic compounds shed some light on the nature of ionic bonds. Ionic solids exhibit a crystalline structure and tend to be rigid and brittle; they also tend to have high melting and boiling points, which suggests that ionic bonds are very strong. Ionic solids are also poor conductors of electricity for the same reason—the strength of ionic bonds prevents ions from moving freely in the solid state. Most ionic solids, however, dissolve readily in water. Once dissolved or melted, ionic compounds are excellent conductors of electricity and heat because the ions can move about freely.

Neutral atoms and their associated ions have very different physical and chemical properties. Sodium *atoms* form sodium metal, a soft, silvery-white metal that burns vigorously in air and reacts explosively with water. Chlorine *atoms* form chlorine gas, Cl_2, a yellow-green gas that is extremely corrosive to most metals and very poisonous to animals and plants. The vigorous reaction between the elements sodium and chlorine forms the white, crystalline compound sodium chloride, common table salt, which contains sodium *cations* and chloride *anions* (Figure Figure 4.1.1). The compound composed of these ions exhibits properties entirely different from the properties of the elements sodium and chlorine. Chlorine is poisonous, but sodium chloride is essential to life; sodium atoms react vigorously with water, but sodium chloride simply dissolves in water.



Figure 4.1.1: (a) Sodium is a soft metal that must be stored in mineral oil to prevent reaction with air or water. (b) Chlorine is a pale yellow-green gas. (c) When combined, they form white crystals of sodium chloride (table salt). (credit a: modification of work by “Jurii”/Wikimedia Commons)

4.1.1: The Formation of Ionic Compounds

Binary ionic compounds are composed of just two elements: a metal (which forms the cations) and a nonmetal (which forms the anions). For example, NaCl is a binary ionic compound. We can think about the formation of such compounds in terms of the periodic properties of the elements. Many metallic elements have relatively low ionization potentials and lose electrons easily. These elements lie to the left in a period or near the bottom of a group on the periodic table. Nonmetal atoms have relatively high electron affinities and thus readily gain electrons lost by metal atoms, thereby filling their valence shells. Nonmetallic elements are found in the upper-right corner of the periodic table.

As all substances must be electrically neutral, the total number of positive charges on the cations of an ionic compound must equal the total number of negative charges on its anions. The formula of an ionic compound represents the simplest ratio of the numbers of ions necessary to give identical numbers of positive and negative charges. For example, the formula for aluminum oxide, Al_2O_3, indicates that this ionic compound contains two aluminum cations, Al^{3+}, for every three oxide anions, O^{2-} [thus, $(2 \times +3) + (3 \times -2) = 0$].

It is important to note, however, that the formula for an ionic compound does *not* represent the physical arrangement of its ions. It is incorrect to refer to a sodium chloride (NaCl) “molecule” because there is not a single ionic bond, per se, between any specific pair of sodium and chloride ions. The attractive forces between ions are isotropic—the same in all directions—meaning that any

particular ion is equally attracted to all of the nearby ions of opposite charge. This results in the ions arranging themselves into a tightly bound, three-dimensional lattice structure. Sodium chloride, for example, consists of a regular arrangement of equal numbers of Na^+ cations and Cl^- anions (Figure Figure 4.1.2).



Figure 4.1.2: The atoms in sodium chloride (common table salt) are arranged to (a) maximize opposite charges interacting. The smaller spheres represent sodium ions, the larger ones represent chloride ions. In the expanded view (b), the geometry can be seen more clearly. Note that each ion is "bonded" to all of the surrounding ions—six in this case.

Two diagrams are shown and labeled "a" and "b." Diagram a shows a cube made up of twenty-seven alternating purple and green spheres. The purple spheres are smaller than the green spheres. Diagram b shows the same spheres, but this time, they are spread out and connected in three dimensions by white rods. The purple spheres are labeled "N superscript postive sign" while the green are labeled "C l superscript negative sign."

The strong electrostatic attraction between Na^+ and Cl^- ions holds them tightly together in solid NaCl. It requires 769 kJ of energy to dissociate one mole of solid NaCl into separate gaseous Na^+ and Cl^- ions:

$$\mathrm{NaCl}(s) \longrightarrow \mathrm{Na}^+(g) + \mathrm{Cl}^-(g) \quad \Delta H = 769\ \mathrm{kJ}$$

4.1.2: Electronic Structures of Cations

When forming a cation, an atom of a main group element tends to lose all of its valence electrons, thus assuming the electronic structure of the noble gas that precedes it in the periodic table. For groups 1 (the alkali metals) and 2 (the alkaline earth metals), the group numbers are equal to the numbers of valence shell electrons and, consequently, to the charges of the cations formed from atoms of these elements when all valence shell electrons are removed. For example, calcium is a group 2 element whose neutral atoms have 20 electrons and a ground state electron configuration of $1s^22s^22p^63s^23p^64s^2$. When a Ca atom loses both of its valence electrons, the result is a cation with 18 electrons, a 2+ charge, and an electron configuration of $1s^22s^22p^63s^23p^6$. The Ca^{2+} ion is therefore isoelectronic with the noble gas Ar.

For groups 12–17, the group numbers exceed the number of valence electrons by 10 (accounting for the possibility of full *d* subshells in atoms of elements in the fourth and greater periods). Thus, the charge of a cation formed by the loss of all valence electrons is equal to the group number minus 10. For example, aluminum (in group 13) forms 3+ ions (Al^{3+}).

Exceptions to the expected behavior involve elements toward the bottom of the groups. In addition to the expected ions Tl^{3+}, Sn^{4+}, Pb^{4+}, and Bi^{5+}, a partial loss of these atoms' valence shell electrons can also lead to the formation of Tl^+, Sn^{2+}, Pb^{2+}, and Bi^{3+} ions. The formation of these 1+, 2+, and 3+ cations is ascribed to the inert pair effect, which reflects the relatively low energy of the valence *s*-electron pair for atoms of the heavy elements of groups 13, 14, and 15. Mercury (group 12) also exhibits an unexpected behavior: it forms a diatomic ion, Hg_2^{2+} (an ion formed from two mercury atoms, with an Hg-Hg bond), in addition to the expected monatomic ion Hg^{2+} (formed from only one mercury atom).

Transition and inner transition metal elements behave differently than main group elements. Most transition metal cations have 2+ or 3+ charges that result from the loss of their outermost *s* electron(s) first, sometimes followed by the loss of one or two *d* electrons from the next-to-outermost shell. For example, iron ($1s^22s^22p^63s^23p^63d^64s^2$) forms the ion Fe^{2+} ($1s^22s^22p^63s^23p^63d^6$) by the loss of the 4*s* electrons and the ion Fe^{3+} ($1s^22s^22p^63s^23p^63d^5$) by the loss of the 4*s* electrons and one of the 3*d* electrons. Although the *d* orbitals of the transition elements are—according to the Aufbau principle—the last to fill when building up electron configurations, the outermost *s* electrons are the first to be lost when these atoms ionize. When the inner transition metals form ions, they usually have a 3+ charge, resulting from the loss of their outermost *s* electrons and a *d* or *f* electron.

Example 4.1.1: Determining the Electronic Structures of Cations

There are at least 14 elements categorized as "essential trace elements" for the human body. They are called "essential" because they are required for healthy bodily functions, "trace" because they are required only in small amounts, and "elements" in spite of the fact that they are really ions. Two of these essential trace elements, chromium and zinc, are required as Cr^{3+} and Zn^{2+}. Write the electron configurations of these cations.

Solution

First, write the electron configuration for the neutral atoms:

- Zn: $[Ar]3d^{10}4s^2$
- Cr: $[Ar]3d^54s^1$

Next, remove electrons from the highest energy orbital. For the transition metals, electrons are removed from the *s* orbital first and then from the *d* orbital. For the *p*-block elements, electrons are removed from the *p* orbitals and then from the *s* orbital. Zinc is a member of group 12, so it should have a charge of 2+, and thus loses only the two electrons in its *s* orbital. Chromium is a transition element and should lose its *s* electrons and then its *d* electrons when forming a cation. Thus, we find the following electron configurations of the ions:

- Zn^{2+}: [Ar]$3d^{10}$
- Cr^{3+}: [Ar]$3d^3$

? Exercise 4.1.1

Potassium and magnesium are required in our diet. Write the electron configurations of the ions expected from these elements.

Answer

K^+: [Ar], Mg^{2+}: [Ne]

4.1.3: Electronic Structures of Anions

Most monatomic anions form when a neutral nonmetal atom gains enough electrons to completely fill its outer *s* and *p* orbitals, thereby reaching the electron configuration of the next noble gas. Thus, it is simple to determine the charge on such a negative ion: The charge is equal to the number of electrons that must be gained to fill the *s* and *p* orbitals of the parent atom. Oxygen, for example, has the electron configuration $1s^2 2s^2 2p^4$, whereas the oxygen anion has the electron configuration of the noble gas neon (Ne), $1s^2 2s^2 2p^6$. The two additional electrons required to fill the valence orbitals give the oxide ion the charge of 2– (O^{2-}).

✓ Example 4.1.2: Determining the Electronic Structure of Anions

Selenium and iodine are two essential trace elements that form anions. Write the electron configurations of the anions.

Solution

Se^{2-}: [Ar]$3d^{10}4s^2 4p^6$

I^-: [Kr]$4d^{10}5s^2 5p^6$

? Exercise 4.1.2

Write the electron configurations of a phosphorus atom and its negative ion. Give the charge on the anion.

Answer

P: [Ne]$3s^2 3p^3$

P^{3-}: [Ne]$3s^2 3p^6$

Summary

Atoms gain or lose electrons to form ions with particularly stable electron configurations. The charges of cations formed by the representative metals may be determined readily because, with few exceptions, the electronic structures of these ions have either a noble gas configuration or a completely filled electron shell. The charges of anions formed by the nonmetals may also be readily determined because these ions form when nonmetal atoms gain enough electrons to fill their valence shells.

Glossary

inert pair effect

tendency of heavy atoms to form ions in which their valence *s* electrons are not lost

ionic bond

strong electrostatic force of attraction between cations and anions in an ionic compound

---

This page titled 4.1: Ionic Bonding is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **7.2: Ionic Bonding** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

4.2: Lattice Enthalpies and Born Haber Cycles

Lattice enthalpy is a measure of the strength of the forces between the ions in an ionic solid. The greater the **lattice enthalpy**, the stronger the forces. This page introduces lattice enthalpies (lattice energies) and Born-Haber cycles.

Defining Lattice Enthalpy

There are two different ways of defining lattice enthalpy which directly contradict each other, and you will find both in common use. In fact, there is a simple way of sorting this out, but many sources do not use it. Lattice enthalpy is a measure of the strength of the forces between the ions in an ionic solid. The greater the lattice enthalpy, the stronger the forces. Those forces are only completely broken when the ions are present as gaseous ions, scattered so far apart that there is negligible attraction between them. You can show this on a simple enthalpy diagram.

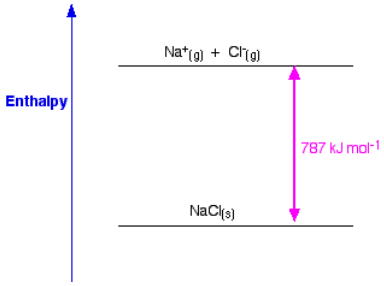


Figure 4.2.1: For sodium chloride, the solid is more stable than the gaseous ions by 787 kJ mol^{-1}, and that is a measure of the strength of the attractions between the ions in the solid. Remember that energy (in this case heat energy) is released when bonds are made, and is required to break bonds.

So lattice enthalpy could be described in either of two ways.

- It could be described as the enthalpy change when 1 mole of sodium chloride (or whatever) was formed from its scattered gaseous ions. In other words, you are looking at a downward arrow on the diagram.
- Or, it could be described as the enthalpy change when 1 mole of sodium chloride (or whatever) is broken up to form its scattered gaseous ions. In other words, you are looking at an upward arrow on the diagram.

Both refer to the same enthalpy diagram, but one looks at it from the point of view of making the lattice, and the other from the point of view of breaking it up. Unfortunately, both of these are often described as "lattice enthalpy".

Definitions

- The *lattice dissociation enthalpy* is the enthalpy change needed to convert 1 mole of solid crystal into its scattered gaseous ions. Lattice dissociation enthalpies are **always positive**.
- The *lattice formation enthalpy* is the enthalpy change when 1 mole of solid crystal is formed from its separated gaseous ions. Lattice formation enthalpies are **always negative**.

This is an absurdly confusing situation which is easily resolved by never using the term "lattice enthalpy" without qualifying it.

- You should talk about "lattice dissociation enthalpy" if you want to talk about the amount of energy needed to split up a lattice into its scattered gaseous ions. For NaCl, the lattice dissociation enthalpy is +787 kJ mol^{-1}.
- You should talk about "lattice formation enthalpy" if you want to talk about the amount of energy released when a lattice is formed from its scattered gaseous ions. For NaCl, the lattice formation enthalpy is -787 kJ mol^{-1}.

That immediately removes any possibility of confusion.

Factors affecting Lattice Enthalpy

The two main factors affecting lattice enthalpy are

- The charges on the ions and
- The ionic radii (which affects the distance between the ions).

The charges on the ions

Sodium chloride and magnesium oxide have exactly the same arrangements of ions in the crystal lattice, but the lattice enthalpies are very different.

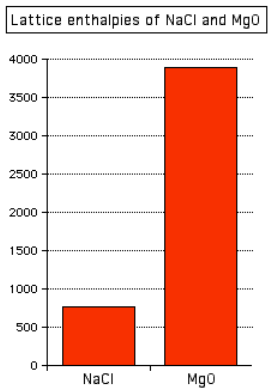


Figure 4.2.2

You can see in Figure 4.2.2 that the lattice enthalpy of magnesium oxide is much greater than that of sodium chloride. That's because in magnesium oxide, 2+ ions are attracting 2- ions; in sodium chloride, the attraction is only between 1+ and 1- ions.

The Radius of the Ions

The lattice enthalpy of magnesium oxide is also increased relative to sodium chloride because magnesium ions are smaller than sodium ions, and oxide ions are smaller than chloride ions. That means that the ions are closer together in the lattice, and that increases the strength of the attractions.

This effect of ion size on lattice enthalpy is clearly observed as you go down a Group in the Periodic Table. For example, as you go down Group 7 of the Periodic Table from fluorine to iodine, you would expect the lattice enthalpies of their sodium salts to fall as the negative ions get bigger - and that is the case:

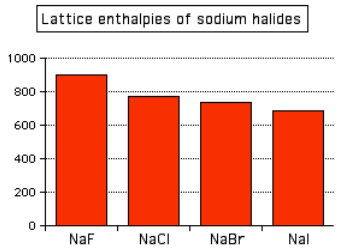


Figure 4.2.3

Attractions are governed by the distances between the centers of the oppositely charged ions, and that distance is obviously greater as the negative ion gets bigger. And you can see exactly the same effect if as you go down Group 1. The next bar chart, Figure 4.2.4 shows the lattice enthalpies of the Group 1 chlorides.

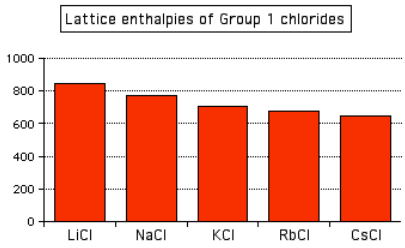


Figure 4.2.4

Calculating Lattice Enthalpy

It is impossible to measure the enthalpy change starting from a solid crystal and converting it into its scattered gaseous ions. It is even more difficult to imagine how you could do the reverse - start with scattered gaseous ions and measure the enthalpy change when these convert to a solid crystal. Instead, lattice enthalpies always have to be calculated, and there are two entirely different ways in which this can be done.

1. You can can use a Hess's Law cycle (in this case called a Born-Haber cycle) involving enthalpy changes which can be measured. Lattice enthalpies calculated in this way are described as experimental values.
2. Or you can do physics-style calculations working out how much energy would be released, for example, when ions considered as point charges come together to make a lattice. These are described as theoretical values. In fact, in this case, what you are actually calculating are properly described as lattice energies.

Born-Haber Cycles

Standard Atomization Enthalpies

Before we start talking about Born-Haber cycles, we need to define the **atomization enthalpy**, ΔH_a^o. The standard atomization enthalpy is the enthalpy change when 1 mole of gaseous atoms is formed from the element in its standard state. Enthalpy change of atomization is always positive. You are always going to have to supply energy to break an element into its separate gaseous atoms. All of the following equations represent changes involving atomization enthalpy:

$$\frac{1}{2}Cl_2(g) \rightarrow Cl(g) \quad \Delta H_a^o = +122\,kJ\,mol^{-1} \tag{4.2.1}$$

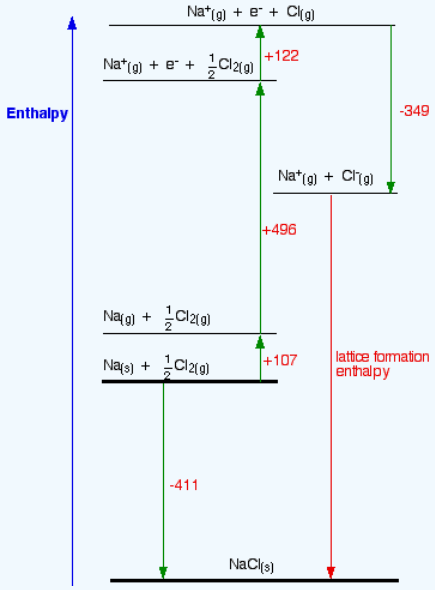
$$\frac{1}{2}Br_2(l) \rightarrow Br(g) \quad \Delta H_a^o = +122\,kJ\,mol^{-1} \tag{4.2.2}$$

$$Na(s) \rightarrow Na(g) \quad \Delta H_a^o = +107\,kJ\,mol^{-1} \tag{4.2.3}$$

Notice particularly that the "mol^{-1}" is per mole of atoms **formed** - NOT per mole of element that you start with. You will quite commonly have to write fractions into the left-hand side of the equation. Getting this wrong is a common mistake.

Example 4.2.1: Born-Haber Cycle for $NaCl$

Consider a Born-Haber cycle for sodium chloride, and then talk it through carefully afterwards. You will see that I have arbitrarily decided to draw this for lattice formation enthalpy. If you wanted to draw it for lattice dissociation enthalpy, the red arrow would be reversed - pointing upwards.



Focus to start with on the higher of the two thicker horizontal lines. We are starting here with the elements sodium and chlorine in their standard states. Notice that we only need half a mole of chlorine gas in order to end up with 1 mole of NaCl. The arrow

pointing down from this to the lower thick line represents the enthalpy change of formation of sodium chloride.

The Born-Haber cycle now imagines this formation of sodium chloride as happening in a whole set of small changes, most of which we know the enthalpy changes for - except, of course, for the lattice enthalpy that we want to calculate.

- The +107 is the atomization enthalpy of sodium. We have to produce gaseous atoms so that we can use the next stage in the cycle.
- The +496 is the first ionization energy of sodium. Remember that first ionization energies go from gaseous atoms to gaseous singly charged positive ions.
- The +122 is the atomization enthalpy of chlorine. Again, we have to produce gaseous atoms so that we can use the next stage in the cycle.
- The -349 is the first electron affinity of chlorine. Remember that first electron affinities go from gaseous atoms to gaseous singly charged negative ions.
- And finally, we have the positive and negative gaseous ions that we can convert into the solid sodium chloride using the lattice formation enthalpy.

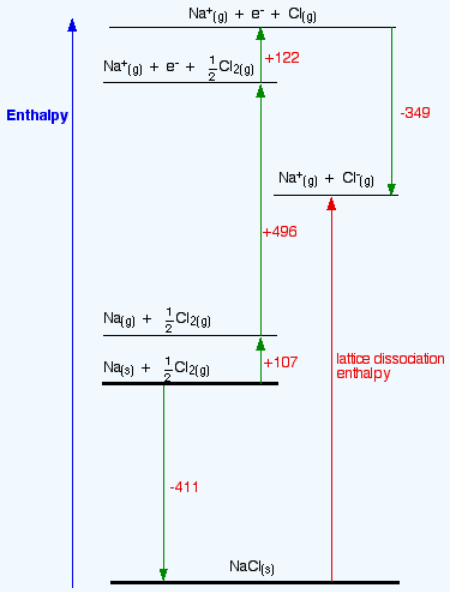
Now we can use Hess' Law and find two different routes around the diagram which we can equate. As drawn, the two routes are obvious. The diagram is set up to provide two different routes between the thick lines. So, from the cycle we get the calculations directly underneath it . . .

$$-411 = +107 + 496 + 122 - 349 + LE$$

$$LE = -411 - 107 - 496 - 122 + 349$$

$$LE = -787 \text{ kJ mol}^{-1}$$

How would this be different if you had drawn a lattice dissociation enthalpy in your diagram? Your diagram would now look like this:



The only difference in the diagram is the direction the lattice enthalpy arrow is pointing. It does, of course, mean that you have to find two new routes. You cannot use the original one, because that would go against the flow of the lattice enthalpy arrow. This time both routes would start from the elements in their standard states, and finish at the gaseous ions.

$$-411 + LE = +107 + 496 + 122 - 349$$

$$LE = +107 + 496 + 122 - 349 + 411$$

$$LE = +787 \text{ kJ mol}^{-1}$$

Once again, the cycle sorts out the sign of the lattice enthalpy.

Theoretical Estimates of Lattice Energies

Let's assume that a compound is fully ionic. Let's also assume that the ions are point charges - in other words that the charge is concentrated at the center of the ion. By doing physics-style calculations, it is possible to calculate a theoretical value for what you would expect the lattice energy to be. Calculations of this sort end up with values of *lattice energy*, and not *lattice enthalpy*. If you know how to do it, you can then fairly easily convert between the two.

There are several different equations, of various degrees of complication, for calculating lattice energy in this way. There are two possibilities:

- There is reasonable agreement between the experimental value (calculated from a Born-Haber cycle) and the theoretical value. Sodium chloride is a case like this - the theoretical and experimental values agree to within a few percent. That means that for sodium chloride, the assumptions about the solid being ionic are fairly good.
- The experimental and theoretical values do not agree. A commonly quoted example of this is silver chloride, AgCl. Depending on where you get your data from, the theoretical value for lattice enthalpy for AgCl is anywhere from about 50 to 150 kJ mol^{-1} less than the value that comes from a Born-Haber cycle. In other words, treating the AgCl as 100% ionic underestimates its lattice enthalpy by quite a lot.

The explanation is that silver chloride actually has a significant amount of covalent bonding between the silver and the chlorine, because there is not enough electronegativity difference between the two to allow for complete transfer of an electron from the silver to the chlorine. Comparing experimental (Born-Haber cycle) and theoretical values for lattice enthalpy is a good way of judging how purely ionic a crystal is.

Example 4.2.2: Born-Haber Cycle for $MgCl_2$

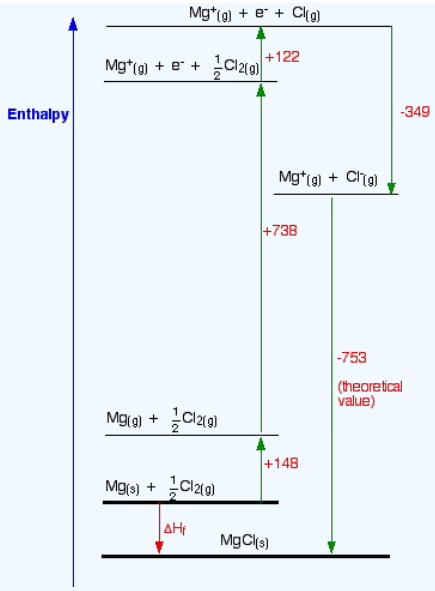
The question arises as to why, from an energetics point of view, magnesium chloride is $MgCl_2$ rather than MgCl or $MgCl_3$ (or any other formula you might like to choose). It turns out that $MgCl_2$ is the formula of the compound which has the most negative enthalpy change of formation - in other words, it is the most stable one relative to the elements magnesium and chlorine.

Let's look at this in terms of Born-Haber cycles of and contrast the enthalpy change of formation for the imaginary compounds MgCl and $MgCl_3$. That means that we will have to use theoretical values of their lattice enthalpies. We ca not use experimental ones, because these compounds obviously do not exist! I'm taking theoretical values for lattice enthalpies for these compounds that I found on the web. I can't confirm these, but all the other values used by that source were accurate. The exact values do not matter too much anyway, because the results are so dramatically clear-cut.

1. The Born-Haber cycle for MgCl

We will start with the compound MgCl, because that cycle is just like the NaCl one we have already looked at.

$$\mathrm{Mg(s)} + \tfrac{1}{2}\mathrm{Cl_2(g)} \rightarrow \mathrm{MgCl(s)} \tag{4.2.4}$$



Find two routes around this without going against the flow of any arrows. That's easy:

$$\Delta H_f = +148 + 738 + 122 - 349 - 753$$

$$\Delta H_f = -94 \text{ kJ mol}^{-1}$$

So the compound MgCl is definitely energetically **more stable** than its elements. I have drawn this cycle very roughly to scale, but that is going to become more and more difficult as we look at the other two possible formulae. So I am going to rewrite it as a table. You can see from the diagram that the enthalpy change of formation can be found just by adding up all the other numbers in the cycle, and we can do this just as well in a table.

	kJ
atomization enthalpy of Mg	+148
1st IE of Mg	+738
atomization enthalpy of Cl	+122
electron affinity of Cl	-349
lattice enthalpy	-753
calculated ΔH_f	-94

2. The Born-Haber cycle for $MgCl_2$

The equation for the enthalpy change of formation this time is

$$\mathrm{Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)} \tag{4.2.5}$$

So how does that change the numbers in the Born-Haber cycle?

- You need to add in the second ionization energy of magnesium, because you are making a 2+ ion.
- You need to multiply the atomization enthalpy of chlorine by 2, because you need 2 moles of gaseous chlorine atoms.
- You need to multiply the electron affinity of chlorine by 2, because you are making 2 moles of chloride ions.
- You obviously need a different value for lattice enthalpy.

	kJ
atomization enthalpy of Mg	+148

	kJ
1st IE of Mg	+738
2nd IE of Mg	+1451
atomization enthalpy of Cl (x 2)	+244
electron affinity of Cl (x 2)	-698
lattice enthalpy	-2526
calculated ΔH_f	-643

You can see that much more energy is released when you make $MgCl_2$ than when you make MgCl. Why is that? You need to put in more energy to ionize the magnesium to give a 2+ ion, but a lot more energy is released as lattice enthalpy. That is because there are stronger ionic attractions between 1- ions and 2+ ions than between the 1- and 1+ ions in MgCl. So what about $MgCl_3$? The lattice energy here would be even greater.

3. The Born-Haber cycle for $MgCl_3$

The equation for the enthalpy change of formation this time is

$$\mathrm{Mg(s)} + \tfrac{3}{2}\mathrm{Cl_2(g)} \rightarrow \mathrm{MgCl_3(s)} \tag{4.2.6}$$

So how does that change the numbers in the Born-Haber cycle this time?

- You need to add in the third ionization energy of magnesium, because you are making a 3+ ion.
- You need to multiply the atomization enthalpy of chlorine by 3, because you need 3 moles of gaseous chlorine atoms.
- You need to multiply the electron affinity of chlorine by 3, because you are making 3 moles of chloride ions.
- You again need a different value for lattice enthalpy.

	kJ
atomization enthalpy of Mg	+148
1st IE of Mg	+738
2nd IE of Mg	+1451
3rd IE of Mg	+7733
atomization enthalpy of Cl (x 3)	+366
electron affinity of Cl (x 3)	-1047
lattice enthalpy	-5440
calculated ΔH_f	+3949

This time, the compound is hugely energetically unstable, both with respect to its elements, and also to other compounds that could be formed. You would need to supply nearly 4000 kJ to get 1 mole of $MgCl_3$ to form!

Look carefully at the reason for this. The lattice enthalpy is the **highest** for all these possible compounds, but it is not high enough to make up for the very large third ionization energy of magnesium.

Why is the third ionization energy so big? The first two electrons to be removed from magnesium come from the 3s level. The third one comes from the 2p. That is closer to the nucleus, and lacks a layer of screening as well - and so much more energy is needed to remove it. The 3s electrons are screened from the nucleus by the 1 level and 2 level electrons. The 2p electrons are only screened by the 1 level (plus a bit of help from the 2s electrons).

Conclusion

> Magnesium chloride is $MgCl_2$ because this is the combination of magnesium and chlorine which produces the most energetically stable compound - the one with the most negative enthalpy change of formation.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

This page titled 4.2: Lattice Enthalpies and Born Haber Cycles is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jim Clark.

4.3: Covalent Bonding

Learning Objectives

- Describe the formation of covalent bonds
- Define electronegativity and assess the polarity of covalent bonds

In ionic compounds, electrons are transferred between atoms of different elements to form ions. But this is not the only way that compounds can be formed. Atoms can also make chemical bonds by sharing electrons between each other. Such bonds are called covalent bonds. Covalent bonds are formed between two atoms when both have similar tendencies to attract electrons to themselves (i.e., when both atoms have identical or fairly similar ionization energies and electron affinities). For example, two hydrogen atoms bond covalently to form an H_2 molecule; each hydrogen atom in the H_2 molecule has two electrons stabilizing it, giving each atom the same number of valence electrons as the noble gas He.

Compounds that contain covalent bonds 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. 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.

4.3.1: Formation of Covalent Bonds

Nonmetal atoms frequently form covalent bonds with other nonmetal atoms. For example, the hydrogen molecule, H_2, contains a covalent bond between its two hydrogen atoms. Figure $4.3.1$ illustrates why this bond is formed. Starting on the far right, we have two separate hydrogen atoms with a particular potential energy, indicated by the red line. Along the *x*-axis is the distance between the two atoms. As the two atoms approach each other (moving left along the *x*-axis), their valence orbitals (1*s*) begin to overlap. The single electrons on each hydrogen atom then interact with both atomic nuclei, occupying the space around both atoms. The strong attraction of each shared electron to both nuclei stabilizes the system, and the potential energy decreases as the bond distance decreases. If the atoms continue to approach each other, the positive charges in the two nuclei begin to repel each other, and the potential energy increases. The bond length is determined by the distance at which the lowest potential energy is achieved.

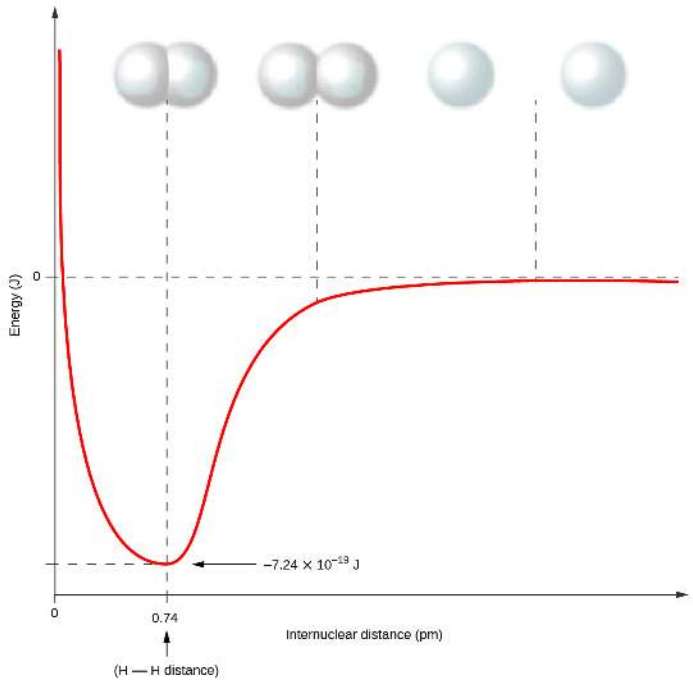


Figure 4.3.1: *The potential energy of two separate hydrogen atoms (right) decreases as they approach each other, and the single electrons on each atom are shared to form a covalent bond. The bond length is the internuclear distance at which the lowest potential energy is achieved.*

It is essential to remember that energy must be added to break chemical bonds (an endothermic process), whereas forming chemical bonds releases energy (an exothermic process). In the case of H_2, the covalent bond is very strong; a large amount of energy, 436 kJ, must be added to break the bonds in one mole of hydrogen molecules and cause the atoms to separate:

$$\mathrm{H_2}(g) \longrightarrow 2\,\mathrm{H}(g) \quad \Delta H = 436\ \mathrm{kJ}$$

Conversely, the same amount of energy is released when one mole of H_2 molecules forms from two moles of H atoms:

$$2\,\mathrm{H}(g) \longrightarrow \mathrm{H_2}(g) \quad \Delta H = -436\ \mathrm{kJ}$$

4.3.2: Pure vs. Polar Covalent Bonds

If the atoms that form a covalent bond are identical, as in H_2, Cl_2, and other diatomic molecules, then the electrons in the bond must be shared equally. We refer to this as a pure covalent bond. Electrons shared in pure covalent bonds have an equal probability of being near each nucleus. In the case of Cl_2, each atom starts off with seven valence electrons, and each Cl shares one electron with the other, forming one covalent bond:

$$\mathrm{Cl} + \mathrm{Cl} \longrightarrow \mathrm{Cl_2}$$

The total number of electrons around each individual atom consists of six nonbonding electrons and two shared (i.e., bonding) electrons for eight total electrons, matching the number of valence electrons in the noble gas argon. Since the bonding atoms are identical, Cl_2 also features a pure covalent bond.

When the atoms linked by a covalent bond are different, the bonding electrons are shared, but no longer equally. Instead, the bonding electrons are more attracted to one atom than the other, giving rise to a shift of electron density toward that atom. This unequal distribution of electrons is known as a polar covalent bond, characterized by a partial positive charge on one atom and a partial negative charge on the other. The atom that attracts the electrons more strongly acquires the partial negative charge and vice versa. For example, the electrons in the H–Cl bond of a hydrogen chloride molecule spend more time near the chlorine atom than near the hydrogen atom. Thus, in an HCl molecule, the chlorine atom carries a partial negative charge and the hydrogen atom has a partial positive charge. Figure 4.3.2 shows the distribution of electrons in the H–Cl bond. Note that the shaded area around Cl is much larger than it is around H. Compare this to Figure 4.3.1, which shows the even distribution of electrons in the H_2 nonpolar bond.

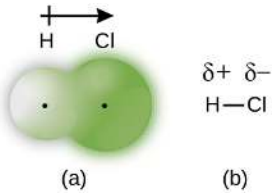


Figure 4.3.2: (a) The distribution of electron density in the HCl molecule is uneven. The electron density is greater around the chlorine nucleus. The small, black dots indicate the location of the hydrogen and chlorine nuclei in the molecule. (b) Symbols δ+ and δ– indicate the polarity of the H–Cl bond.

We sometimes designate the positive and negative atoms in a polar covalent bond using a lowercase Greek letter "delta," δ, with a plus sign or minus sign to indicate whether the atom has a partial positive charge (δ+) or a partial negative charge (δ–). This symbolism is shown for the H–Cl molecule in Figure 4.3.2b.

4.3.3: Electronegativity

Whether a bond is nonpolar or polar covalent is determined by a property of the bonding atoms called electronegativity. Electronegativity is a measure of the tendency of an atom to attract electrons (or electron density) towards itself. It determines how the shared electrons are distributed between the two atoms in a bond. The more strongly an atom attracts the electrons in its bonds, the larger its electronegativity. Electrons in a polar covalent bond are shifted toward the more electronegative atom; thus, the more electronegative atom is the one with the partial negative charge. The greater the difference in electronegativity, the more polarized the electron distribution and the larger the partial charges of the atoms.

Figure 4.3.3 shows the electronegativity values of the elements as proposed by one of the most famous chemists of the twentieth century: Linus Pauling. In general, electronegativity increases from left to right across a period in the periodic table and decreases down a group. Thus, the nonmetals, which lie in the upper right, tend to have the highest electronegativities, with fluorine the most electronegative element of all (EN = 4.0). Metals tend to be less electronegative elements, and the group 1 metals have the lowest electronegativities. Note that noble gases are excluded from this figure because these atoms usually do not share electrons with others atoms since they have a full valence shell. (While noble gas compounds such as XeO_2 do exist, they can only be formed under extreme conditions, and thus they do not fit neatly into the general model of electronegativity.)

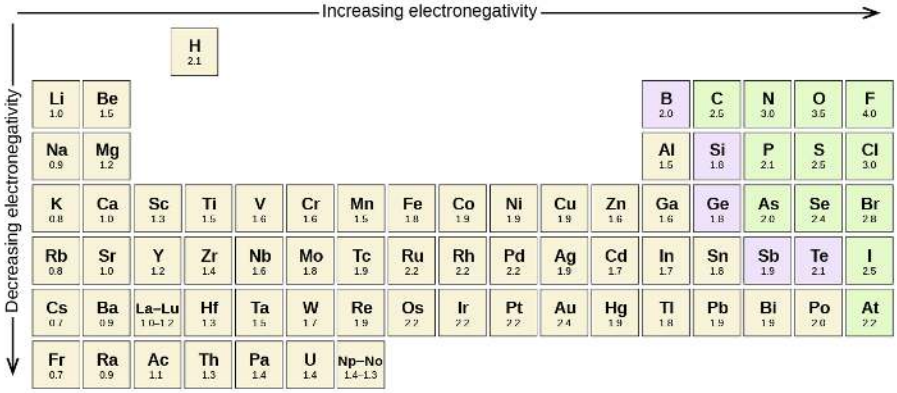


Figure 4.3.3: The electronegativity values derived by Pauling follow predictable periodic trends with the higher electronegativities toward the upper right of the periodic table.

Linus Pauling

Linus Pauling is the only person to have received two unshared (individual) Nobel Prizes: one for chemistry in 1954 for his work on the nature of chemical bonds and one for peace in 1962 for his opposition to weapons of mass destruction. He developed many of the theories and concepts that are foundational to our current understanding of chemistry, including electronegativity and resonance structures.



Linus Pauling (1901–1994) made many important contributions to the field of chemistry. He was also a prominent activist, publicizing issues related to health and nuclear weapons.

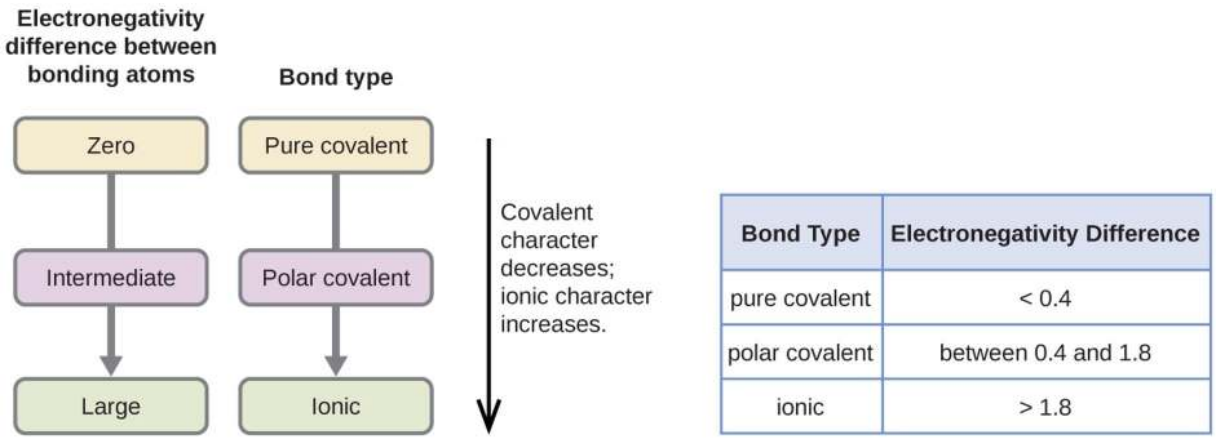
Pauling also contributed to many other fields besides chemistry. His research on sickle cell anemia revealed the cause of the disease—the presence of a genetically inherited abnormal protein in the blood—and paved the way for the field of molecular genetics. His work was also pivotal in curbing the testing of nuclear weapons; he proved that radioactive fallout from nuclear testing posed a public health risk.

4.3.4: Electronegativity versus Electron Affinity

We must be careful not to confuse electronegativity and electron affinity. The electron affinity of an element is a measurable physical quantity, namely, the energy released or absorbed when an isolated gas-phase atom acquires an electron, measured in kJ/mol. Electronegativity, on the other hand, describes how tightly an atom attracts electrons in a bond. It is a dimensionless quantity that is calculated, not measured. Pauling derived the first electronegativity values by comparing the amounts of energy required to break different types of bonds. He chose an arbitrary relative scale ranging from 0 to 4.

4.3.5: Electronegativity and Bond Type

The absolute value of the difference in electronegativity (ΔEN) of two bonded atoms provides a rough measure of the polarity to be expected in the bond and, thus, the bond type. When the difference is very small or zero, the bond is covalent and nonpolar. When it is large, the bond is polar covalent or ionic. The absolute values of the electronegativity differences between the atoms in the bonds H–H, H–Cl, and Na–Cl are 0 (nonpolar), 0.9 (polar covalent), and 2.1 (ionic), respectively. The degree to which electrons are shared between atoms varies from completely equal (pure covalent bonding) to not at all (ionic bonding). Figure 4.3.4 shows the relationship between electronegativity difference and bond type.



Bond Type	Electronegativity Difference
pure covalent	< 0.4
polar covalent	between 0.4 and 1.8
ionic	> 1.8

Figure 4.3.4: As the electronegativity difference increases between two atoms, the bond becomes more ionic.

A rough approximation of the electronegativity differences associated with covalent, polar covalent, and ionic bonds is shown in Figure 4.3.4. This table is just a general guide, however, with many exceptions. For example, the H and F atoms in HF have an electronegativity difference of 1.9, and the N and H atoms in NH_3 a difference of 0.9, yet both of these compounds form bonds that are considered polar covalent. Likewise, the Na and Cl atoms in NaCl have an electronegativity difference of 2.1, and the Mn and I atoms in MnI_2 have a difference of 1.0, yet both of these substances form ionic compounds.

The best guide to the covalent or ionic character of a bond is to consider the types of atoms involved and their relative positions in the periodic table. Bonds between two nonmetals are generally covalent; bonding between a metal and a nonmetal is often ionic.

Some compounds contain both covalent and ionic bonds. The atoms in polyatomic ions, such as OH^-, NO_3^-, and NH_4^+, are held together by polar covalent bonds. However, these polyatomic ions form ionic compounds by combining with ions of opposite charge. For example, potassium nitrate, KNO_3, contains the K^+ cation and the polyatomic NO_3^- anion. Thus, bonding in potassium nitrate is ionic, resulting from the electrostatic attraction between the ions K^+ and NO_3^-, as well as covalent between the nitrogen and oxygen atoms in NO_3^-.

Example 4.3.1: Electronegativity and Bond Polarity

Bond polarities play an important role in determining the structure of proteins. Using the electronegativity values in Table A2, arrange the following covalent bonds—all commonly found in amino acids—in order of increasing polarity. Then designate the positive and negative atoms using the symbols δ+ and δ–:

C–H, C–N, C–O, N–H, O–H, S–H

Solution

The polarity of these bonds increases as the absolute value of the electronegativity difference increases. The atom with the δ– designation is the more electronegative of the two. Table 4.3.1 shows these bonds in order of increasing polarity.

Table 4.3.1: Bond Polarity and Electronegativity Difference

Bond	ΔEN	Polarity
C–H	0.4	$\overset{\delta-}{\mathrm{C}}-\overset{\delta+}{\mathrm{H}}$
S–H	0.4	$\overset{\delta-}{\mathrm{S}}-\overset{\delta+}{\mathrm{H}}$
C–N	0.5	$\overset{\delta+}{\mathrm{C}}-\overset{\delta-}{\mathrm{N}}$
N–H	0.9	$\overset{\delta-}{\mathrm{N}}-\overset{\delta+}{\mathrm{H}}$
C–O	1.0	$\overset{\delta+}{\mathrm{C}}-\overset{\delta-}{\mathrm{O}}$
O–H	1.4	$\overset{\delta-}{\mathrm{O}}-\overset{\delta+}{\mathrm{H}}$

Exercise 4.3.1

Silicones are polymeric compounds containing, among others, the following types of covalent bonds: Si–O, Si–C, C–H, and C–C. Using the electronegativity values in Figure 4.3.3, arrange the bonds in order of increasing polarity and designate the positive and negative atoms using the symbols δ+ and δ–.

Answer

Bond	Electronegativity Difference	Polarity
C–C	0.0	nonpolar
C–H	0.4	$\overset{\delta-}{\mathrm{C}}-\overset{\delta+}{\mathrm{H}}$
Si–C	0.7	$\overset{\delta+}{\mathrm{Si}}-\overset{\delta-}{\mathrm{C}}$
Si–O	1.7	$\overset{\delta+}{\mathrm{Si}}-\overset{\delta-}{\mathrm{O}}$

Summary

Covalent bonds form when electrons are shared between atoms and are attracted by the nuclei of both atoms. In pure covalent bonds, the electrons are shared equally. In polar covalent bonds, the electrons are shared unequally, as one atom exerts a stronger force of attraction on the electrons than the other. The ability of an atom to attract a pair of electrons in a chemical bond is called its

electronegativity. The difference in electronegativity between two atoms determines how polar a bond will be. In a diatomic molecule with two identical atoms, there is no difference in electronegativity, so the bond is nonpolar or pure covalent. When the electronegativity difference is very large, as is the case between metals and nonmetals, the bonding is characterized as ionic.

4.3.5.1: Contrasting 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. **Covalent compounds**, sometimes called molecular compounds, display a wide range of physical properties due to the many different sizes, shapes, and compositions of molecules. The melting and boiling points of covalent compounds are generally quite low compared to those of **ionic compounds**. This is because melting of ionic compounds involves breaking ionic bonds whereas the melting of covalent compounds involves disrupting the weak forces between molecules. When covalent compounds melt, the covalent bonds in the molecules are not broken.

Since covalent 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 covalent compounds is variable and depends on the structure of the molecule. Many, but not all, ionic compounds are quite soluble in water. The table below summarizes some of the differences between ionic and covalent compounds.

Also note that the chemical formula of a covalent compound represents something slightly different than the chemical formula of an ionic compound. The chemical formula of a covalent compound represents the identity and actual number of atoms that compose a molecule. The chemical formula of an ionic compound, on the other hand, represents the simplist whole number ratio of anions to cations in the crystal.

Property	Ionic Compounds	Covalent Compounds
Type of elements	Metal and nonmetal	Nonmetals only
Bonding	Ionic - attraction between anions and cations	Covalent - sharing of pair(s) of electrons between atoms
Representative unit	Formula unit	Molecule
What the formula represents	The ratio of cations to anions	The type and number of atoms in the 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
State when dissolved in water	Separates into ions	Remains molecules

Table 4.3.1: Comparison of Ionic and Molecular Compounds

Glossary

bond length
distance between the nuclei of two bonded atoms at which the lowest potential energy is achieved

covalent bond
bond formed when electrons are shared between atoms

electronegativity
tendency of an atom to attract electrons in a bond to itself

polar covalent bond
covalent bond between atoms of different electronegativities; a covalent bond with a positive end and a negative end

pure covalent bond

(also, nonpolar covalent bond) covalent bond between atoms of identical electronegativities

---

This page titled 4.3: Covalent Bonding is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **7.3: Covalent Bonding** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

4.4: Lewis Symbols and Structures

Learning Objectives

- Write Lewis symbols for neutral atoms and ions
- Draw Lewis structures depicting the bonding in simple molecules

Thus far, we have discussed the various types of bonds that form between atoms and/or ions. In all cases, these bonds involve the sharing or transfer of valence shell electrons between atoms. In this section, we will explore the typical method for depicting valence shell electrons and chemical bonds, namely Lewis symbols and Lewis structures.

4.4.1: Lewis Symbols

We use Lewis symbols to describe valence electron configurations of atoms and monatomic ions. A Lewis symbol consists of an elemental symbol surrounded by one dot for each of its valence electrons:



Figure 4.4.1 shows the Lewis symbols for the elements of the third period of the periodic table. Electron dots are typically arranged in four pairs located on the four "sides" of the atomic symbol.

Atoms	Electronic Configuration	Lewis Symbol
sodium	$[Ne]3s^1$	Na•
magnesium	$[Ne]3s^2$	•Mg•
aluminum	$[Ne]3s^23p^1$	•Al•
silicon	$[Ne]3s^23p^2$	•Si•
phosphorus	$[Ne]3s^23p^3$	•P•
sulfur	$[Ne]3s^23p^4$	:S•
chlorine	$[Ne]3s^23p^5$	:Cl•
argon	$[Ne]3s^23p^6$	:Ar:

Figure 4.4.1: Lewis symbols illustrating the number of valence electrons for each element in the third period of the periodic table.

Lewis symbols can be used to illustrate the formation of cations from atoms, as shown here for sodium and calcium:



Likewise, they can be used to show the formation of anions from atoms, as shown here for chlorine and sulfur:



Figure 4.4.2 demonstrates the use of Lewis symbols to show the transfer of electrons during the formation of ionic compounds.

https://chem.libretexts.org/@go/page/393225

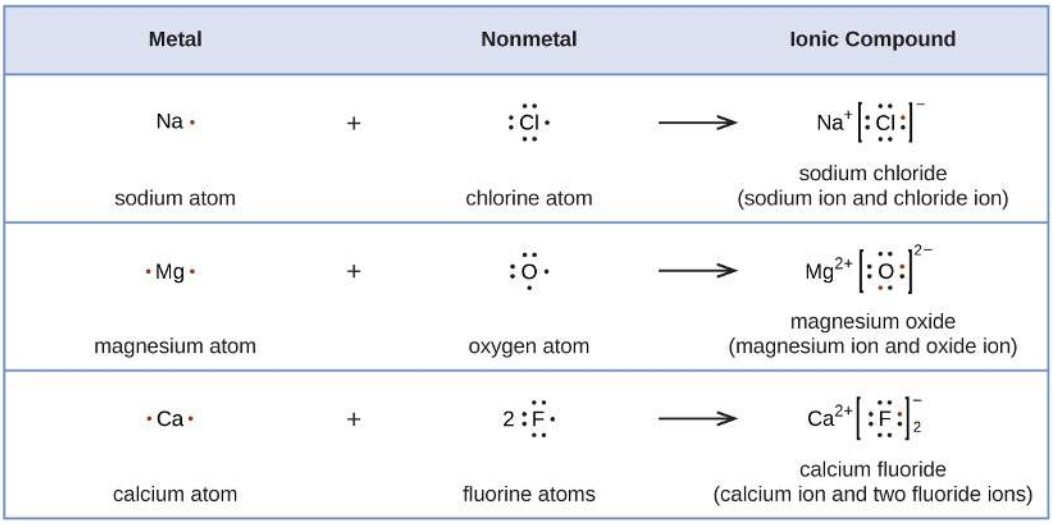
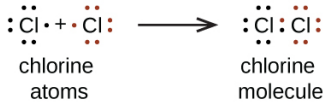


Figure 4.4.2: Cations are formed when atoms lose electrons, represented by fewer Lewis dots, whereas anions are formed by atoms gaining electrons. The total number of electrons does not change.

4.4.2: Lewis Structures

We also use Lewis symbols to indicate the formation of covalent bonds, which are shown in Lewis structures, drawings that describe the bonding in molecules and polyatomic ions. For example, when two chlorine atoms form a chlorine molecule, they share one pair of electrons:



The Lewis structure indicates that each Cl atom has three pairs of electrons that are not used in bonding (called lone pairs) and one shared pair of electrons (written between the atoms). A dash (or line) is usually used to indicate a shared pair of electrons:

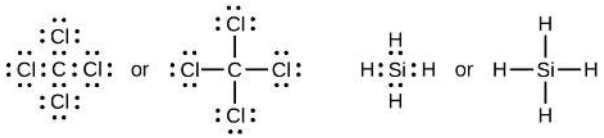


In the Lewis model, a single shared pair of electrons is a single bond. Each Cl atom interacts with eight valence electrons total: the six in the lone pairs and the two in the single bond.

4.4.3: The Octet Rule

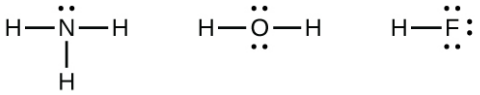
The other halogen molecules (F_2, Br_2, I_2, and At_2) form bonds like those in the chlorine molecule: one single bond between atoms and three lone pairs of electrons per atom. This allows each halogen atom to have a noble gas electron configuration. The tendency of main group atoms to form enough bonds to obtain eight valence electrons is known as the octet rule.

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); this is especially true of the nonmetals of the second period of the periodic table (C, N, O, and F). For example, each atom of a group 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 CCl_4 (carbon tetrachloride) and silicon in SiH_4 (silane). Because hydrogen only needs two electrons to fill its valence shell, it is an exception to the octet rule and only needs to form one bond. 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.



carbon tetrachloride silane

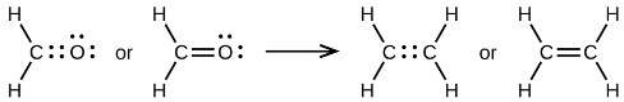
Group 15 elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form three covalent bonds, as in NH_3 (ammonia). Oxygen and other atoms in group 16 obtain an octet by forming two covalent bonds:



ammonia Water hydrogen fluoride

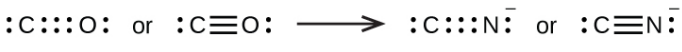
4.4.4: Double and Triple Bonds

As previously mentioned, when a pair of atoms shares one pair of electrons, we call this a single bond. However, a pair of atoms may need to share more than one pair of electrons in order to achieve the requisite octet. A double bond forms when two pairs of electrons are shared between a pair of atoms, as between the carbon and oxygen atoms in CH_2O (formaldehyde) and between the two carbon atoms in C_2H_4 (ethylene):



formaldehyde ethylene

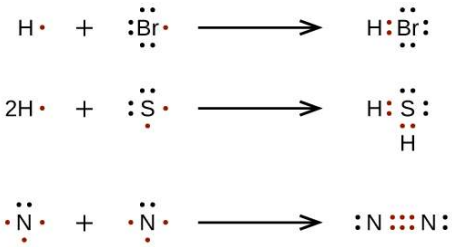
A triple bond forms when three electron pairs are shared by a pair of atoms, as in carbon monoxide (CO) and the cyanide ion (CN^-):



carbon monoxide cyanide ion

4.4.5: Writing Lewis Structures with the Octet Rule

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 SiH_4, CHO_2^-, NO^+, and OF_2 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 on each atom in the molecule:

$$\begin{aligned} &SiH_4 && (4.4.1)\\ &\text{Si: } 4 \text{ valence electrons/atom} \times 1 \text{ atom} = 4 && (4.4.2)\\ &+\text{H: } 1 \text{ valence electron/atom} \times 4 \text{ atoms} = 4 && (4.4.3)\\ &\qquad = 8 \text{ valence electrons} && (4.4.4)\end{aligned}$$

   - For a *negative ion*, such as CHO_2^-, we add the number of valence electrons on the atoms to the number of negative charges on the ion (one electron is gained for each single negative charge):

$$\begin{aligned} &CHO_2^-\\ &\text{C: } 4 \text{ valence electrons/atom} \times 1 \text{ atom} = 4\\ &\text{H: } 1 \text{ valence electron/atom} \times 1 \text{ atom} = 1\\ &\text{O: } 6 \text{ valence electrons/atom} \times 2 \text{ atoms} = 12\\ &+ \qquad 1 \text{ additional electron} = 1\\ &\qquad = 18 \text{ valence electrons}\end{aligned}$$

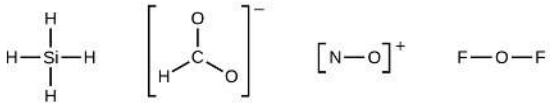
   - For a *positive ion*, such as NO^+, we add the number of valence electrons on the atoms in the ion and then subtract the number of positive charges on the ion (one electron is lost for each single positive charge) from the total number of valence electrons:

$$\begin{aligned} &NO^+\\ &\text{N: } 5 \text{ valence electrons/atom} \times 1 \text{ atom} = 5\\ &\text{O: } 6 \text{ valence electron/atom} \times 1 \text{ atom} = 6\\ &+ -1 \text{ electron (positive charge)} = -1\\ &\qquad = 10 \text{ valence electrons}\end{aligned}$$

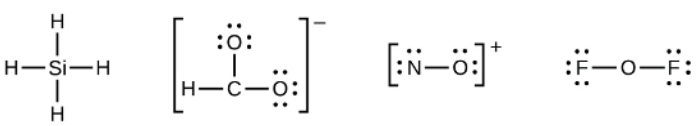
   - Since OF_2 is a neutral molecule, we simply add the number of valence electrons:

$$\begin{aligned} &OF_2\\ &\text{O: } 6 \text{ valence electrons/atom} \times 1 \text{ atom} = 6\\ &+\text{F: } 7 \text{ valence electrons/atom} \times 2 \text{ atoms} = 14\\ &\qquad = 20 \text{ valence electrons}\end{aligned}$$

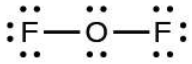
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond. (Note that we denote ions with brackets around the structure, indicating the charge outside the brackets:)



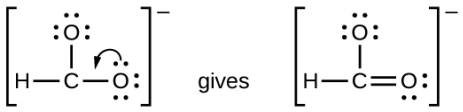
3. When several arrangements of atoms are possible, as for CHO_2^-, we must use experimental evidence to choose the correct one. In general, the less electronegative elements are more likely to be central atoms. In CHO_2^-, the less electronegative carbon atom occupies the central position with the oxygen and hydrogen atoms surrounding it. Other examples include P in $POCl_3$, S in SO_2, and Cl in ClO_4^-. An exception is that hydrogen is almost never a central atom. As the most electronegative element, fluorine also cannot be a central atom.
4. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.
   - There are no remaining electrons on SiH_4, so it is unchanged:



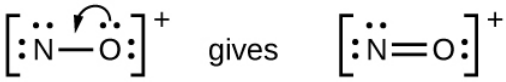
5. Place all remaining electrons on the central atom.
   - For SiH_4, CHO_2^-, and NO^+, there are no remaining electrons; we already placed all of the electrons determined in Step 1.
   - For OF_2, we had 16 electrons remaining in Step 3, and we placed 12, leaving 4 to be placed on the central atom:



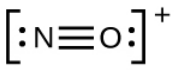
6. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.
   - SiH_4: Si already has an octet, so nothing needs to be done.
   - CHO_2^-: We have distributed the valence electrons as lone pairs on the oxygen atoms, but the carbon atom lacks an octet:



- NO^+: For this ion, we added eight outer electrons, but neither atom has an octet. We cannot add any more electrons since we have already used the total that we found in Step 1, so we must move electrons to form a multiple bond:



- This still does not produce an octet, so we must move another pair, forming a triple bond:



- In OF_2, each atom has an octet as drawn, so nothing changes.

Example 4.4.1: Writing Lewis Structures

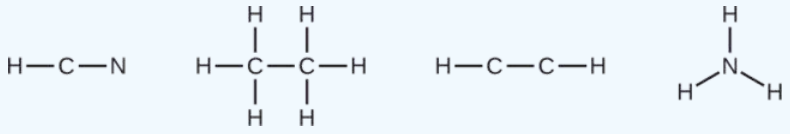
NASA's Cassini-Huygens mission detected a large cloud of toxic hydrogen cyanide (HCN) on Titan, one of Saturn's moons. Titan also contains ethane (H_3CCH_3), acetylene (HCCH), and ammonia (NH_3). What are the Lewis structures of these molecules?

Solution

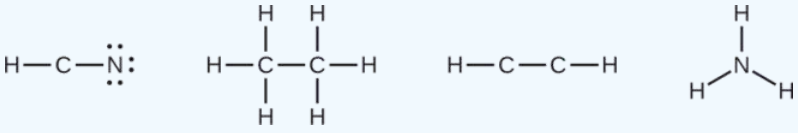
Calculate the number of valence electrons.

- HCN: (1 × 1) + (4 × 1) + (5 × 1) = 10
- H_3CCH_3: (1 × 3) + (2 × 4) + (1 × 3) = 14
- HCCH: (1 × 1) + (2 × 4) + (1 × 1) = 10
- NH_3: (5 × 1) + (3 × 1) = 8

Draw a skeleton and connect the atoms with single bonds. Remember that H is never a central atom:



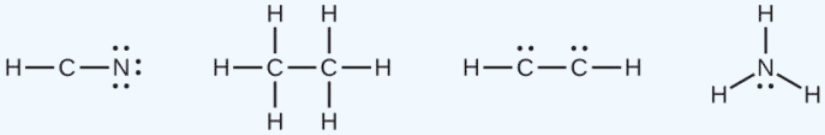
Where needed, distribute electrons to the terminal atoms:



- HCN: six electrons placed on N
- H_3CCH_3: no electrons remain

- HCCH: no terminal atoms capable of accepting electrons
- NH_3: no terminal atoms capable of accepting electrons

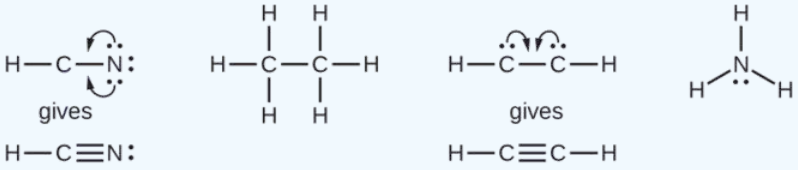
Where needed, place remaining electrons on the central atom:



- HCN: no electrons remain
- H_3CCH_3: no electrons remain
- HCCH: four electrons placed on carbon
- NH_3: two electrons placed on nitrogen

Where needed, rearrange electrons to form multiple bonds in order to obtain an octet on each atom:

- HCN: form two more C–N bonds
- H_3CCH_3: all atoms have the correct number of electrons
- HCCH: form a triple bond between the two carbon atoms
- NH_3: all atoms have the correct number of electrons



? Exercise 4.4.1

Both carbon monoxide, CO, and carbon dioxide, CO_2, are products of the combustion of fossil fuels. Both of these gases also cause problems: CO is toxic and CO_2 has been implicated in global climate change. What are the Lewis structures of these two molecules?

Answer



Fullerene Chemistry

Carbon soot has been known to man since prehistoric times, but it was not until fairly recently that the molecular structure of the main component of soot was discovered. In 1996, the Nobel Prize in Chemistry was awarded to Richard Smalley, Robert Curl, and Harold Kroto for their work in discovering a new form of carbon, the C_{60} buckminsterfullerene molecule. An entire class of compounds, including spheres and tubes of various shapes, were discovered based on C_{60}. This type of molecule, called a fullerene, consists of a complex network of single- and double-bonded carbon atoms arranged in such a way that each carbon atom obtains a full octet of electrons. Because of their size and shape, fullerenes can encapsulate other molecules, so they have shown potential in various applications from hydrogen storage to targeted drug delivery systems. They also possess unique electronic and optical properties that have been put to good use in solar powered devices and chemical sensors.

4.4.6: Exceptions to the Octet Rule

Many covalent molecules have central atoms that do not have eight electrons in their Lewis structures. These molecules fall into three categories:

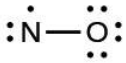
- Odd-electron molecules have an odd number of valence electrons, and therefore have an unpaired electron.
- Electron-deficient molecules have a central atom that has fewer electrons than needed for a noble gas configuration.
- Hypervalent molecules have a central atom that has more electrons than needed for a noble gas configuration.

4.4.6.1: Odd-electron Molecules

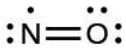
We call molecules that contain an odd number of electrons free radicals. Nitric oxide, NO, is an example of an odd-electron molecule; it is produced in internal combustion engines when oxygen and nitrogen react at high temperatures.

To draw the Lewis structure for an odd-electron molecule like NO, we follow the same five steps we would for other molecules, but with a few minor changes:

1. *Determine the total number of valence (outer shell) electrons*. The sum of the valence electrons is 5 (from N) + 6 (from O) = 11. The odd number immediately tells us that we have a free radical, so we know that not every atom can have eight electrons in its valence shell.
2. *Draw a skeleton structure of the molecule*. We can easily draw a skeleton with an N–O single bond: N–O
3. *Distribute the remaining electrons as lone pairs on the terminal atoms*. In this case, there is no central atom, so we distribute the electrons around both atoms. We give eight electrons to the more electronegative atom in these situations; thus oxygen has the filled valence shell:

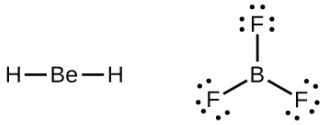


4. *Place all remaining electrons on the central atom*. Since there are no remaining electrons, this step does not apply.
5. *Rearrange the electrons to make multiple bonds with the central atom in order to obtain octets wherever possible.* We know that an odd-electron molecule cannot have an octet for every atom, but we want to get each atom as close to an octet as possible. In this case, nitrogen has only five electrons around it. To move closer to an octet for nitrogen, we take one of the lone pairs from oxygen and use it to form a NO double bond. (We cannot take another lone pair of electrons on oxygen and form a triple bond because nitrogen would then have nine electrons:)

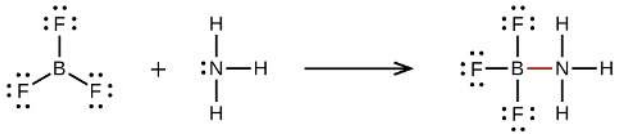


4.4.6.2: Electron-deficient Molecules

We will also encounter a few molecules that contain central atoms that do not have a filled valence shell. Generally, these are molecules with central atoms from groups 2 and 13 and outer atoms that are hydrogen or other atoms that do not form multiple bonds. For example, in the Lewis structures of beryllium dihydride, BeH_2, and boron trifluoride, BF_3, the beryllium and boron atoms each have only four and six electrons, respectively. It is possible to draw a structure with a double bond between a boron atom and a fluorine atom in BF_3, satisfying the octet rule, but experimental evidence indicates the bond lengths are closer to that expected for B–F single bonds. This suggests the best Lewis structure has three B–F single bonds and an electron deficient boron. The reactivity of the compound is also consistent with an electron deficient boron. However, the B–F bonds are slightly shorter than what is actually expected for B–F single bonds, indicating that some double bond character is found in the actual molecule.



An atom like the boron atom in BF_3, which does not have eight electrons, is very reactive. It readily combines with a molecule containing an atom with a lone pair of electrons. For example, NH_3 reacts with BF_3 because the lone pair on nitrogen can be shared with the boron atom:



4.4.6.3: Hypervalent Molecules

Elements in the second period of the periodic table (n = 2) can accommodate only eight electrons in their valence shell orbitals because they have only four valence orbitals (one 2*s* and three 2*p* orbitals). Elements in the third and higher periods ($n \geq 3$) have more than four valence orbitals and can share more than four pairs of electrons with other atoms because they have empty *d* orbitals

in the same shell. Molecules formed from these elements are sometimes called hypervalent molecules.Table 4.4.5 shows the Lewis structures for two hypervalent molecules, PCl_5 and SF_6.

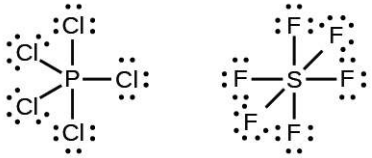
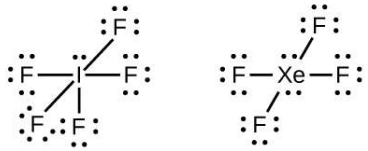


Table **4.4.5***: In PCl_5, the central atom phosphorus shares five pairs of electrons. In SF_6, sulfur shares six pairs of electrons.*

In some hypervalent molecules, such as IF_5 and XeF_4, some of the electrons in the outer shell of the central atom are lone pairs:



When we write the Lewis structures for these molecules, we find that we have electrons left over after filling the valence shells of the outer atoms with eight electrons. These additional electrons must be assigned to the central atom.

Example 4.4.2: Octet Rule Violations

Xenon is a noble gas, but it forms a number of stable compounds. We examined XeF_4 earlier. What are the Lewis structures of XeF_2 and XeF_6?

Solution

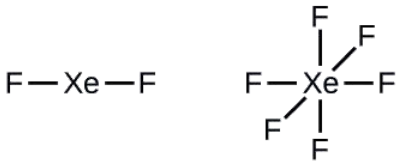
We can draw the Lewis structure of any covalent molecule by following the six steps discussed earlier. In this case, we can condense the last few steps, since not all of them apply.

Step 1: Calculate the number of valence electrons:

$$XeF_2: 8 + (2 \times 7) = 22$$

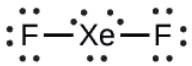
$$XeF_6: 8 + (6 \times 7) = 50$$

Step 2: Draw a skeleton joining the atoms by single bonds. **Xenon will be the central atom because fluorine cannot be a central atom:**

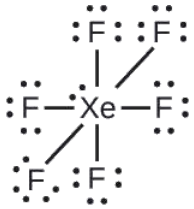


Step 3: Distribute the remaining electrons.

XeF_2: We place three lone pairs of electrons around each F atom, accounting for 12 electrons and giving each F atom 8 electrons. Thus, six electrons (three lone pairs) remain. These lone pairs must be placed on the Xe atom. This is acceptable because Xe atoms have empty valence shell *d* orbitals and can accommodate more than eight electrons. The Lewis structure of XeF_2 shows two bonding pairs and three lone pairs of electrons around the Xe atom:



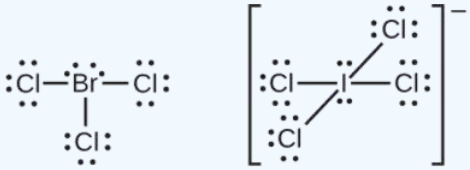
XeF_6: We place three lone pairs of electrons around each F atom, accounting for 36 electrons. Two electrons remain, and this lone pair is placed on the Xe atom:



? Exercise 4.4.2: interhalogens

The halogens form a class of compounds called the interhalogens, in which halogen atoms covalently bond to each other. Write the Lewis structures for the interhalogens $BrCl_3$ and ICl_4^-.

Answer



Summary

Valence electronic structures can be visualized by drawing Lewis symbols (for atoms and monatomic ions) and Lewis structures (for molecules and polyatomic ions). Lone pairs, unpaired electrons, and single, double, or triple bonds are used to indicate where the valence electrons are located around each atom in a Lewis structure. Most structures—especially those containing second row elements—obey the octet rule, in which every atom (except H) is surrounded by eight electrons. Exceptions to the octet rule occur for odd-electron molecules (free radicals), electron-deficient molecules, and hypervalent molecules.

Glossary

double bond
covalent bond in which two pairs of electrons are shared between two atoms

free radical
molecule that contains an odd number of electrons

hypervalent molecule
molecule containing at least one main group element that has more than eight electrons in its valence shell

Lewis structure
diagram showing lone pairs and bonding pairs of electrons in a molecule or an ion

Lewis symbol
symbol for an element or monatomic ion that uses a dot to represent each valence electron in the element or ion

lone pair
two (a pair of) valence electrons that are not used to form a covalent bond

octet rule
guideline that states main group atoms will form structures in which eight valence electrons interact with each nucleus, counting bonding electrons as interacting with both atoms connected by the bond

single bond

bond in which a single pair of electrons is shared between two atoms

triple bond

bond in which three pairs of electrons are shared between two atoms

---

This page titled 4.4: Lewis Symbols and Structures is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **7.4: Lewis Symbols and Structures** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

4.5: Formal Charges and Resonance

Learning Objectives

- Compute formal charges for atoms in any Lewis structure
- Use formal charges to identify the most reasonable Lewis structure for a given molecule
- Explain the concept of resonance and draw Lewis structures representing resonance forms for a given molecule

Previously, we discussed how to write Lewis structures for molecules and polyatomic ions. In some cases, however, there is seemingly more than one valid structure for a molecule. We can use the concept of formal charges to help us predict the most appropriate Lewis structure when more than one is reasonable.

4.5.1: Calculating Formal Charge

The formal charge of an atom in a molecule is the *hypothetical* charge the atom would have if we could redistribute the electrons in the bonds evenly between the atoms. Another way of saying this is that formal charge results when we take the number of valence electrons of a neutral atom, subtract the nonbonding electrons, and then subtract the number of bonds connected to that atom in the Lewis structure.

Thus, we calculate formal charge as follows:

$$\text{formal charge} = \#\text{ valence shell electrons (free atom)} - \#\text{ lone pair electrons} - \frac{1}{2}\#\text{ bonding electrons}$$

We can double-check formal charge calculations by determining the sum of the formal charges for the whole structure. The sum of the formal charges of all atoms in a molecule must be zero; the sum of the formal charges in an ion should equal the charge of the ion.

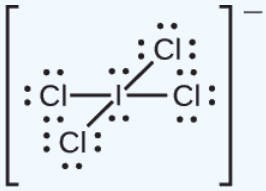
We must remember that the formal charge calculated for an atom is not the *actual* charge of the atom in the molecule. Formal charge is only a useful bookkeeping procedure; it does not indicate the presence of actual charges.

Example 4.5.1: Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen ion ICl_4^-.

Solution

We divide the bonding electron pairs equally for all I– Cl bonds:



We assign lone pairs of electrons to their atoms. Each Cl atom now has seven electrons assigned to it, and the I atom has eight.

Subtract this number from the number of valence electrons for the neutral atom:

- I: 7 – 8 = –1
- Cl: 7 – 7 = 0

The sum of the formal charges of all the atoms equals –1, which is identical to the charge of the ion (–1).

Exercise 4.5.1

Calculate the formal charge for each atom in the carbon monoxide molecule:



Answer

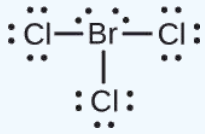
C −1, O +1

Example 4.5.2: Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen molecule $BrCl_3$.

Solution

Assign one of the electrons in each Br–Cl bond to the Br atom and one to the Cl atom in that bond:



Assign the lone pairs to their atom. Now each Cl atom has seven electrons and the Br atom has seven electrons.

Subtract this number from the number of valence electrons for the neutral atom. This gives the formal charge:

- Br: 7 – 7 = 0
- Cl: 7 – 7 = 0

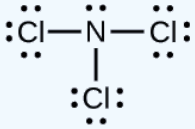
All atoms in $BrCl_3$ have a formal charge of zero, and the sum of the formal charges totals zero, as it must in a neutral molecule.

Exercise 4.5.2

Determine the formal charge for each atom in NCl_3.

Answer

N: 0; all three Cl atoms: 0



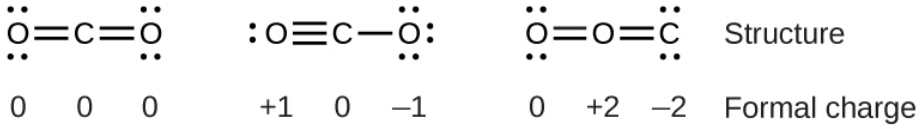
4.5.2: Using Formal Charge to Predict Molecular Structure

The arrangement of atoms in a molecule or ion is called its molecular structure. In many cases, following the steps for writing Lewis structures may lead to more than one possible molecular structure—different multiple bond and lone-pair electron placements or different arrangements of atoms, for instance. A few guidelines involving formal charge can be helpful in deciding which of the possible structures is most likely for a particular molecule or ion.

Predicting Molecular Structure Guidelines

1. A molecular structure in which all formal charges are zero is preferable to one in which some formal charges are not zero.
2. If the Lewis structure must have nonzero formal charges, the arrangement with the smallest nonzero formal charges is preferable.
3. Lewis structures are preferable when adjacent formal charges are zero or of the opposite sign.
4. When we must choose among several Lewis structures with similar distributions of formal charges, the structure with the negative formal charges on the more electronegative atoms is preferable.

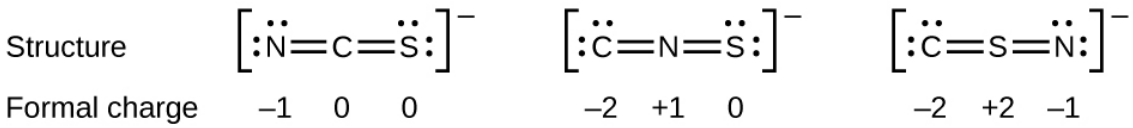
To see how these guidelines apply, let us consider some possible structures for carbon dioxide, CO_2. We know from our previous discussion that the less electronegative atom typically occupies the central position, but formal charges allow us to understand *why* this occurs. We can draw three possibilities for the structure: carbon in the center and double bonds, carbon in the center with a single and triple bond, and oxygen in the center with double bonds:



Three Lewis structures are shown. The left and right structures show a carbon atom double bonded to two oxygen atoms, each of which has two lone pairs of electrons. The center structure shows a carbon atom that is triple bonded to an oxygen atom with one lone pair of electrons and single bonded to an oxygen atom with three lone pairs of electrons. The third structure shows an oxygen atom double bonded to another oxygen atom with to lone pairs of electrons. The first oxygen atom is also double bonded to a carbon atom with two lone pairs of electrons.

Comparing the three formal charges, we can definitively identify the structure on the left as preferable because it has only formal charges of zero (Guideline 1).

As another example, the thiocyanate ion, an ion formed from a carbon atom, a nitrogen atom, and a sulfur atom, could have three different molecular structures: CNS^-, NCS^-, or CSN^-. The formal charges present in each of these molecular structures can help us pick the most likely arrangement of atoms. Possible Lewis structures and the formal charges for each of the three possible structures for the thiocyanate ion are shown here:

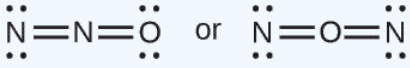


Two rows of structures and numbers are shown. The top row is labeled, “Structure” and depicts three Lewis structures and the bottom row is labeled, “Formal charge.” The left structure shows a carbon atom double bonded to a nitrogen atom with two lone electron pairs on one side and double bonded to a sulfur atom with two lone electron pairs on the other. The structure is surrounded by brackets and has a superscripted negative sign. Below this structure are the numbers negative one, zero, and zero. The middle structure shows a carbon atom with two lone pairs of electrons double bonded to a nitrogen atom that is double bonded to a sulfur atom with two lone electron pairs. The structure is surrounded by brackets and has a superscripted negative sign. Below this structure are the numbers negative two, positive one, and zero. The right structure shows a carbon atom with two lone electron pairs double bonded to a sulfur atom that is double bonded to a nitrogen atom with two lone electron pairs. The structure is surrounded by brackets and has a superscripted negative sign. Below this structure are the numbers negative two, positive two, and one.

Note that the sum of the formal charges in each case is equal to the charge of the ion (–1). However, the first arrangement of atoms is preferred because it has the lowest number of atoms with nonzero formal charges (Guideline 2). Also, it places the least electronegative atom in the center, and the negative charge on the more electronegative element (Guideline 4).

Example 4.5.3: Using Formal Charge to Determine Molecular Structure

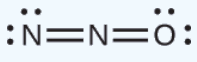
Nitrous oxide, N_2O, commonly known as laughing gas, is used as an anesthetic in minor surgeries, such as the routine extraction of wisdom teeth. Which is the likely structure for nitrous oxide?



Solution Determining formal charge yields the following:



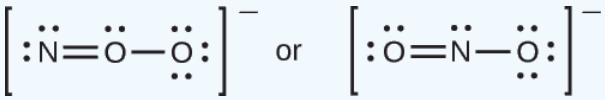
The structure with a terminal oxygen atom best satisfies the criteria for the most stable distribution of formal charge:



The number of atoms with formal charges are minimized (Guideline 2), and there is no formal charge larger than one (Guideline 2). This is again consistent with the preference for having the less electronegative atom in the central position.

? Exercise 4.5.3

Which is the most likely molecular structure for the nitrite (NO_2^-) ion?



Answer

ONO^-

4.5.3: Resonance

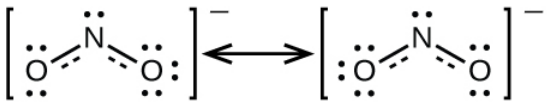
You may have noticed that the nitrite anion in Example 4.5.3 can have two possible structures with the atoms in the same positions. The electrons involved in the N–O double bond, however, are in different positions:



Two Lewis structures are shown. The left structure shows an oxygen atom with three lone pairs of electrons single bonded to a nitrogen atom with one lone pair of electrons that is double bonded to an oxygen with two lone pairs of electrons. Brackets surround this structure, and there is a superscripted negative sign. The right structure shows an oxygen atom with two lone pairs of electrons double bonded to a nitrogen atom with one lone pair of electrons that is single bonded to an oxygen atom with three lone pairs of electrons. Brackets surround this structure, and there is a superscripted negative sign.

If nitrite ions do indeed contain a single and a double bond, we would expect for the two bond lengths to be different. A double bond between two atoms is shorter (and stronger) than a single bond between the same two atoms. Experiments show, however, that both N–O bonds in NO_2^- have the same strength and length, and are identical in all other properties.

It is not possible to write a single Lewis structure for NO_2^- in which nitrogen has an octet and both bonds are equivalent. Instead, we use the concept of resonance: if two or more Lewis structures with the same arrangement of atoms can be written for a molecule or ion, the actual distribution of electrons is an *average* of that shown by the various Lewis structures. The actual distribution of electrons in each of the nitrogen-oxygen bonds in NO_2^- is the average of a double bond and a single bond. We call the individual Lewis structures resonance forms. The actual electronic structure of the molecule (the average of the resonance forms) is called a resonance hybrid of the individual resonance forms. A double-headed arrow between Lewis structures indicates that they are resonance forms. Thus, the electronic structure of the NO_2^- ion is shown as:

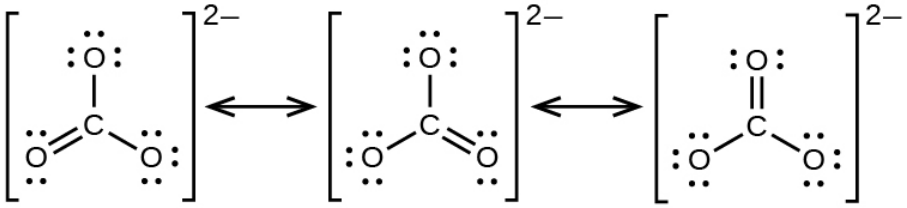


Two Lewis structures are shown with a double headed arrow drawn between them. The left structure shows an oxygen atom with two lone pairs of electrons double bonded to a nitrogen atom with one lone pair of electrons that is single bonded to an oxygen atom with three lone pairs of electrons. Brackets surround this structure, and there is a superscripted negative sign. The right structure shows an oxygen atom with three lone pairs of electrons single bonded to a nitrogen atom with one lone pair of electrons that is double bonded to an oxygen atom with two lone pairs of electrons. Brackets surround this structure, and there is a superscripted negative sign.

We should remember that a molecule described as a resonance hybrid *never* possesses an electronic structure described by either resonance form. It does not fluctuate between resonance forms; rather, the actual electronic structure is *always* the average of that shown by all resonance forms. George Wheland, one of the pioneers of resonance theory, used a historical analogy to describe the relationship between resonance forms and resonance hybrids. A medieval traveler, having never before seen a rhinoceros, described it as a hybrid of a dragon and a unicorn because it had many properties in common with both. Just as a rhinoceros is neither a

dragon sometimes nor a unicorn at other times, a resonance hybrid is neither of its resonance forms at any given time. Like a rhinoceros, it is a real entity that experimental evidence has shown to exist. It has some characteristics in common with its resonance forms, but the resonance forms themselves are convenient, imaginary images (like the unicorn and the dragon).

The carbonate anion, CO_3^{2-}, provides a second example of resonance:



Three Lewis structures are shown with double headed arrows in between. Each structure is surrounded by brackets, and each has a superscripted two negative sign. The left structure depicts a carbon atom bonded to three oxygen atoms. It is single bonded to two of these oxygen atoms, each of which has three lone pairs of electrons, and double bonded to the third, which has two lone pairs of electrons. The double bond is located between the lower left oxygen atom and the carbon atom. The central and right structures are the same as the first, but the position of the double bonded oxygen has moved to the lower right oxygen in the central structure and to the top oxygen in the right structure.

One oxygen atom must have a double bond to carbon to complete the octet on the central atom. All oxygen atoms, however, are equivalent, and the double bond could form from any one of the three atoms. This gives rise to three resonance forms of the carbonate ion. Because we can write three identical resonance structures, we know that the actual arrangement of electrons in the carbonate ion is the average of the three structures. Again, experiments show that all three C–O bonds are exactly the same.

Summary

In a Lewis structure, formal charges can be assigned to each atom by treating each bond as if one-half of the electrons are assigned to each atom. These hypothetical formal charges are a guide to determining the most appropriate Lewis structure. A structure in which the formal charges are as close to zero as possible is preferred. Resonance occurs in cases where two or more Lewis structures with identical arrangements of atoms but different distributions of electrons can be written. The actual distribution of electrons (the resonance hybrid) is an average of the distribution indicated by the individual Lewis structures (the resonance forms).

4.5.4: Key Equations

- $\text{formal charge} = \#\text{ valence shell electrons (free atom)} - \#\text{ one pair electrons} - \frac{1}{2}\#\text{ bonding electrons}$

Glossary

formal charge

charge that would result on an atom by taking the number of valence electrons on the neutral atom and subtracting the nonbonding electrons and the number of bonds (one-half of the bonding electrons)

molecular structure

arrangement of atoms in a molecule or ion

resonance

situation in which one Lewis structure is insufficient to describe the bonding in a molecule and the average of multiple structures is observed

resonance forms

two or more Lewis structures that have the same arrangement of atoms but different arrangements of electrons

resonance hybrid

average of the resonance forms shown by the individual Lewis structures

This page titled 4.5: Formal Charges and Resonance is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **7.5: Formal Charges and Resonance** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

https://chem.libretexts.org/@go/page/393230

4.6: Strengths of Ionic and Covalent Bonds

Learning Objectives

- Describe the energetics of covalent and ionic bond formation and breakage
- Use the Born-Haber cycle to compute lattice energies for ionic compounds
- Use average covalent bond energies to estimate enthalpies of reaction

A bond's strength describes how strongly each atom is joined to another atom, and therefore how much energy is required to break the bond between the two atoms. In this section, you will learn about the bond strength of covalent bonds, and then compare that to the strength of ionic bonds, which is related to the lattice energy of a compound.

4.6.1: Bond Strength: Covalent Bonds

Stable molecules exist because covalent bonds hold the atoms together. We measure the strength of a covalent bond by the energy required to break it, that is, the energy necessary to separate the bonded atoms. Separating any pair of bonded atoms requires energy; *the stronger a bond, the greater the energy required to break it.* The energy required to break a specific covalent bond in one mole of gaseous molecules is called the bond energy or the bond dissociation energy. The bond energy for a diatomic molecule, D_{X-Y}, is defined as the standard enthalpy change for the endothermic reaction:

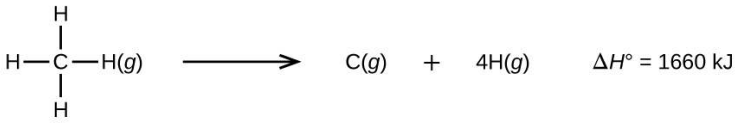
$$XY_{(g)} \longrightarrow X_{(g)} + Y_{(g)} \quad D_{X-Y} = \Delta H^\circ \tag{4.6.1}$$

For example, the bond energy of the pure covalent H–H bond, Δ_{H-H}, is 436 kJ per mole of H–H bonds broken:

$$H_{2(g)} \longrightarrow 2H_{(g)} \quad D_{H-H} = \Delta H^\circ = 436kJ \tag{4.6.2}$$

> *Breaking a bond **always** require energy to be added to the molecule. Correspondingly, making a bond **always** releases energy.*

Molecules with three or more atoms have two or more bonds. The sum of all bond energies in such a molecule is equal to the standard enthalpy change for the endothermic reaction that breaks all the bonds in the molecule. For example, the sum of the four C–H bond energies in CH_4, 1660 kJ, is equal to the standard enthalpy change of the reaction:



A reaction is shown with Lewis structures. The first structure shows a carbon atom single bonded to four hydrogen atoms with the symbol, "(g)" written next to it. A right-facing arrow points to the letter "C" and the symbol "(g)," which is followed by a plus sign. Next is the number 4, the letter "H" and the symbol, "(g)." To the right of this equation is another equation: capital delta H superscript degree symbol equals 1660 k J.

The average C–H bond energy, D_{C-H}, is 1660/4 = 415 kJ/mol because there are four moles of C–H bonds broken per mole of the reaction. Although the four C–H bonds are equivalent in the original molecule, they do not each require the same energy to break; once the first bond is broken (which requires 439 kJ/mol), the remaining bonds are easier to break. The 415 kJ/mol value is the average, not the exact value required to break any one bond.

The strength of a bond between two atoms increases as the number of electron pairs in the bond increases. Generally, as the bond strength increases, the bond length decreases. Thus, we find that triple bonds are stronger and shorter than double bonds between the same two atoms; likewise, double bonds are stronger and shorter than single bonds between the same two atoms. Average bond energies for some common bonds appear in Table 4.6.2, and a comparison of bond lengths and bond strengths for some common bonds appears in Table 4.6.2. When one atom bonds to various atoms in a group, the bond strength typically decreases as we move down the group. For example, C–F is 439 kJ/mol, C–Cl is 330 kJ/mol, and C–Br is 275 kJ/mol.

Table 4.6.1: Bond Energies (kJ/mol)

Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Energy

Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Energy
H–H	436	C–S	260	F–Cl	255
H–C	415	C–Cl	330	F–Br	235
H–N	390	C–Br	275	Si–Si	230
H–O	464	C–I	240	Si–P	215
H–F	569	N–N	160	Si–S	225
H–Si	395	$N=N$	418	Si–Cl	359
H–P	320	$N\equiv N$	946	Si–Br	290
H–S	340	N–O	200	Si–I	215
H–Cl	432	N–F	270	P–P	215
H–Br	370	N–P	210	P–S	230
H–I	295	N–Cl	200	P–Cl	330
C–C	345	N–Br	245	P–Br	270
$C=C$	611	O–O	140	P–I	215
$C\equiv C$	837	$O=O$	498	S–S	215
C–N	290	O–F	160	S–Cl	250
$C=N$	615	O–Si	370	S–Br	215
$C\equiv N$	891	O–P	350	Cl–Cl	243
C–O	350	O–Cl	205	Cl–Br	220
$C=O$	741	O–I	200	Cl–I	210
$C\equiv O$	1080	F–F	160	Br–Br	190
C–F	439	F–Si	540	Br–I	180
C–Si	360	F–P	489	I–I	150
C–P	265	F–S	285		

Table 4.6.2: Average Bond Lengths and Bond Energies for Some Common Bonds

Bond	Bond Length (Å)	Bond Energy (kJ/mol)
C–C	1.54	345
$C=C$	1.34	611
$C\equiv C$	1.20	837
C–N	1.43	290
$C=N$	1.38	615
$C\equiv N$	1.16	891
C–O	1.43	350
$C=O$	1.23	741
$C\equiv O$	1.13	1080

We can use bond energies to calculate approximate enthalpy changes for reactions where enthalpies of formation are not available. Calculations of this type will also tell us whether a reaction is exothermic or endothermic.

- An **exothermic reaction** (ΔH negative, heat produced) results when the bonds in the products are stronger than the bonds in the reactants.
- An **endothermic reaction** (ΔH positive, heat absorbed) results when the bonds in the products are weaker than those in the reactants.

The enthalpy change, ΔH, for a chemical reaction is approximately equal to the sum of the energy required to break all bonds in the reactants (energy "in", positive sign) plus the energy released when all bonds are formed in the products (energy "out," negative sign). This can be expressed mathematically in the following way:

$$\Delta H = \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}} \tag{4.6.3}$$

In this expression, the symbol Σ means "the sum of" and D represents the bond energy in kilojoules per mole, which is always a positive number. The bond energy is obtained from a table and will depend on whether the particular bond is a single, double, or triple bond. Thus, in calculating enthalpies in this manner, it is important that we consider the bonding in all reactants and products. Because D values are typically averages for one type of bond in many different molecules, this calculation provides a rough estimate, not an exact value, for the enthalpy of reaction.

Consider the following reaction:

$$\mathrm{H_{2\,(g)} + Cl_{2\,(g)} \longrightarrow 2\,HCl_{(g)}} \tag{4.6.4}$$

or

$$\mathrm{H\text{–}H_{(g)} + Cl\text{–}Cl_{(g)} \longrightarrow 2\,H\text{–}Cl_{(g)}} \tag{4.6.5}$$

To form two moles of HCl, one mole of H–H bonds and one mole of Cl–Cl bonds must be broken. The energy required to break these bonds is the sum of the bond energy of the H–H bond (436 kJ/mol) and the Cl–Cl bond (243 kJ/mol). During the reaction, two moles of H–Cl bonds are formed (bond energy = 432 kJ/mol), releasing 2 × 432 kJ; or 864 kJ. Because the bonds in the products are stronger than those in the reactants, the reaction releases more energy than it consumes:

$$\begin{aligned}\Delta H &= \sum \mathrm{D_{bonds\ broken}} - \sum \mathrm{D_{bonds\ formed}} \\ &= [\mathrm{D_{H-H}} + \mathrm{D_{Cl-Cl}}] - 2\mathrm{D_{H-Cl}} \\ &= [436 + 243] - 2(432) = -185\ \mathrm{kJ}\end{aligned}$$

This excess energy is released as heat, so the reaction is exothermic. Table T2 gives a value for the standard molar enthalpy of formation of HCl(g), ΔH_f°, of –92.307 kJ/mol. Twice that value is –184.6 kJ, which agrees well with the answer obtained earlier for the formation of two moles of HCl.

Example 4.6.1: Using Bond Energies to Approximate Enthalpy Changes

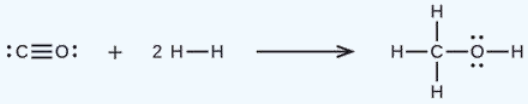
Methanol, CH_3OH, may be an excellent alternative fuel. The high-temperature reaction of steam and carbon produces a mixture of the gases carbon monoxide, CO, and hydrogen, H_2, from which methanol can be produced. Using the bond energies in Table 4.6.2, calculate the approximate enthalpy change, ΔH, for the reaction here:

$$CO_{(g)} + 2H2_{(g)} \longrightarrow CH_3OH_{(g)}$$

Solution

First, we need to write the Lewis structures of the reactants and the products:

https://chem.libretexts.org/@go/page/393231



A set of Lewis diagrams show a chemical reaction. The first structure shows a carbon atom with a lone pair of electrons triple bonded to an oxygen with a lone pair of electrons. To the right of this structure is a plus sign, then the number 2 followed by a hydrogen atom single bonded to a hydrogen atom. To the right of this structure is a right-facing arrow followed by a hydrogen atom single bonded to a carbon atom that is single bonded to two hydrogen atoms and an oxygen atom with two lone pairs of electrons. The oxygen atom is also single bonded to a hydrogen atom.

From this, we see that ΔH for this reaction involves the energy required to break a C–O triple bond and two H–H single bonds, as well as the energy produced by the formation of three C–H single bonds, a C–O single bond, and an O–H single bond. We can express this as follows (via Equation 4.6.3):

$$\begin{aligned}\Delta H &= \sum D_{bonds\ broken} - \sum D_{bonds\ formed} \\ \Delta H &= [\mathrm{D_{C\equiv O} + 2(D_{H-H})}] - [\mathrm{3(D_{C-H}) + D_{C-O} + D_{O-H}}]\end{aligned}$$

Using the bond energy values in Table 4.6.2, we obtain:

$$\begin{aligned}\Delta H &= [1080 + 2(436)] - [3(415) + 350 + 464] \\ &= -107\ \mathrm{kJ}\end{aligned}$$

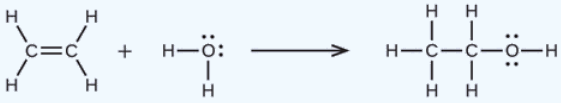
We can compare this value to the value calculated based on $\Delta H_\mathrm{f}^\circ$ data from Appendix G:

$$\begin{aligned}\Delta H &= [\Delta H_\mathrm{f}^\circ \mathrm{CH_3OH}(g)] - [\Delta H_\mathrm{f}^\circ \mathrm{CO}(g) + 2 \times \Delta H_\mathrm{f}^\circ \mathrm{H_2}] \\ &= [-201.0] - [-110.52 + 2 \times 0] \\ &= -90.5\ \mathrm{kJ}\end{aligned}$$

Note that there is a fairly significant gap between the values calculated using the two different methods. This occurs because D values are the *average* of different bond strengths; therefore, they often give only rough agreement with other data.

? Exercise 4.6.1

Ethyl alcohol, CH_3CH_2OH, was one of the first organic chemicals deliberately synthesized by humans. It has many uses in industry, and it is the alcohol contained in alcoholic beverages. It can be obtained by the fermentation of sugar or synthesized by the hydration of ethylene in the following reaction:



A set of Lewis structures show a chemical reaction. The first structure shows two carbon atoms that are double bonded together and are each single bonded to two hydrogen atoms. This structure is followed by a plus sign, then an oxygen atom with two lone pairs of electrons single bonded to two hydrogen atoms. A right-facing arrow leads to a carbon atom single bonded to three hydrogen atoms and a second carbon atom. The second carbon atom is single bonded to two hydrogen atoms and an oxygen atom with two lone pairs of electrons. The oxygen atom is single bonded to a hydrogen atom as well.

Using the bond energies in Table 4.6.2, calculate an approximate enthalpy change, ΔH, for this reaction.

Answer

–35 kJ

4.6.2: Ionic Bond Strength and Lattice Energy

An ionic compound is stable because of the electrostatic attraction between its positive and negative ions. The lattice energy of a compound is a measure of the strength of this attraction. The lattice energy ($\Delta H_{lattice}$) of an ionic compound is defined as the energy required to separate one mole of the solid into its component gaseous ions. For the ionic solid MX, the lattice energy is the enthalpy change of the process:

$$MX_{(s)} \longrightarrow Mn^{+}_{(g)} + X^{n-}_{(g)} \qquad \Delta H_{lattice} \tag{4.6.6}$$

Note that we are using the convention where the ionic solid is separated into ions, so our lattice energies will be endothermic (positive values). Some texts use the equivalent but opposite convention, defining lattice energy as the energy released when separate ions combine to form a lattice and giving negative (exothermic) values. Thus, if you are looking up lattice energies in another reference, be certain to check which definition is being used. In both cases, a larger magnitude for lattice energy indicates a more stable ionic compound. For sodium chloride, $\Delta H_{\text{lattice}}$ = 769 kJ. Thus, it requires 769 kJ to separate one mole of solid NaCl into gaseous Na^+ and Cl^- ions. When one mole each of gaseous Na^+ and Cl^- ions form solid NaCl, 769 kJ of heat is released.

The lattice energy $\Delta H_{lattice}$ of an ionic crystal can be expressed by the following equation (derived from Coulomb's law, governing the forces between electric charges):

$$\Delta H_{lattice} = \frac{C(Z^+)(Z^-)}{R_o} \tag{4.6.7}$$

in which

- C is a constant that depends on the type of crystal structure;
- Z^+ and Z^- are the charges on the ions; and
- R_o is the interionic distance (the sum of the radii of the positive and negative ions).

Thus, the lattice energy of an ionic crystal increases rapidly as the charges of the ions increase and the sizes of the ions decrease. When all other parameters are kept constant, doubling the charge of both the cation and anion quadruples the lattice energy. For example, the lattice energy of LiF (Z^+ and Z^- = 1) is 1023 kJ/mol, whereas that of MgO (Z^+ and Z^- = 2) is 3900 kJ/mol (R_o is nearly the same—about 200 pm for both compounds).

Different interatomic distances produce different lattice energies. For example, we can compare the lattice energy of MgF_2 (2957 kJ/mol) to that of MgI_2 (2327 kJ/mol) to observe the effect on lattice energy of the smaller ionic size of F^- as compared to I^-.

Example 4.6.2: Lattice Energy Comparisons

The precious gem ruby is aluminum oxide, Al_2O_3, containing traces of Cr^{3+}. The compound Al_2Se_3 is used in the fabrication of some semiconductor devices. Which has the larger lattice energy, Al_2O_3 or Al_2Se_3?

Solution

In these two ionic compounds, the charges Z^+ and Z^- are the same, so the difference in lattice energy will mainly depend upon R_o. The O^{2-} ion is smaller than the Se^{2-} ion. Thus, Al_2O_3 would have a shorter interionic distance than Al_2Se_3, and Al_2O_3 would have the larger lattice energy.

Exercise 4.6.2

Zinc oxide, ZnO, is a very effective sunscreen. How would the lattice energy of ZnO compare to that of NaCl?

Answer

ZnO would have the larger lattice energy because the Z values of both the cation and the anion in ZnO are greater, and the interionic distance of ZnO is smaller than that of NaCl.

4.6.3: The Born-Haber Cycle

It is not possible to measure lattice energies directly. However, the lattice energy can be calculated using the equation given in the previous section or by using a thermochemical cycle. The Born-Haber cycle is an application of Hess's law that breaks down the formation of an ionic solid into a series of individual steps:

- ΔH_f°, the standard enthalpy of formation of the compound
- IE, the ionization energy of the metal
- EA, the electron affinity of the nonmetal
- ΔH_s°, the enthalpy of sublimation of the metal
- D, the bond dissociation energy of the nonmetal

- $\Delta H_{lattice}$, the lattice energy of the compound

Figure 4.6.1 diagrams the Born-Haber cycle for the formation of solid cesium fluoride.

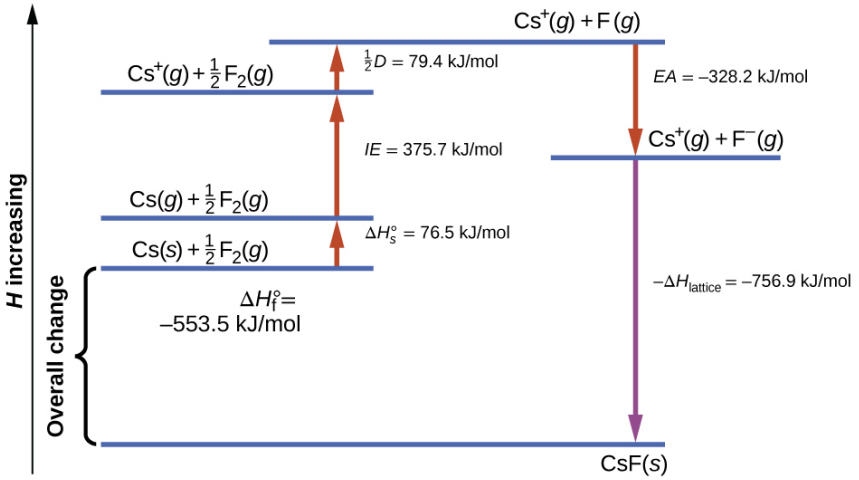


Figure 4.6.1: The Born-Haber cycle shows the relative energies of each step involved in the formation of an ionic solid from the necessary elements in their reference states.

A diagram is shown. An upward facing arrow is drawn to the far left of the chart and is labeled “H increasing.” A horizontal line is drawn at the bottom of the chart. A downward-facing, vertical arrow to the left side of this line is labeled, “Overall change.” Beside this arrow is another label, “capital delta H subscript f, equals negative 553.5 k J per mol, (Enthalpy of formation).” Three horizontal lines, one above the other, and all above the bottom line, are labeled, from bottom to top, as: “C s (s), plus sign, one half F subscript 2, (g),” “C s (g), plus sign, one half F subscript 2, (g),” and “C s, superscript positive sign, (g), plus sign, one half F subscript 2, (g).” Each of these lines is connected by an upward-facing vertical arrow. Each arrow is labeled, “capital delta H subscript 1, equals 76.5 k J per mol, (Enthalpy of sublimation),” “capital delta H subscript 2, equals 375.7 k J per mol, (ionization energy),” and “capital delta H subscript 3 equals 79.4 k J / mol (one half dissociation energy).” Another horizontal line is drawn in the center top portion of the diagram and is labeled “C s, superscript positive sign, (g), plus sign, F, (g).” There is one more horizontal line drawn to the right of the overall diagram and located halfway down the image. An arrow connects the top line to this line and is labeled, “capital delta H equals negative 328.2 k J / mol (electron affinity).” The line is labeled, “C s superscript positive sign (g) plus F superscript negative sign (g).” The arrow connecting this line to the bottom line is labeled, “negative capital delta H subscript lattice equals negative 756.9 k J / mol.” The arrow points to a label on the bottom line which reads, “C s F (s).”

We begin with the elements in their most common states, Cs(*s*) and $F_2(g)$. The ΔH_s° represents the conversion of solid cesium into a gas, and then the ionization energy converts the gaseous cesium atoms into cations. In the next step, we account for the energy required to break the F–F bond to produce fluorine atoms. Converting one mole of fluorine atoms into fluoride ions is an exothermic process, so this step gives off energy (the electron affinity) and is shown as decreasing along the *y*-axis. We now have one mole of Cs cations and one mole of F anions. These ions combine to produce solid cesium fluoride. The enthalpy change in this step is the negative of the lattice energy, so it is also an exothermic quantity. The total energy involved in this conversion is equal to the experimentally determined enthalpy of formation, ΔH_f°, of the compound from its elements. In this case, the overall change is exothermic.

Hess’s law can also be used to show the relationship between the enthalpies of the individual steps and the enthalpy of formation. Table 4.6.3 shows this for cesium fluoride, CsF.

Table 4.6.3: Enthalpies of Select Transitions

Enthalpy of sublimation of Cs(*s*)	$\mathrm{Cs}(s) \longrightarrow \mathrm{Cs}(g) \quad \Delta H = \Delta H_s^\circ = 77\ \mathrm{kJ/mol}$
One-half of the bond energy of F_2	$\frac{1}{2}\mathrm{F}_2(g) \longrightarrow \mathrm{F}(g) \quad \Delta H = \frac{1}{2}D = 79\ \mathrm{kJ/mol}$
Ionization energy of Cs(*g*)	$\mathrm{Cs}(g) \longrightarrow \mathrm{Cs}^+(g) + \mathrm{e}^- \quad \Delta H = IE = 376\ \mathrm{kJ/mol}$
Negative of the electron affinity of F	$\mathrm{F}(g) + \mathrm{e}^- \longrightarrow \mathrm{F}^-(g) \quad \Delta H = -EA = -328\ \mathrm{kJ/mol}$
Negative of the lattice energy of CsF(*s*)	$\mathrm{Cs}^+(g) + \mathrm{F}^-(g) \longrightarrow \mathrm{CsF}(s) \quad \Delta H = -\Delta H_{\text{lattice}} = ?$
Enthalpy of formation of CsF(*s*), add steps 1–5	$\Delta H = \Delta H_f^\circ = \Delta H_s^\circ + \frac{1}{2}D + IE + (-EA) + (-\Delta H_{\text{lattice}})$ $\mathrm{Cs}(s) + \frac{1}{2}\mathrm{F}_2(g) \longrightarrow \mathrm{CsF}(s) = -554\ \mathrm{kJ/mol}$

Thus, the lattice energy can be calculated from other values. For cesium chloride, using this data, the lattice energy is:

$$\Delta H_{\text{lattice}} = (411 + 109 + 122 + 496 + 368)\ \text{kJ} = 770\ \text{kJ}$$

The Born-Haber cycle may also be used to calculate any one of the other quantities in the equation for lattice energy, provided that the remainder is known. For example, if the relevant enthalpy of sublimation ΔH_s°, ionization energy (IE), bond dissociation enthalpy (D), lattice energy $\Delta H_{\text{lattice}}$, and standard enthalpy of formation ΔH_f° are known, the Born-Haber cycle can be used to determine the electron affinity of an atom.

Lattice energies calculated for ionic compounds are typically much larger than bond dissociation energies measured for covalent bonds. Whereas lattice energies typically fall in the range of 600–4000 kJ/mol (some even higher), covalent bond dissociation energies are typically between 150–400 kJ/mol for single bonds. Keep in mind, however, that these are not directly comparable values. For ionic compounds, lattice energies are associated with many interactions, as cations and anions pack together in an extended lattice. For covalent bonds, the bond dissociation energy is associated with the interaction of just two atoms.

Summary

The strength of a covalent bond is measured by its bond dissociation energy, that is, the amount of energy required to break that particular bond in a mole of molecules. Multiple bonds are stronger than single bonds between the same atoms. The enthalpy of a reaction can be estimated based on the energy input required to break bonds and the energy released when new bonds are formed. For ionic bonds, the lattice energy is the energy required to separate one mole of a compound into its gas phase ions. Lattice energy increases for ions with higher charges and shorter distances between ions. Lattice energies are often calculated using the Born-Haber cycle, a thermochemical cycle including all of the energetic steps involved in converting elements into an ionic compound.

4.6.3.1: Key Equations

- Bond energy for a diatomic molecule: $\mathrm{XY}(g) \longrightarrow \mathrm{X}(g) + \mathrm{Y}(g) \quad \mathrm{D}_{\mathrm{X–Y}} = \Delta H^\circ$
- Enthalpy change: $\Delta H = \Sigma \mathrm{D}_{\text{bonds broken}} - \Sigma \mathrm{D}_{\text{bonds formed}}$
- Lattice energy for a solid MX: $\mathrm{MX}(s) \longrightarrow \mathrm{M}^{n+}(g) + \mathrm{X}^{n-}(g) \quad \Delta H_{\text{lattice}}$
- Lattice energy for an ionic crystal: $\Delta H_{\text{lattice}} = \dfrac{\mathrm{C}(\mathrm{Z}^+)(\mathrm{Z}^-)}{\mathrm{R_o}}$

Footnotes

1. This question is taken from the Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

Glossary

bond energy

(also, bond dissociation energy) energy required to break a covalent bond in a gaseous substance

Born-Haber cycle

thermochemical cycle relating the various energetic steps involved in the formation of an ionic solid from the relevant elements

lattice energy ($\Delta H_{\text{lattice}}$)

energy required to separate one mole of an ionic solid into its component gaseous ions

This page titled 4.6: Strengths of Ionic and Covalent Bonds is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **7.6: Strengths of Ionic and Covalent Bonds** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

4.E: Chemical Bonding and Molecular Geometry (Exercises)

4.E.1: Ionic Bonding

Exercise 4.E.1

Does a cation gain protons to form a positive charge or does it lose electrons?

Answer

The protons in the nucleus do not change during normal chemical reactions. Only the outer electrons move. Positive charges form when electrons are lost.

Exercise 4.E.2

Iron(III) sulfate [$Fe_2(SO_4)_3$] is composed of Fe^{3+} and SO_4^{2-} ions. Explain why a sample of iron(III) sulfate is uncharged.

Answer

Add texts here. Do not delete this text first.

Exercise 4.E.3

Which of the following atoms would be expected to form negative ions in binary ionic compounds and which would be expected to form positive ions: P, I, Mg, Cl, In, Cs, O, Pb, Co?

Answer

P, I, Cl, and O would form anions because they are nonmetals. Mg, In, Cs, Pb, and Co would form cations because they are metals.

Exercise 4.E.4

Which of the following atoms would be expected to form negative ions in binary ionic compounds and which would be expected to form positive ions: Br, Ca, Na, N, F, Al, Sn, S, Cd?

Answer

Add texts here. Do not delete this text first.

Exercise 4.E.5

Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:

a. P
b. Mg
c. Al
d. O
e. Cl
f. Cs

Answer

P^{3-}; Mg^{2+}; Al^{3+}; O^{2-}; Cl^{-}; Cs^{+}

Exercise $4.E.6$

Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:

1. I
2. Sr
3. K
4. N
5. S
6. In

Answer

I^-

Sr^{2+}

K^+

N^{3-}

S^{2-}

In^{3+}

Exercise $4.E.7$

Write the electron configuration for each of the following ions:

1. As^{3-}
2. I^-
3. Be^{2+}
4. Cd^{2+}
5. O^{2-}
6. Ga^{3+}
7. Li^+
8. N^{3-}
9. Sn^{2+}
10. Co^{2+}
11. Fe^{2+}
12. As^{3+}

Answer

$[Ar]4s^23d^{10}4p^6$

$[Kr]4d^{10}5s^25p^6$ $1s^2$ $[Kr]4d^{10}$

[He]

[Kr] 5s0 4d10

$[He]2s^22p^6$;

$[Ar]3d^{10}$

$1s^2$

$[He]2s^22p^6$

$[Kr]4d^{10}5s^2$

$[Ar]3d^7$

https://chem.libretexts.org/@go/page/393232

[Ar]$3d^6$

[Ar]$3d^{10}4s^2$

Exercise 4.E.8

Write the electron configuration for the monatomic ions formed from the following elements (which form the greatest concentration of monatomic ions in seawater):

1. Cl
2. Na
3. Mg
4. Ca
5. K
6. Br
7. Sr
8. F

Answer

Add texts here. Do not delete this text first.

Exercise 4.E.9

Write out the full electron configuration for each of the following atoms and for the monatomic ion found in binary ionic compounds containing the element:

a. Al
b. Br
c. Sr
d. Li
e. As
f. S

Answer

$1s^22s^22p^63s^23p^1$; Al^{3+}: $1s^22s^22p^6$;

$1s^22s^22p^63s^23p^63d^{10}4s^24p^5$; Br^-: $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$;

$1s^22s^22p^63s^23p^63d^{10}4s^24p^65s^2$; Sr^{2+}: $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$;

$1s^22s^1$; Li^+: $1s^2$;

$1s^22s^22p^63s^23p^63d^{10}4s^24p^3$; As^{3-}: $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$;

$1s^22s^22p^63s^23p^4$; S^{2-}: $1s^22s^22p^63s^23p^6$

Exercise 4.E.10

From the labels of several commercial products, prepare a list of six ionic compounds in the products. For each compound, write the formula. (You may need to look up some formulas in a suitable reference.)

Answer

Add texts here. Do not delete this text first.

4.E.2: Covalent Bonding

Exercise 4.E.11

Why is it incorrect to speak of a molecule of solid NaCl?

Answer

NaCl consists of discrete ions arranged in a crystal lattice, not covalently bonded molecules.

Exercise 4.E.12

What information can you use to predict whether a bond between two atoms is covalent or ionic?

Answer

Add texts here. Do not delete this text first.

Exercise 4.E.13

Predict which of the following compounds are ionic and which are covalent, based on the location of their constituent atoms in the periodic table:

1. Cl_2CO
2. MnO
3. NCl_3
4. $CoBr_2$
5. K_2S
6. CO
7. CaF_2
8. HI
9. CaO
10. IBr
11. CO_2

Answer

ionic: (2), (4), (5), (7), and (9); covalent: (1), (3), (6), (8), (10), and (11)

Exercise 4.E.14

Explain the difference between a nonpolar covalent bond, a polar covalent bond, and an ionic bond.

Answer

Add texts here. Do not delete this text first.

Exercise 4.E.15

From its position in the periodic table, determine which atom in each pair is more electronegative:

1. Br or Cl
2. N or O
3. S or O
4. P or S
5. Si or N
6. Ba or P

7. N or K

Answer

Cl; O; O; S; N; P; N

Exercise 4.E.16

From its position in the periodic table, determine which atom in each pair is more electronegative:

1. N or P
2. N or Ge
3. S or F
4. Cl or S
5. H or C
6. Se or P
7. C or Si

Answer

Add texts here. Do not delete this text first.

Exercise 4.E.17

From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:

1. C, F, H, N, O
2. Br, Cl, F, H, I
3. F, H, O, P, S
4. Al, H, Na, O, P
5. Ba, H, N, O, As

Answer

H, C, N, O, F;

H, I, Br, Cl, F;

H, P, S, O, F;

Na, Al, H, P, O;

Ba, H, As, N, O

Exercise 4.E.18

From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:

1. As, H, N, P, Sb
2. Cl, H, P, S, Si
3. Br, Cl, Ge, H, Sr
4. Ca, H, K, N, Si
5. Cl, Cs, Ge, H, Sr

Answer

Add texts here. Do not delete this text first.

Exercise 4.E.19

Which atoms can bond to sulfur so as to produce a positive partial charge on the sulfur atom?

Answer

N, O, F, and Cl

Exercise 4.E.20

Which is the most polar bond?

1. C–C
2. C–H
3. N–H
4. O–H
5. Se–H

Answer

O–H

Exercise 4.E.21

Identify the more polar bond in each of the following pairs of bonds:

1. HF or HCl
2. NO or CO
3. SH or OH
4. PCl or SCl
5. CH or NH
6. SO or PO
7. CN or NN

Answer

HF; CO; OH; PCl; NH; PO; CN

Exercise 4.E.22

Which of the following molecules or ions contain polar bonds?

Answer

O_3

S_8

O_2^{2-}

NO_3^-

CO_2

H_2S

BH_4^-

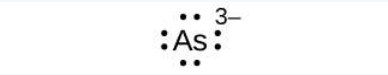
4.E.3: Lewis Symbols and Structures

Exercise 4.E.23

Write the Lewis symbols for each of the following ions:

a. As^{3-}
b. I^{-}
c. Be^{2+}
d. O^{2-}
e. Ga^{3+}
f. Li^{+}
g. N^{3-}

Answer

eight electrons: 

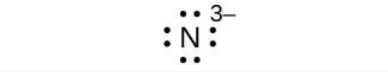
eight electrons: 

no electrons: Be^{2+}

eight electrons: 

no electrons: Ga^{3+}

no electrons: Li^{+}

eight electrons: 

Exercise 4.E.24

Many monatomic ions are found in seawater, including the ions formed from the following list of elements. Write the Lewis symbols for the monatomic ions formed from the following elements:

a. Cl
b. Na
c. Mg
d. Ca
e. K
f. Br
g. Sr
h. F

Answer

Add texts here. Do not delete this text first.

Exercise 4.E.25

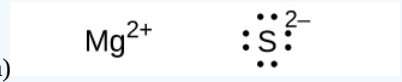
Write the Lewis symbols of the ions in each of the following ionic compounds and the Lewis symbols of the atom from which they are formed:

1. MgS

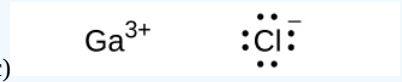
https://chem.libretexts.org/@go/page/393232

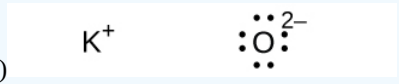
2. Al_2O_3
3. $GaCl_3$
4. K_2O
5. Li_3N
6. KF

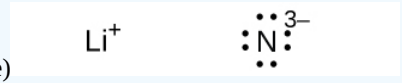
Answer

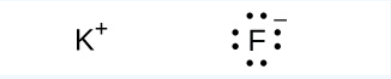
(a) 

(b) 

(c) 

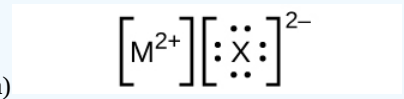
(d) 

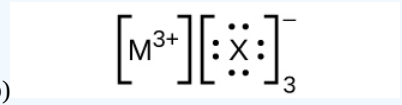
(e) 

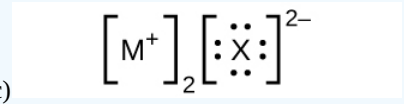
(f) 

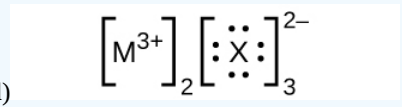
Exercise 4.E.26

In the Lewis structures listed here, M and X represent various elements in the third period of the periodic table. Write the formula of each compound using the chemical symbols of each element:Add exercises text here.

(a) 

(b) 

(c) 

(d) 

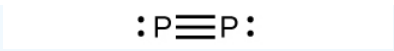
Answer

Add texts here. Do not delete this text first.

Exercise 4.E.27

Write the Lewis structure for the diatomic molecule P_2, an unstable form of phosphorus found in high-temperature phosphorus vapor.

Answer



Exercise 4.E.28

Write Lewis structures for the following:

a. H_2
b. HBr
c. PCl_3
d. SF_2
e. H_2CCH_2
f. HNNH
g. H_2CNH
h. (h) NO^-
i. (i) N_2
j. (j) CO
k. (k) CN^-

Answer

Add texts here. Do not delete this text first.

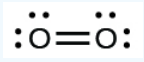
Exercise 4.E.29

Write Lewis structures for the following:

a. O_2
b. H_2CO
c. AsF_3
d. ClNO
e. $SiCl_4$
f. H_3O^+
g. NH_4^+
h. (h) BF_4^-
i. (i) HCCH
j. (j) ClCN
k. (k) C_2^{2+}

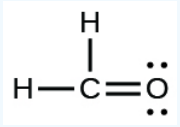
Answer

(a)



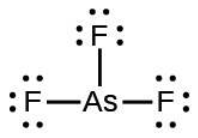
In this case, the Lewis structure is inadequate to depict the fact that experimental studies have shown two unpaired electrons in each oxygen molecule.

(b)


;

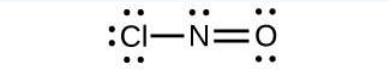
(c)

https://chem.libretexts.org/@go/page/393232



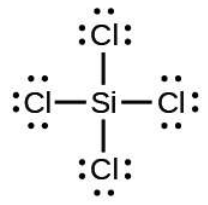
;

(d)



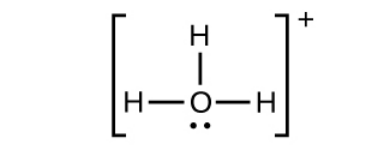
;

(e)



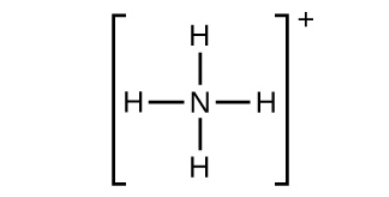
;

(f)



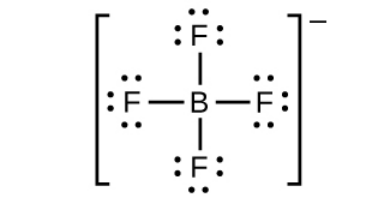
;

(g)



;

(h)



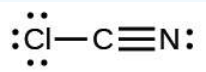
;

(i)



;

(j)



;

(k)



https://chem.libretexts.org/@go/page/393232

Exercise 4.E.30

Write Lewis structures for the following:

1. ClF_3
2. PCl_5
3. BF_3
4. PF_6^-

Answer

Add texts here. Do not delete this text first.

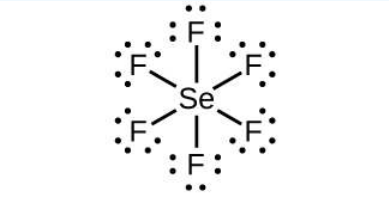
Exercise 4.E.31

Write Lewis structures for the following:

1. SeF_6
2. XeF_4
3. $SeCl_3^+$
4. Cl_2BBCl_2 (contains a B–B bond)

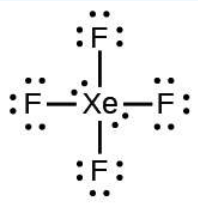
Answer

SeF_6:



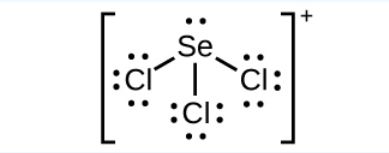
;

XeF_4:



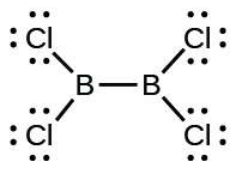
;

$SeCl_3^+$:



;

Cl_2BBCl_2:



https://chem.libretexts.org/@go/page/393232

Exercise 4.E.32

Write Lewis structures for:

1. PO_4^{3-}
2. ICl_4^-
3. SO_3^{2-}
4. HONO

Answer

Add texts here. Do not delete this text first.

Exercise 4.E.33

Correct the following statement: “The bonds in solid $PbCl_2$ are ionic; the bond in a HCl molecule is covalent. Thus, all of the valence electrons in $PbCl_2$ are located on the Cl^- ions, and all of the valence electrons in a HCl molecule are shared between the H and Cl atoms.”

Answer

Two valence electrons per Pb atom are transferred to Cl atoms; the resulting Pb^{2+} ion has a $6s^2$ valence shell configuration. Two of the valence electrons in the HCl molecule are shared, and the other six are located on the Cl atom as lone pairs of electrons.

Exercise 4.E.34

Write Lewis structures for the following molecules or ions:

1. SbH_3
2. XeF_2
3. Se_8 (a cyclic molecule with a ring of eight Se atoms)

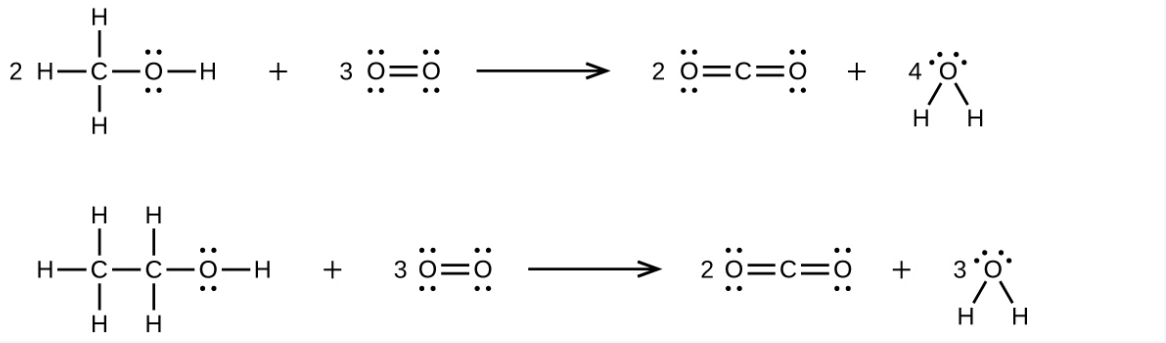
Answer

Add texts here. Do not delete this text first.

Exercise 4.E.35

Methanol, H_3COH, is used as the fuel in some race cars. Ethanol, C_2H_5OH, is used extensively as motor fuel in Brazil. Both methanol and ethanol produce CO_2 and H_2O when they burn. Write the chemical equations for these combustion reactions using Lewis structures instead of chemical formulas.

Answer



https://chem.libretexts.org/@go/page/393232

Exercise 4.E.36

Many planets in our solar system contain organic chemicals including methane (CH_4) and traces of ethylene (C_2H_4), ethane (C_2H_6), propyne (H_3CCCH), and diacetylene (HCCCCH). Write the Lewis structures for each of these molecules.

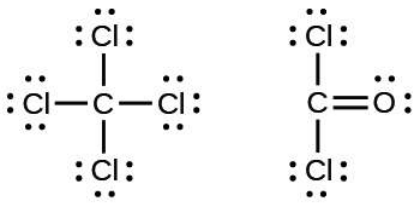
Answer

Add texts here. Do not delete this text first.

Exercise 4.E.37

Carbon tetrachloride was formerly used in fire extinguishers for electrical fires. It is no longer used for this purpose because of the formation of the toxic gas phosgene, Cl_2CO. Write the Lewis structures for carbon tetrachloride and phosgene.

Answer



Exercise 4.E.38

Identify the atoms that correspond to each of the following electron configurations. Then, write the Lewis symbol for the common ion formed from each atom:

1. $1s^2 2s^2 2p^5$
2. $1s^2 2s^2 2p^6 3s^2$
3. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$
4. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^4$
5. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$

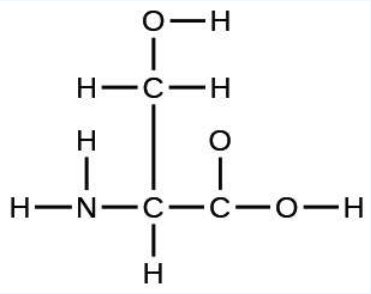
Answer

Add texts here. Do not delete this text first.

Exercise 4.E.39

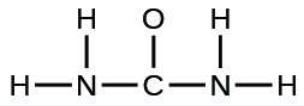
The arrangement of atoms in several biologically important molecules is given here. Complete the Lewis structures of these molecules by adding multiple bonds and lone pairs. Do not add any more atoms.

the amino acid serine:

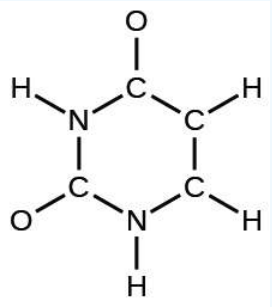


urea:

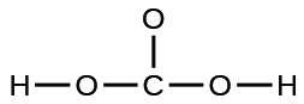
https://chem.libretexts.org/@go/page/393232



uracil:

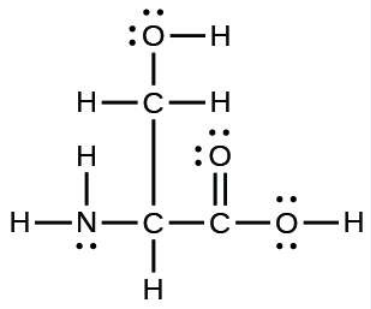


carbonic acid:

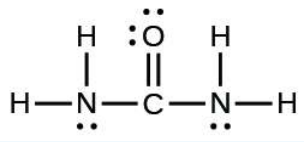


Answer

(a)

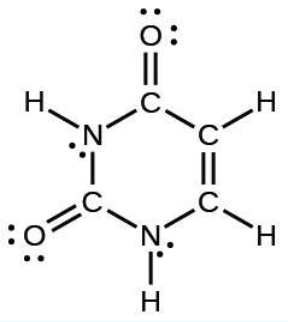

;

(b)


;

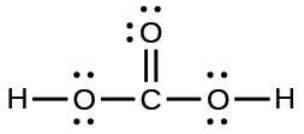
(c)

https://chem.libretexts.org/@go/page/393232



;

(d)



Exercise 4.E.40

A compound with a molar mass of about 28 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.

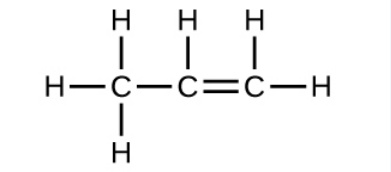
Answer

Add texts here. Do not delete this text first.

Exercise 4.E.41

A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.

Answer



Exercise 4.E.42

Two arrangements of atoms are possible for a compound with a molar mass of about 45 g/mol that contains 52.2% C, 13.1% H, and 34.7% O by mass. Write the Lewis structures for the two molecules.

Answer

Add texts here. Do not delete this text first.

Exercise 4.E.43

How are single, double, and triple bonds similar? How do they differ?

Answer

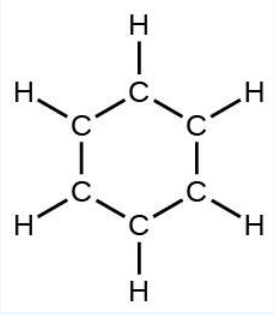
https://chem.libretexts.org/@go/page/393232

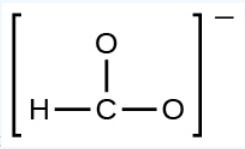
Each bond includes a sharing of electrons between atoms. Two electrons are shared in a single bond; four electrons are shared in a double bond; and six electrons are shared in a triple bond.

4.E.4: Formal Charges and Resonance

? Exercise 4.E. 44

Write resonance forms that describe the distribution of electrons in each of these molecules or ions.

1. selenium dioxide, OSeO
2. nitrate ion, NO_3^-
3. nitric acid, HNO_3 (N is bonded to an OH group and two O atoms)
4. benzene, C_6H_6: 

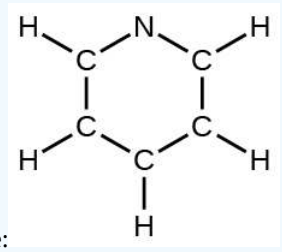
the formate ion: 

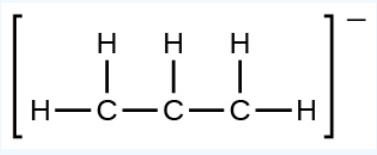
Answer

Add texts here. Do not delete this text first.

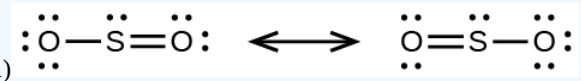
? Exercise 4.E. 45

Write resonance forms that describe the distribution of electrons in each of these molecules or ions.

1. sulfur dioxide, SO_2
2. pyridine: 

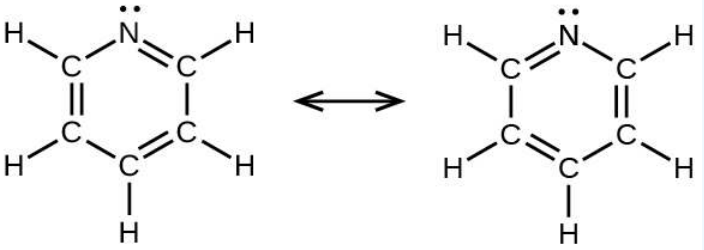
3. the allyl ion: 

Answer

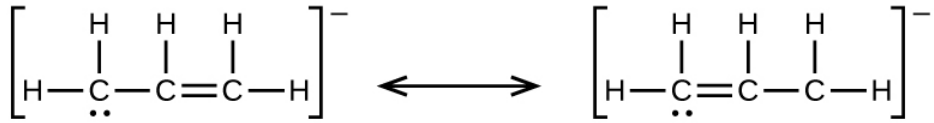
(1) 

https://chem.libretexts.org/@go/page/393232

(2)



(3)



Exercise 4.E.46

Write the resonance forms of ozone, O_3, the component of the upper atmosphere that protects the Earth from ultraviolet radiation.

Answer

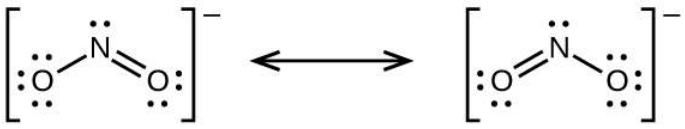
Add texts here. Do not delete this text first.

Exercise 4.E.47

Sodium nitrite is used to preserve bacon and other meats. Write the resonance forms of the nitrite ion, NO_2^-.

Answer

For NO_2^-



For O_3



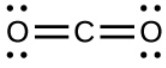
Exercise 4.E.49

Write the Lewis structures for the following, and include resonance structures where appropriate. Indicate which has the strongest carbon-oxygen bond.

1. CO_2
2. CO

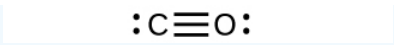
Answer

(a)



(b)

https://chem.libretexts.org/@go/page/393232



CO has the strongest carbon-oxygen bond because there is a triple bond joining C and O. CO_2 has double bonds.

Exercise 4.E.50

Toothpastes containing sodium hydrogen carbonate (sodium bicarbonate) and hydrogen peroxide are widely used. Write Lewis structures for the hydrogen carbonate ion and hydrogen peroxide molecule, with resonance forms where appropriate.

Answer

Add texts here. Do not delete this text first.

Exercise 4.E.51

Determine the formal charge of each element in the following:

1. HCl
2. CF_4
3. PCl_3
4. PF_5

Answer

H: 0, Cl: 0;

C: 0, F: 0;

P: 0, Cl 0;

P: 0, F: 0

Exercise 4.E.52

Determine the formal charge of each element in the following:

1. H_3O^+
2. SO_4^{2-}
3. NH_3
4. O_2^{2-}
5. H_2O_2

Answer

Add texts here. Do not delete this text first.

Exercise 4.E.53

Calculate the formal charge of chlorine in the molecules Cl_2, $BeCl_2$, and ClF_5.

Answer

Cl in Cl_2: 0; Cl in $BeCl_2$: 0; Cl in ClF_5: 0

Exercise $4.E.54$

Calculate the formal charge of each element in the following compounds and ions:

1. F_2CO
2. NO^-
3. BF_4^-
4. $SnCl_3^-$
5. H_2CCH_2
6. ClF_3
7. SeF_6
8. PO_4^{3-}

Answer

Add texts here. Do not delete this text first.

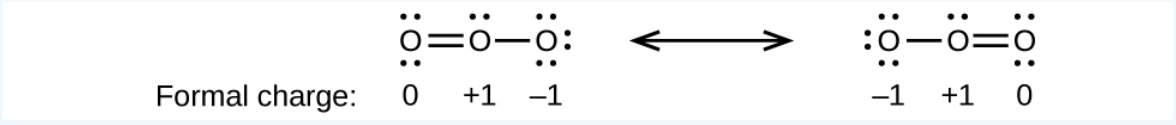
Exercise $4.E.55$

Draw all possible resonance structures for each of these compounds. Determine the formal charge on each atom in each of the resonance structures:

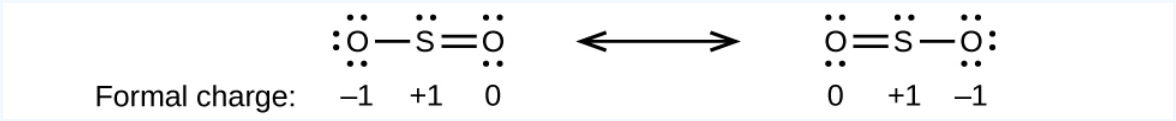
1. O_3
2. SO_2
3. NO_2^-
4. NO_3^-

Answer

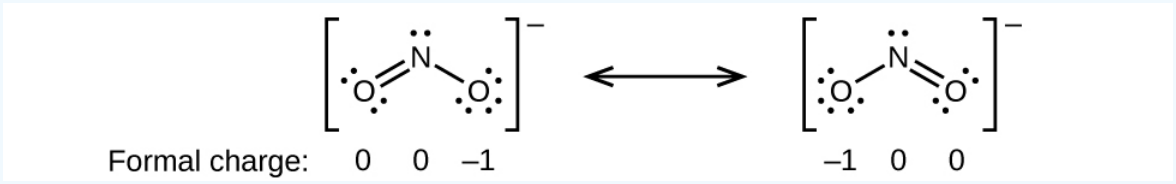
1.



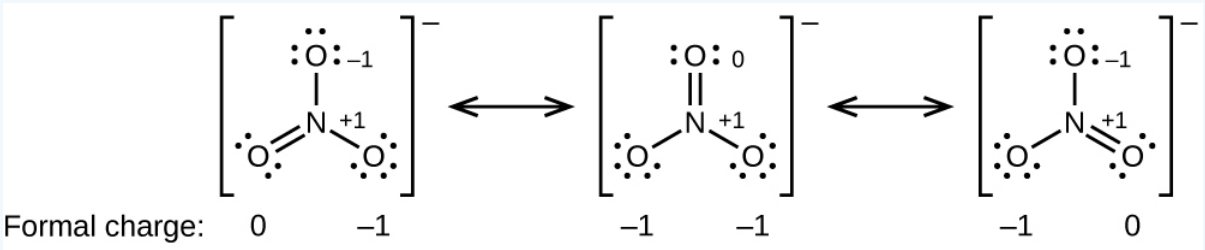
2.



3.



4.



https://chem.libretexts.org/@go/page/393232

Exercise 4.E.56

Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in nitrosyl chloride: ClNO or ClON?

Answer

Add texts here. Do not delete this text first.

Exercise 4.E.57

Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in hypochlorous acid: HOCl or OClH?

Answer

HOCl

Exercise 4.E.58

Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in sulfur dioxide: OSO or SOO?

Answer

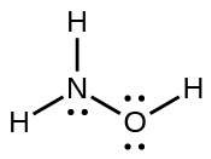
Add texts here. Do not delete this text first.

Exercise 4.E.59

Draw the structure of hydroxylamine, H_3NO, and assign formal charges; look up the structure. Is the actual structure consistent with the formal charges?

Answer

The structure that gives zero formal charges is consistent with the actual structure:



Exercise 4.E.60

Iodine forms a series of fluorides (listed here). Write Lewis structures for each of the four compounds and determine the formal charge of the iodine atom in each molecule:

1. IF
2. IF_3
3. IF_5
4. IF_7

Answer

Add texts here. Do not delete this text first.

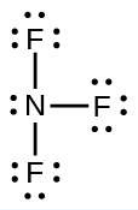
https://chem.libretexts.org/@go/page/393232

Exercise 4.E.61

Write the Lewis structure and chemical formula of the compound with a molar mass of about 70 g/mol that contains 19.7% nitrogen and 80.3% fluorine by mass, and determine the formal charge of the atoms in this compound.

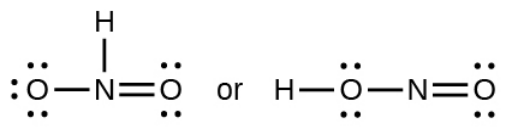
Answer

NF_3;



Exercise 4.E.62

Which of the following structures would we expect for nitrous acid? Determine the formal charges:



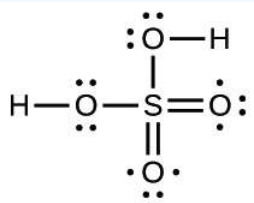
Answer

Add texts here. Do not delete this text first.

Exercise 4.E.63

Sulfuric acid is the industrial chemical produced in greatest quantity worldwide. About 90 billion pounds are produced each year in the United States alone. Write the Lewis structure for sulfuric acid, H_2SO_4, which has two oxygen atoms and two OH groups bonded to the sulfur.

Answer



4.E.5: Strengths of Ionic and Covalent Bonds

Exercise 4.E.64

Which bond in each of the following pairs of bonds is the strongest?

1. C–C or $C=C$
2. C–N or $C\equiv N$
3. $C\equiv O$ or $C=O$
4. H–F or H–Cl
5. C–H or O–H
6. C–N or C–O

Answer

Add texts here. Do not delete this text first.

Exercise 4.E.65

Using the bond energies in Table 4.6.1, determine the approximate enthalpy change for each of the following reactions:

1. $\mathrm{H_2}(g) + \mathrm{Br_2}(g) \longrightarrow 2\,\mathrm{HBr}(g)$
2. $\mathrm{CH_4}(g) + \mathrm{I_2}(g) \longrightarrow \mathrm{CH_3I}(g) + \mathrm{HI}(g)$
3. $\mathrm{C_2H_4}(g) + 3\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(g)$

Answer

−114 kJ;

30 kJ;

−1055 kJ

Exercise 4.E.66

Using the bond energies in Table, determine the approximate enthalpy change for each of the following reactions:

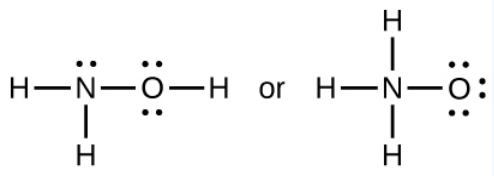
1. $\mathrm{Cl_2}(g) + 3\,\mathrm{F_2}(g) \longrightarrow 2\,\mathrm{ClF_3}(g)$
2. $\mathrm{H_2C{=}CH_2}(g) + \mathrm{H_2}(g) \longrightarrow \mathrm{H_3CCH_3}(g)$
3. (c) $2\,\mathrm{C_2H_6}(g) + 7\,\mathrm{O_2}(g) \longrightarrow 4\,\mathrm{CO_2}(g) + 6\,\mathrm{H_2O}(g)$

Answer

Add texts here. Do not delete this text first.

Exercise 4.E.67

When a molecule can form two different structures, the structure with the stronger bonds is usually the more stable form. Use bond energies to predict the correct structure of the hydroxylamine molecule:



Answer

The greater bond energy is in the figure on the left. It is the more stable form.

Exercise 4.E.68

How does the bond energy of HCldiffer from the standard enthalpy of formation of HCl(g)?

Answer

Add texts here. Do not delete this text first.

https://chem.libretexts.org/@go/page/393232

Exercise 4.E.69

Using the standard enthalpy of formation data in Appendix G, show how the standard enthalpy of formation of HCl(g) can be used to determine the bond energy.

Answer

$$\begin{aligned}
&\mathrm{HCl}(g) \longrightarrow \frac{1}{2}\mathrm{H_2}(g) + \frac{1}{2}\mathrm{Cl_2}(g) && \Delta H_1^\circ = -\Delta H^\circ_{\mathrm{f[HCl}(g)]} \\
&\frac{1}{2}\mathrm{H_2}(g) \longrightarrow \mathrm{H}(g) && \Delta H_2^\circ = \Delta H^\circ_{\mathrm{f[H}(g)]} \\
&\frac{1}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{Cl}(g) && \Delta H_3^\circ = \Delta H^\circ_{\mathrm{f[Cl}(g)]} \\
&\mathrm{HCl}(g) \longrightarrow \mathrm{H}(g) + \mathrm{Cl}(g) && \Delta H^\circ_{298} = \Delta H_1^\circ + \Delta H_2^\circ + \Delta H_3^\circ
\end{aligned}$$

$$D_{\mathrm{HCl}} = \Delta H^\circ_{298} = \Delta H^\circ_{\mathrm{f[HCl}(g)]} + \Delta H^\circ_{\mathrm{f[H}(g)]} + \Delta H^\circ_{\mathrm{f[Cl}(g)]} \tag{4.E.1}$$

$$= -(-92.307\ \mathrm{kJ}) + 217.97\ \mathrm{kJ} + 121.3\ \mathrm{kJ} \tag{4.E.2}$$

$$= 431.6\ \mathrm{kJ} \tag{4.E.3}$$

Exercise 4.E.70

Using the standard enthalpy of formation data in Appendix G, calculate the bond energy of the carbon-sulfur double bond in CS_2.

Answer

Add texts here. Do not delete this text first.

Exercise 4.E.71

Using the standard enthalpy of formation data in Appendix G, determine which bond is stronger: the S–F bond in $SF_4(g)$ or in $SF_6(g)$?Add exercises text here.

Answer

The S–F bond in SF_4 is stronger.

Exercise 4.E.72

Using the standard enthalpy of formation data in Appendix G, determine which bond is stronger: the P–Cl bond in $PCl_3(g)$ or in $PCl_5(g)$?

Answer

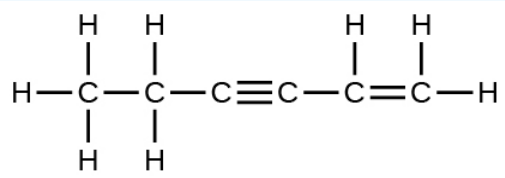
Add texts here. Do not delete this text first.

Exercise 4.E.73

Complete the following Lewis structure by adding bonds (not atoms), and then indicate the longest bond:



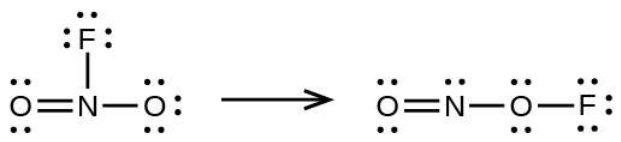
Answer



The C–C single bonds are longest.

Exercise 4.E.74

Use the bond energy to calculate an approximate value of ΔH for the following reaction. Which is the more stable form of FNO_2?



Answer

Add texts here. Do not delete this text first.

Exercise 4.E.75

Use principles of atomic structure to answer each of the following:[1]

1. The radius of the Ca atom is 197 pm; the radius of the Ca^{2+} ion is 99 pm. Account for the difference.
2. The lattice energy of CaO(*s*) is –3460 kJ/mol; the lattice energy of K_2O is –2240 kJ/mol. Account for the difference.
3. Given these ionization values, explain the difference between Ca and K with regard to their first and second ionization energies.

Element	First Ionization Energy (kJ/mol)	Second Ionization Energy (kJ/mol)
K	419	3050
Ca	590	1140

The first ionization energy of Mg is 738 kJ/mol and that of Al is 578 kJ/mol. Account for this difference.

Answer

When two electrons are removed from the valence shell, the Ca radius loses the outermost energy level and reverts to the lower $n = 3$ level, which is much smaller in radius.

The +2 charge on calcium pulls the oxygen much closer compared with K, thereby increasing the lattice energy relative to a less charged ion.

Removal of the 4*s* electron in Ca requires more energy than removal of the 4*s* electron in K because of the stronger attraction of the nucleus and the extra energy required to break the pairing of the electrons. The second ionization energy for K requires that an electron be removed from a lower energy level, where the attraction is much stronger from the nucleus for the electron. In addition, energy is required to unpair two electrons in a full orbital. For Ca, the second ionization potential requires removing only a lone electron in the exposed outer energy level.

In Al, the removed electron is relatively unprotected and unpaired in a *p* orbital. The higher energy for Mg mainly reflects the unpairing of the 2*s* electron.

https://chem.libretexts.org/@go/page/393232

Exercise 4.E.76

The lattice energy of LiF is 1023 kJ/mol, and the Li–F distance is 200.8 pm. NaF crystallizes in the same structure as LiF but with a Na–F distance of 231 pm. Which of the following values most closely approximates the lattice energy of NaF: 510, 890, 1023, 1175, or 4090 kJ/mol?

Answer

Add texts here. Do not delete this text first.

Exercise 4.E.77

For which of the following substances is the least energy required to convert one mole of the solid into separate ions?

1. MgO
2. SrO
3. KF
4. CsF
5. MgF_2

Answer

CsF

Exercise 4.E.78

The reaction of a metal, M, with a halogen, X_2, proceeds by an exothermic reaction as indicated by this equation: $M(s) + X_2(g) \longrightarrow MX_2(s)$. For each of the following, indicate which option will make the reaction more exothermic. Explain your answers.

1. a large radius vs. a small radius for M^{+2}
2. a high ionization energy vs. a low ionization energy for M
3. an increasing bond energy for the halogen
4. a decreasing electron affinity for the halogen
5. an increasing size of the anion formed by the halogen

Answer

Add texts here. Do not delete this text first.

Exercise 4.E.79

The lattice energy of LiF is 1023 kJ/mol, and the Li–F distance is 201 pm. MgO crystallizes in the same structure as LiF but with a Mg–O distance of 205 pm. Which of the following values most closely approximates the lattice energy of MgO: 256 kJ/mol, 512 kJ/mol, 1023 kJ/mol, 2046 kJ/mol, or 4008 kJ/mol? Explain your choice.

Answer

4008 kJ/mol; both ions in MgO have twice the charge of the ions in LiF; the bond length is very similar and both have the same structure; a quadrupling of the energy is expected based on the equation for lattice energy

Exercise 4.E.80

Which compound in each of the following pairs has the larger lattice energy? Note: Mg^{2+} and Li^+ have similar radii; O^{2-} and F^- have similar radii. Explain your choices.

1. MgO or MgSe

2. LiF or MgO
3. Li_2O or LiCl
4. Li_2Se or MgO

Answer

Add texts here. Do not delete this text first.

Exercise 4.E.81

Which compound in each of the following pairs has the larger lattice energy? Note: Ba^{2+} and K^+ have similar radii; S^{2-} and Cl^- have similar radii. Explain your choices.

1. K_2O or Na_2O
2. K_2S or BaS
3. KCl or BaS
4. BaS or $BaCl_2$

Answer

1. Na_2O; Na^+ has a smaller radius than K^+
2. BaS; Ba has a larger charge than K
3. BaS; Ba and S have larger charges
4. BaS; S has a larger charge

Exercise 4.E.82

Which of the following compounds requires the most energy to convert one mole of the solid into separate ions?

1. MgO
2. SrO
3. (c) KF
4. CsF
5. MgF_2

Answer

Add texts here. Do not delete this text first.

Exercise 4.E.83

Which of the following compounds requires the most energy to convert one mole of the solid into separate ions?

1. K_2S
2. K_2O
3. CaS
4. Cs_2S
5. CaO

Answer

CaO

https://chem.libretexts.org/@go/page/393232

Exercise 4.E.84

The lattice energy of KF is 794 kJ/mol, and the interionic distance is 269 pm. The Na–F distance in NaF, which has the same structure as KF, is 231 pm. Which of the following values is the closest approximation of the lattice energy of NaF:

- 682 kJ/mol,
- 794 kJ/mol,
- 924 kJ/mol,
- 1588 kJ/mol, or
- 3175 kJ/mol?

Explain your answer.

Answer

Add texts here. Do not delete this text first.

This page titled 4.E: Chemical Bonding and Molecular Geometry (Exercises) is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

4.S: Study Guide

4: Chemical Bonding I - Basic Concepts

Key Topics for TRU students taking CHEM1500

- Lewis Dot symbols
- the ionic bond; lattice energy
- covalent and polar covalent bonds
- electronegativity
- writing Lewis structures
- formal charge and Lewis structure
- resonance
- exceptions to the octet rule
- bond enthalpy

Key Learning Outcomes (Examples)

- draw acceptable Lewis structures for molecules and polyatomic ions based on formal charges and the octet rule
- identify sigma and pi bonding within a Lewis structure
- draw major resonance structures for molecules and polyatomic ions and determine the bond-orders for all the bonds

4.S: Study Guide is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

5: Chemical Bonding II- Molecular Geometry and Hybridization of Atomic Orbitals

Topic hierarchy

5.1: Molecular Structure and Polarity
5.2: Valence Bond Theory
5.3: Hybrid Atomic Orbitals
5.4: Multiple Bonds
5.5: Molecular Orbital Theory
5.E: Advanced Theories of Covalent Bonding (Exercises)
5.S: Study Guide

5: Chemical Bonding II- Molecular Geometry and Hybridization of Atomic Orbitals is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

5.1: Molecular Structure and Polarity

Learning Objectives

- Predict the structures of small molecules using valence shell electron pair repulsion (VSEPR) theory
- Explain the concepts of polar covalent bonds and molecular polarity
- Assess the polarity of a molecule based on its bonding and structure

Thus far, we have used two-dimensional Lewis structures to represent molecules. However, molecular structure is actually three-dimensional, and it is important to be able to describe molecular bonds in terms of their distances, angles, and relative arrangements in space (Figure 5.1.1). A bond angle is the angle between any two bonds that include a common atom, usually measured in degrees. A bond distance (or bond length) is the distance between the nuclei of two bonded atoms along the straight line joining the nuclei. Bond distances are measured in Ångstroms (1 Å = 10^{-10} m) or picometers (1 pm = 10^{-12} m, 100 pm = 1 Å).

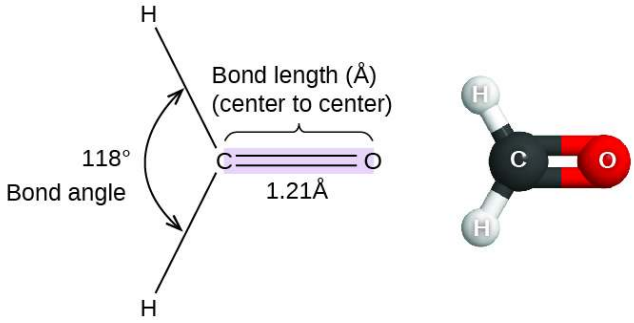


Figure 5.1.1: Bond distances (lengths) and angles are shown for the formaldehyde molecule, H_2CO.

5.1.1: VSEPR Theory

Valence shell electron-pair repulsion theory (VSEPR theory) enables us to predict the molecular structure, including approximate bond angles around a central atom, of a molecule from an examination of the number of bonds and lone electron pairs in its Lewis structure. The VSEPR model assumes that electron pairs in the valence shell of a central atom will adopt an arrangement that minimizes repulsions between these electron pairs by maximizing the distance between them. The electrons in the valence shell of a central atom form either bonding pairs of electrons, located primarily between bonded atoms, or lone pairs. The electrostatic repulsion of these electrons is reduced when the various regions of high electron density assume positions as far from each other as possible.

VSEPR theory predicts the arrangement of electron pairs around each central atom and, usually, the correct arrangement of atoms in a molecule. We should understand, however, that the theory only considers electron-pair repulsions. Other interactions, such as nuclear-nuclear repulsions and nuclear-electron attractions, are also involved in the final arrangement that atoms adopt in a particular molecular structure.

As a simple example of VSEPR theory, let us predict the structure of a gaseous BeF_2 molecule. The Lewis structure of BeF_2 (Figure 5.1.2) shows only two electron pairs around the central beryllium atom. With two bonds and no lone pairs of electrons on the central atom, the bonds are as far apart as possible, and the electrostatic repulsion between these regions of high electron density is reduced to a minimum when they are on opposite sides of the central atom. The bond angle is 180° (Figure 5.1.2).

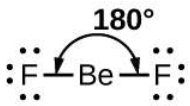


Figure 5.1.2: The BeF_2 molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the Be atom.

Figure 5.1.3 illustrates this and other electron-pair geometries that minimize the repulsions among regions of high electron density (bonds and/or lone pairs). Two regions of electron density around a central atom in a molecule form a linear geometry; three regions form a trigonal planar geometry; four regions form a tetrahedral geometry; five regions form a trigonal bipyramidal geometry; and six regions form an octahedral geometry.

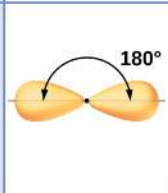
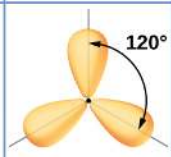
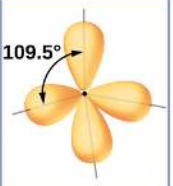
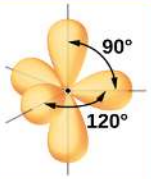
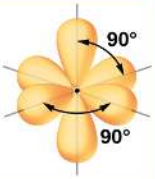
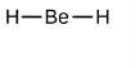
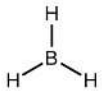
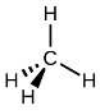
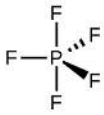
Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions of high electron density (bonds and/or unshared pairs)
Spatial arrangement					
Line-dash-wedge notation					
Electron pair geometry	Linear; 180° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angles of 90° or 120° An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).	Octahedral; all angles 90° or 180°

Figure 5.1.3: The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs).

5.1.2: Electron-pair Geometry versus Molecular Structure

It is important to note that electron-pair geometry around a central atom is *not* the same thing as its molecular structure. The electron-pair geometries shown in Figure 5.1.3 describe all regions where electrons are located, bonds as well as lone pairs. Molecular structure describes the location of the *atoms*, not the electrons.

We differentiate between these two situations by naming the geometry that includes *all* electron pairs the electron-pair geometry. The structure that includes only the placement of the atoms in the molecule is called the molecular structure. The electron-pair geometries will be the same as the molecular structures when there are no lone electron pairs around the central atom, but they will be different when there are lone pairs present on the central atom.

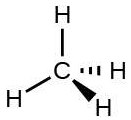


Figure 5.1.4: The molecular structure of the methane molecule, CH_4, is shown with a tetrahedral arrangement of the hydrogen atoms. VSEPR structures like this one are often drawn using the wedge and dash notation, in which solid lines represent bonds in the plane of the page, solid wedges represent bonds coming up out of the plane, and dashed lines represent bonds going down into the plane.

For example, the methane molecule, CH_4, which is the major component of natural gas, has four bonding pairs of electrons around the central carbon atom; the electron-pair geometry is tetrahedral, as is the molecular structure (Figure 5.1.4). On the other hand, the ammonia molecule, NH_3, also has four electron pairs associated with the nitrogen atom, and thus has a tetrahedral electron-pair

geometry. One of these regions, however, is a lone pair, which is not included in the molecular structure, and this lone pair influences the shape of the molecule (Figure 5.1.5).

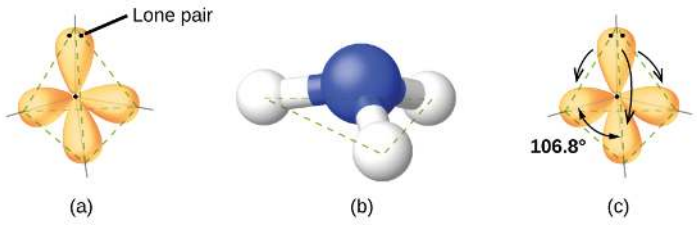


Figure 5.1.5: (a) The electron-pair geometry for the ammonia molecule is tetrahedral with one lone pair and three single bonds. (b) The trigonal pyramidal molecular structure is determined from the electron-pair geometry. (c) The actual bond angles deviate slightly from the idealized angles because the lone pair takes up a larger region of space than do the single bonds, causing the HNH angle to be slightly smaller than 109.5°.

Small distortions from the ideal angles in Figure 5.1.5 can result from differences in repulsion between various regions of electron density. VSEPR theory predicts these distortions by establishing an order of repulsions and an order of the amount of space occupied by different kinds of electron pairs. The order of electron-pair repulsions from greatest to least repulsion is:

lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair

This order of repulsions determines the amount of space occupied by different regions of electrons. A lone pair of electrons occupies a larger region of space than the electrons in a triple bond; in turn, electrons in a triple bond occupy more space than those in a double bond, and so on. The order of sizes from largest to smallest is:

lone pair > triple bond > double bond > single bond

Consider formaldehyde, H_2CO, which is used as a preservative for biological and anatomical specimens. This molecule has regions of high electron density that consist of two single bonds and one double bond. The basic geometry is trigonal planar with 120° bond angles, but we see that the double bond causes slightly larger angles (121°), and the angle between the single bonds is slightly smaller (118°).

In the ammonia molecule, the three hydrogen atoms attached to the central nitrogen are not arranged in a flat, trigonal planar molecular structure, but rather in a three-dimensional trigonal pyramid (Figure 5.1.6) with the nitrogen atom at the apex and the three hydrogen atoms forming the base. The ideal bond angles in a trigonal pyramid are based on the tetrahedral electron pair geometry. Again, there are slight deviations from the ideal because lone pairs occupy larger regions of space than do bonding electrons. The H–N–H bond angles in NH_3 are slightly smaller than the 109.5° angle in a regular tetrahedron (Figure 5.1.6) because the lone pair-bonding pair repulsion is greater than the bonding pair-bonding pair repulsion. The ideal molecular structures are predicted based on the electron-pair geometries for various combinations of lone pairs and bonding pairs.

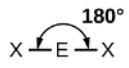
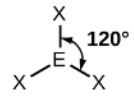
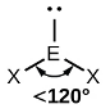
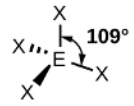
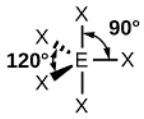
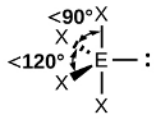
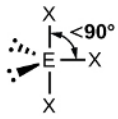
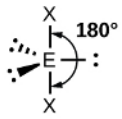
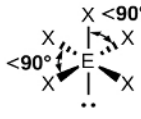
Number of electron pairs	Electron pair geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal planar	 Bent or angular			
4	 Tetrahedral	 Trigonal pyramid	 Bent or angular		
5	 Trigonal bipyramid	 Sawhorse or seesaw	 T-shape	 Linear	
6	 Octahedral	 Square pyramid	 Square planar	 T-shape	 Linear

Figure 5.1.6: The molecular structures are identical to the electron-pair geometries when there are no lone pairs present (first column). For a particular number of electron pairs (row), the molecular structures for one or more lone pairs are determined based on modifications of the corresponding electron-pair geometry.

According to VSEPR theory, the terminal atom locations (Xs in Figure 5.1.7) are equivalent within the linear, trigonal planar, and tetrahedral electron-pair geometries (the first three rows of the table). It does not matter which X is replaced with a lone pair because the molecules can be rotated to convert positions. For trigonal bipyramidal electron-pair geometries, however, there are two distinct X positions (Figure 5.1.7a): an axial position (if we hold a model of a trigonal bipyramid by the two axial positions, we have an axis around which we can rotate the model) and an equatorial position (three positions form an equator around the middle of the molecule). The axial position is surrounded by bond angles of 90°, whereas the equatorial position has more space available because of the 120° bond angles. In a trigonal bipyramidal electron-pair geometry, lone pairs always occupy equatorial positions because these more spacious positions can more easily accommodate the larger lone pairs.

Theoretically, we can come up with three possible arrangements for the three bonds and two lone pairs for the ClF_3 molecule (Figure 5.1.7). The stable structure is the one that puts the lone pairs in equatorial locations, giving a T-shaped molecular structure.

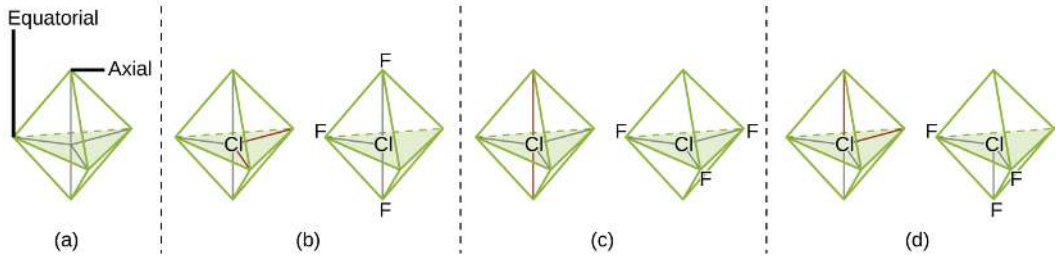


Figure 5.1.7: (a) In a trigonal bipyramid, the two axial positions are located directly across from one another, whereas the three equatorial positions are located in a triangular arrangement. (b–d) The two lone pairs (red lines) in ClF_3 have several possible arrangements, but the T-shaped molecular structure (b) is the one actually observed, consistent with the larger lone pairs both occupying equatorial positions.

When a central atom has two lone electron pairs and four bonding regions, we have an octahedral electron-pair geometry. The two lone pairs are on opposite sides of the octahedron (180° apart), giving a square planar molecular structure that minimizes lone pair-lone pair repulsions.

Predicting Electron Pair Geometry and Molecular Structure

The following procedure uses VSEPR theory to determine the electron pair geometries and the molecular structures:

1. Write the Lewis structure of the molecule or polyatomic ion.
2. Count the number of regions of electron density (lone pairs and bonds) around the central atom. A single, double, or triple bond counts as one region of electron density.
3. Identify the electron-pair geometry based on the number of regions of electron density: linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral (Figure 5.1.7, first column).
4. Use the number of lone pairs to determine the molecular structure (Figure 5.1.7). If more than one arrangement of lone pairs and chemical bonds is possible, choose the one that will minimize repulsions, remembering that lone pairs occupy more space than multiple bonds, which occupy more space than single bonds. In trigonal bipyramidal arrangements, repulsion is minimized when every lone pair is in an equatorial position. In an octahedral arrangement with two lone pairs, repulsion is minimized when the lone pairs are on opposite sides of the central atom.

The following examples illustrate the use of VSEPR theory to predict the molecular structure of molecules or ions that have no lone pairs of electrons. In this case, the molecular structure is identical to the electron pair geometry.

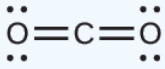
Example 5.1.1: Predicting Electron-pair Geometry and Molecular Structure

Predict the electron-pair geometry and molecular structure for each of the following:

a. carbon dioxide, CO_2, a molecule produced by the combustion of fossil fuels
b. boron trichloride, BCl_3, an important industrial chemical

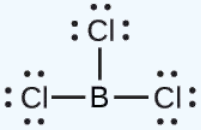
Solution

(a) We write the Lewis structure of CO_2 as:

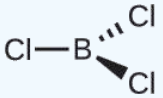


This shows us two regions of high electron density around the carbon atom—each double bond counts as one region, and there are no lone pairs on the carbon atom. Using VSEPR theory, we predict that the two regions of electron density arrange themselves on opposite sides of the central atom with a bond angle of 180°. The electron-pair geometry and molecular structure are identical, and CO_2 molecules are linear.

(b) We write the Lewis structure of BCl_3 as:



Thus we see that BCl_3 contains three bonds, and there are no lone pairs of electrons on boron. The arrangement of three regions of high electron density gives a trigonal planar electron-pair geometry. The B–Cl bonds lie in a plane with 120° angles between them. BCl_3 also has a trigonal planar molecular structure.



The electron-pair geometry and molecular structure of BCl_3 are both trigonal planar. Note that the VSEPR geometry indicates the correct bond angles (120°), unlike the Lewis structure shown above.

Exercise 5.1.1

Carbonate, CO_3^{2-}, is a common polyatomic ion found in various materials from eggshells to antacids. What are the electron-pair geometry and molecular structure of this polyatomic ion?

Answer

The electron-pair geometry is trigonal planar and the molecular structure is trigonal planar. Due to resonance, all three C–O bonds are identical. Whether they are single, double, or an average of the two, each bond counts as one region of electron density.

Example 5.1.2: Predicting Electron-pair Geometry and Molecular Structure

Two of the top 50 chemicals produced in the United States, ammonium nitrate and ammonium sulfate, both used as fertilizers, contain the ammonium ion. Predict the electron-pair geometry and molecular structure of the NH_4^+ cation.

Solution

We write the Lewis structure of NH_4^+ as:

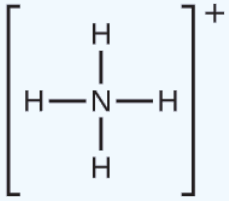


Figure 5.1.7).

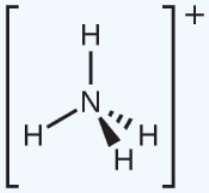


Figure 5.1.8: *The ammonium ion displays a tetrahedral electron-pair geometry as well as a tetrahedral molecular structure.*

Exercise 5.1.2

Identify a molecule with trigonal bipyramidal molecular structure.

Answer

Any molecule with five electron pairs around the central atoms including no lone pairs will be trigonal bipyramidal. PF_5 is a common example

The next several examples illustrate the effect of lone pairs of electrons on molecular structure.

Example 5.1.3: Lone Pairs on the Central Atom

Predict the electron-pair geometry and molecular structure of a water molecule.

Solution

The Lewis structure of H_2O indicates that there are four regions of high electron density around the oxygen atom: two lone pairs and two chemical bonds:

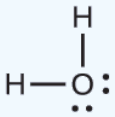


Figure 5.1.9. Thus, the electron-pair geometry is tetrahedral and the molecular structure is bent with an angle slightly less than 109.5°. In fact, the bond angle is 104.5°.

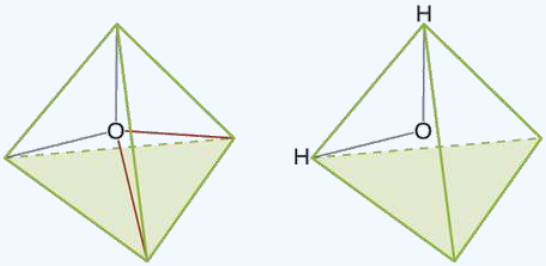


Figure 5.1.9: (a) H_2O has four regions of electron density around the central atom, so it has a tetrahedral electron-pair geometry. (b) Two of the electron regions are lone pairs, so the molecular structure is bent.

Exercise 5.1.3

The hydronium ion, H_3O^+, forms when acids are dissolved in water. Predict the electron-pair geometry and molecular structure of this cation.

Answer

electron pair geometry: tetrahedral; molecular structure: trigonal pyramidal

Example 5.1.4: SF_4 Sulfur tetrafluoride,

Predicting Electron-pair Geometry and Molecular Structure: SF_4, is extremely valuable for the preparation of fluorine-containing compounds used as herbicides (i.e., SF_4 is used as a fluorinating agent). Predict the electron-pair geometry and molecular structure of a SF_4 molecule.

Solution

The Lewis structure of SF_4 indicates five regions of electron density around the sulfur atom: one lone pair and four bonding pairs:

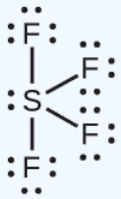


Figure 5.1.10).

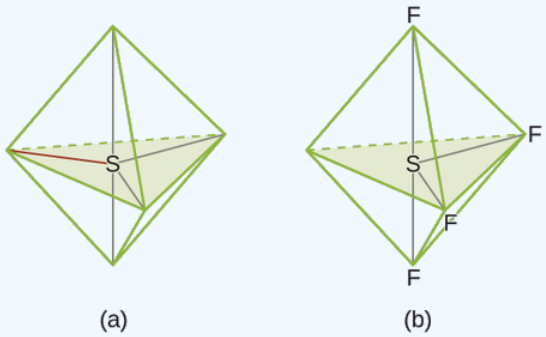


Figure 5.1.10: (a) SF_4 has a trigonal bipyramidal arrangement of the five regions of electron density. (b) One of the regions is a lone pair, which results in a seesaw-shaped molecular structure.

Exercise 5.1.4

Predict the electron pair geometry and molecular structure for molecules of XeF_2.

Answer

The electron-pair geometry is trigonal bipyramidal. The molecular structure is linear.

Example 5.1.4: XeF_4

Of all the noble gases, xenon is the most reactive, frequently reacting with elements such as oxygen and fluorine. Predict the electron-pair geometry and molecular structure of the XeF_4 molecule.

Solution

The Lewis structure of XeF_4 indicates six regions of high electron density around the xenon atom: two lone pairs and four bonds:

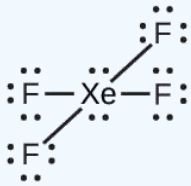


Figure 5.1.11: The five atoms are all in the same plane and have a square planar molecular structure.

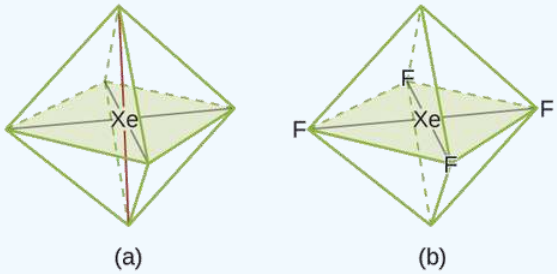


Figure 5.1.11: (a) XeF_4 adopts an octahedral arrangement with two lone pairs (red lines) and four bonds in the electron-pair geometry. (b) The molecular structure is square planar with the lone pairs directly across from one another.

Exercise 5.1.4

In a certain molecule, the central atom has three lone pairs and two bonds. What will the electron pair geometry and molecular structure be?

Answer

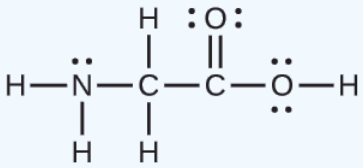
electron pair geometry: trigonal bipyramidal; molecular structure: linear

5.1.3: Molecular Structure for Multicenter Molecules

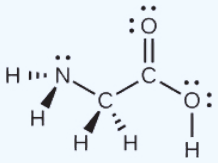
When a molecule or polyatomic ion has only one central atom, the molecular structure completely describes the shape of the molecule. Larger molecules do not have a single central atom, but are connected by a chain of interior atoms that each possess a "local" geometry. The way these local structures are oriented with respect to each other also influences the molecular shape, but such considerations are largely beyond the scope of this introductory discussion. For our purposes, we will only focus on determining the local structures.

Example 5.1.5: Predicting Structure in Multicenter Molecules

The Lewis structure for the simplest amino acid, glycine, $H_2NCH_2CO_2H$, is shown here. Predict the local geometry for the nitrogen atom, the two carbon atoms, and the oxygen atom with a hydrogen atom attached:



Solution



Consider each central atom independently. The electron-pair geometries:

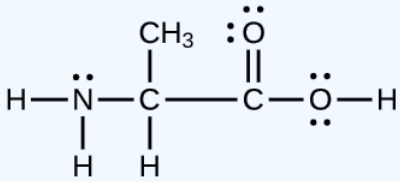
- nitrogen—four regions of electron density; tetrahedral
- carbon ($\underline{C}H_2$)—four regions of electron density; tetrahedral
- carbon ($\underline{C}O_2$)—three regions of electron density; trigonal planar
- oxygen ($\underline{O}H$)—four regions of electron density; tetrahedral

The local structures:

- nitrogen—three bonds, one lone pair; trigonal pyramidal
- carbon ($\underline{C}H_2$)—four bonds, no lone pairs; tetrahedral
- carbon ($\underline{C}O_2$)—three bonds (double bond counts as one bond), no lone pairs; trigonal planar
- oxygen ($\underline{O}H$)—two bonds, two lone pairs; bent (109°)

Exercise 5.1.5

Another amino acid is alanine, which has the Lewis structure shown here. Predict the electron-pair geometry and local structure of the nitrogen atom, the three carbon atoms, and the oxygen atom with hydrogen attached:



Answer

electron-pair geometries: nitrogen—tetrahedral; carbon ($\underline{C}H$)—tetrahedral; carbon ($\underline{C}H_3$)—tetrahedral; carbon ($\underline{C}O_2$)—trigonal planar; oxygen ($\underline{O}H$)—tetrahedral; local structures: nitrogen—trigonal pyramidal; carbon ($\underline{C}H$)—tetrahedral;

carbon ($\underline{C}H_3$)—tetrahedral; carbon ($\underline{C}O_2$)—trigonal planar; oxygen ($\underline{O}H$)—bent (109°)

Example 5.1.6: Molecular Simulation

Using this molecular shape simulator allows us to control whether bond angles and/or lone pairs are displayed by checking or unchecking the boxes under "Options" on the right. We can also use the "Name" checkboxes at bottom-left to display or hide the electron pair geometry (called "electron geometry" in the simulator) and/or molecular structure (called "molecular shape" in the simulator).

Build the molecule HCN in the simulator based on the following Lewis structure:

$$\mathrm{H{-}C{\equiv}N}$$

Click on each bond type or lone pair at right to add that group to the central atom. Once you have the complete molecule, rotate it to examine the predicted molecular structure. What molecular structure is this?

Solution

The molecular structure is linear.

Exercise 5.1.6

Build a more complex molecule in the simulator. Identify the electron-group geometry, molecular structure, and bond angles. Then try to find a chemical formula that would match the structure you have drawn.

Answer

Answers will vary. For example, an atom with four single bonds, a double bond, and a lone pair has an octahedral electron-group geometry and a square pyramidal molecular structure. $XeOF_4$ is a molecule that adopts this structure.

5.1.4: Molecular Polarity and Dipole Moment

As discussed previously, polar covalent bonds connect two atoms with differing electronegativities, leaving one atom with a partial positive charge (δ+) and the other atom with a partial negative charge (δ–), as the electrons are pulled toward the more electronegative atom. This separation of charge gives rise to a bond dipole moment. The magnitude of a bond dipole moment is represented by the Greek letter mu (μ) and is given by

$$\mu = Qr \tag{5.1.1}$$

where

- Q is the magnitude of the partial charges (determined by the electronegativity difference) and
- r is the distance between the charges:

This bond moment can be represented as a vector, a quantity having both direction and magnitude (Figure 5.1.12). Dipole vectors are shown as arrows pointing along the bond from the less electronegative atom toward the more electronegative atom. A small plus sign is drawn on the less electronegative end to indicate the partially positive end of the bond. The length of the arrow is proportional to the magnitude of the electronegativity difference between the two atoms.

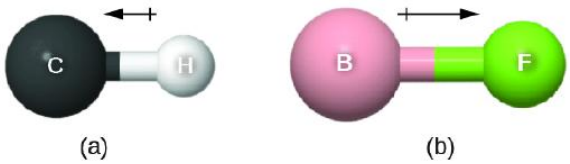


Figure 5.1.12: (a) There is a small difference in electronegativity between C and H, represented as a short vector. (b) The electronegativity difference between B and F is much larger, so the vector representing the bond moment is much longer.

A whole molecule may also have a separation of charge, depending on its molecular structure and the polarity of each of its bonds. If such a charge separation exists, the molecule is said to be a polar molecule (or dipole); otherwise the molecule is said to be nonpolar. The dipole moment measures the extent of net charge separation in the molecule as a whole. We determine the dipole moment by adding the bond moments in three-dimensional space, taking into account the molecular structure.

For diatomic molecules, there is only one bond, so its bond dipole moment determines the molecular polarity. Homonuclear diatomic molecules such as Br_2 and N_2 have no difference in electronegativity, so their dipole moment is zero. For heteronuclear molecules such as CO, there is a small dipole moment. For HF, there is a larger dipole moment because there is a larger difference in electronegativity.

When a molecule contains more than one bond, the geometry must be taken into account. If the bonds in a molecule are arranged such that their bond moments cancel (vector sum equals zero), then the molecule is nonpolar. This is the situation in CO_2 (Figure 5.1.13*A*). Each of the bonds is polar, but the molecule as a whole is nonpolar. From the Lewis structure, and using VSEPR theory, we determine that the CO_2 molecule is linear with polar C=O bonds on opposite sides of the carbon atom. The bond moments cancel because they are pointed in opposite directions. In the case of the water molecule (Figure 5.1.13*B*), the Lewis structure again shows that there are two bonds to a central atom, and the electronegativity difference again shows that each of these bonds has a nonzero bond moment. In this case, however, the molecular structure is bent because of the lone pairs on O, and the two bond moments do not cancel. Therefore, water does have a net dipole moment and is a polar molecule (dipole).

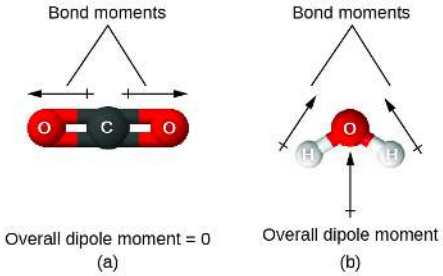
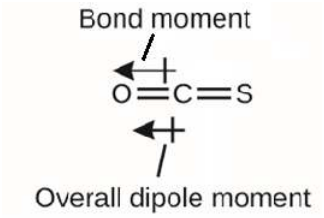


Figure 5.1.13: The overall dipole moment of a molecule depends on the individual bond dipole moments and how they are arranged. (a) Each CO bond has a bond dipole moment, but they point in opposite directions so that the net CO_2 molecule is nonpolar. (b) In contrast, water is polar because the OH bond moments do not cancel out.

The OCS molecule has a structure similar to CO_2, but a sulfur atom has replaced one of the oxygen atoms. To determine if this molecule is polar, we draw the molecular structure. VSEPR theory predicts a linear molecule:

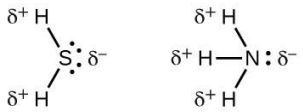


The C–O bond is considerably polar. C and S have the same electronegativity values, and so the C-S bond is non-polar. Because oxygen is more electronegative than sulfur, the oxygen end of the molecule is the negative end.

Chloromethane, CH_3Cl, is another example of a polar molecule. Although the polar C–Cl and C–H bonds are arranged in a tetrahedral geometry, the C–Cl bonds have a larger bond moment than the C–H bond, and the bond moments do not completely cancel each other. All of the dipoles have a upward component in the orientation shown, since carbon is more electronegative than hydrogen and less electronegative than chlorine:



When we examine the highly symmetrical molecules BF_3 (trigonal planar), CH_4 (tetrahedral), PF_5 (trigonal bipyramidal), and SF_6 (octahedral), in which all the polar bonds are identical, the molecules are nonpolar. The bonds in these molecules are arranged such that their dipoles cancel. However, just because a molecule contains identical bonds does not mean that the dipoles will always cancel. Many molecules that have identical bonds and lone pairs on the central atoms have bond dipoles that do not cancel. Examples include H_2S and NH_3. A hydrogen atom is at the positive end and a nitrogen or sulfur atom is at the negative end of the polar bonds in these molecules:



Other examples of molecules with polar bonds are shown in Figure 5.1.14. In molecular geometries that are highly symmetrical (most notably tetrahedral and square planar, trigonal bipyramidal, and octahedral), individual bond dipole moments completely cancel, and there is no net dipole moment. Although a molecule like $CHCl_3$ is best described as tetrahedral, the atoms bonded to carbon are not identical. Consequently, the bond dipole moments cannot cancel one another, and the molecule has a dipole moment. Due to the arrangement of the bonds in molecules that have V-shaped, trigonal pyramidal, seesaw, T-shaped, and square pyramidal geometries, the bond dipole moments cannot cancel one another. Consequently, molecules with these geometries always have a nonzero dipole moment. Molecules with asymmetrical charge distributions have a net dipole moment.

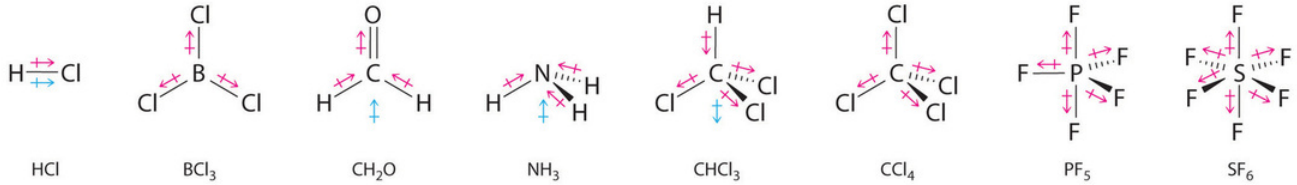


Figure 5.1.14: Molecules with Polar Bonds. Individual bond dipole moments are indicated in red. Due to their different three-dimensional structures, some molecules with polar bonds have a net dipole moment (HCl, CH_2O, NH_3, and $CHCl_3$), indicated in blue, whereas others do not because the bond dipole moments cancel (BCl_3, CCl_4, PF_5, and SF_6).

To summarize, to be polar, a molecule must:

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

5.1.5: Properties of Polar Molecules

Polar molecules tend to align when placed in an electric field with the positive end of the molecule oriented toward the negative plate and the negative end toward the positive plate (Figure 5.1.15). We can use an electrically charged object to attract polar molecules, but nonpolar molecules are not attracted. Also, polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances.

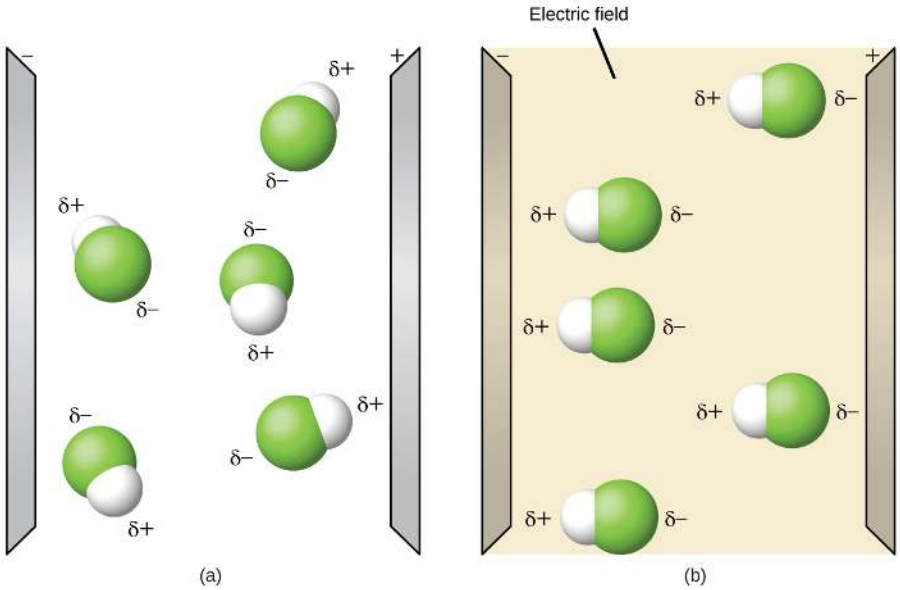


Figure 5.1.15: (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction.

https://chem.libretexts.org/@go/page/393234

Example 5.1.7: Polarity Simulations

Open the molecule polarity simulation and select the "Three Atoms" tab at the top. This should display a molecule ABC with three electronegativity adjustors. You can display or hide the bond moments, molecular dipoles, and partial charges at the right. Turning on the Electric Field will show whether the molecule moves when exposed to a field, similar to Figure 5.1.14

Use the electronegativity controls to determine how the molecular dipole will look for the starting bent molecule if:

a. A and C are very electronegative and B is in the middle of the range.
b. A is very electronegative, and B and C are not.

Solution

a. Molecular dipole moment points immediately between A and C.
b. Molecular dipole moment points along the A–B bond, toward A.

Exercise 5.1.7

Determine the partial charges that will give the largest possible bond dipoles.

Answer

The largest bond moments will occur with the largest partial charges. The two solutions above represent how unevenly the electrons are shared in the bond. The bond moments will be maximized when the electronegativity difference is greatest. The controls for A and C should be set to one extreme, and B should be set to the opposite extreme. Although the magnitude of the bond moment will not change based on whether B is the most electronegative or the least, the direction of the bond moment will.

Summary

VSEPR theory predicts the three-dimensional arrangement of atoms in a molecule. It states that valence electrons will assume an electron-pair geometry that minimizes repulsions between areas of high electron density (bonds and/or lone pairs). Molecular structure, which refers only to the placement of atoms in a molecule and not the electrons, is equivalent to electron-pair geometry only when there are no lone electron pairs around the central atom. A dipole moment measures a separation of charge. For one bond, the bond dipole moment is determined by the difference in electronegativity between the two atoms. For a molecule, the overall dipole moment is determined by both the individual bond moments and how these dipoles are arranged in the molecular structure. Polar molecules (those with an appreciable dipole moment) interact with electric fields, whereas nonpolar molecules do not.

Glossary

axial position
location in a trigonal bipyramidal geometry in which there is another atom at a 180° angle and the equatorial positions are at a 90° angle

bond angle
angle between any two covalent bonds that share a common atom

bond distance
(also, bond length) distance between the nuclei of two bonded atoms

bond dipole moment
separation of charge in a bond that depends on the difference in electronegativity and the bond distance represented by partial charges or a vector

dipole moment

property of a molecule that describes the separation of charge determined by the sum of the individual bond moments based on the molecular structure

electron-pair geometry
arrangement around a central atom of all regions of electron density (bonds, lone pairs, or unpaired electrons)

equatorial position
one of the three positions in a trigonal bipyramidal geometry with 120° angles between them; the axial positions are located at a 90° angle

linear
shape in which two outside groups are placed on opposite sides of a central atom

molecular structure
structure that includes only the placement of the atoms in the molecule

octahedral
shape in which six outside groups are placed around a central atom such that a three-dimensional shape is generated with four groups forming a square and the other two forming the apex of two pyramids, one above and one below the square plane

polar molecule
(also, dipole) molecule with an overall dipole moment

tetrahedral
shape in which four outside groups are placed around a central atom such that a three-dimensional shape is generated with four corners and 109.5° angles between each pair and the central atom

trigonal bipyramidal
shape in which five outside groups are placed around a central atom such that three form a flat triangle with 120° angles between each pair and the central atom, and the other two form the apex of two pyramids, one above and one below the triangular plane

trigonal planar
shape in which three outside groups are placed in a flat triangle around a central atom with 120° angles between each pair and the central atom

valence shell electron-pair repulsion theory (VSEPR)
theory used to predict the bond angles in a molecule based on positioning regions of high electron density as far apart as possible to minimize electrostatic repulsion

vector
quantity having magnitude and direction

This page titled 5.1: Molecular Structure and Polarity is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **7.7: Molecular Structure and Polarity** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

5.2: Valence Bond Theory

Learning Objectives

- Describe the formation of covalent bonds in terms of atomic orbital overlap
- Define and give examples of σ and π bonds

As we know, a scientific theory is a strongly supported explanation for observed natural laws or large bodies of experimental data. For a theory to be accepted, it must explain experimental data and be able to predict behavior. For example, VSEPR theory has gained widespread acceptance because it predicts three-dimensional molecular shapes that are consistent with experimental data collected for thousands of different molecules. However, VSEPR theory does not provide an explanation of chemical bonding.

There are successful theories that describe the electronic structure of atoms. We can use quantum mechanics to predict the specific regions around an atom where electrons are likely to be located: A spherical shape for an *s* orbital, a dumbbell shape for a *p* orbital, and so forth. However, these predictions only describe the orbitals around free atoms. When atoms bond to form molecules, atomic orbitals are not sufficient to describe the regions where electrons will be located in the molecule. A more complete understanding of electron distributions requires a model that can account for the electronic structure of molecules. One popular theory holds that a covalent bond forms when a pair of electrons is shared by two atoms and is simultaneously attracted by the nuclei of both atoms. In the following sections, we will discuss how such bonds are described by valence bond theory and hybridization.

Valence bond theory describes a covalent bond as the overlap of half-filled atomic orbitals (each containing a single electron) that yield a pair of electrons shared between the two bonded atoms. We say that orbitals on two different atoms overlap when a portion of one orbital and a portion of a second orbital occupy the same region of space. According to valence bond theory, a covalent bond results when two conditions are met:

1. an orbital on one atom overlaps an orbital on a second atom and
2. the single electrons in each orbital combine to form an electron pair.

The mutual attraction between this negatively charged electron pair and the two atoms' positively charged nuclei serves to physically link the two atoms through a force we define as a covalent bond. The strength of a covalent bond depends on the extent of overlap of the orbitals involved. Orbitals that overlap extensively form bonds that are stronger than those that have less overlap.

The energy of the system depends on how much the orbitals overlap. Figure 5.2.1 illustrates how the sum of the energies of two hydrogen atoms (the colored curve) changes as they approach each other. When the atoms are far apart there is no overlap, and by convention we set the sum of the energies at zero. As the atoms move together, their orbitals begin to overlap. Each electron begins to feel the attraction of the nucleus in the other atom. In addition, the electrons begin to repel each other, as do the nuclei. While the atoms are still widely separated, the attractions are slightly stronger than the repulsions, and the energy of the system decreases. (A bond begins to form.) As the atoms move closer together, the overlap increases, so the attraction of the nuclei for the electrons continues to increase (as do the repulsions among electrons and between the nuclei). At some specific distance between the atoms, which varies depending on the atoms involved, the energy reaches its lowest (most stable) value. This optimum distance between the two bonded nuclei is the bond distance between the two atoms. The bond is stable because at this point, the attractive and repulsive forces combine to create the lowest possible energy configuration. If the distance between the nuclei were to decrease further, the repulsions between nuclei and the repulsions as electrons are confined in closer proximity to each other would become stronger than the attractive forces. The energy of the system would then rise (making the system destabilized), as shown at the far left of Figure 5.2.1.

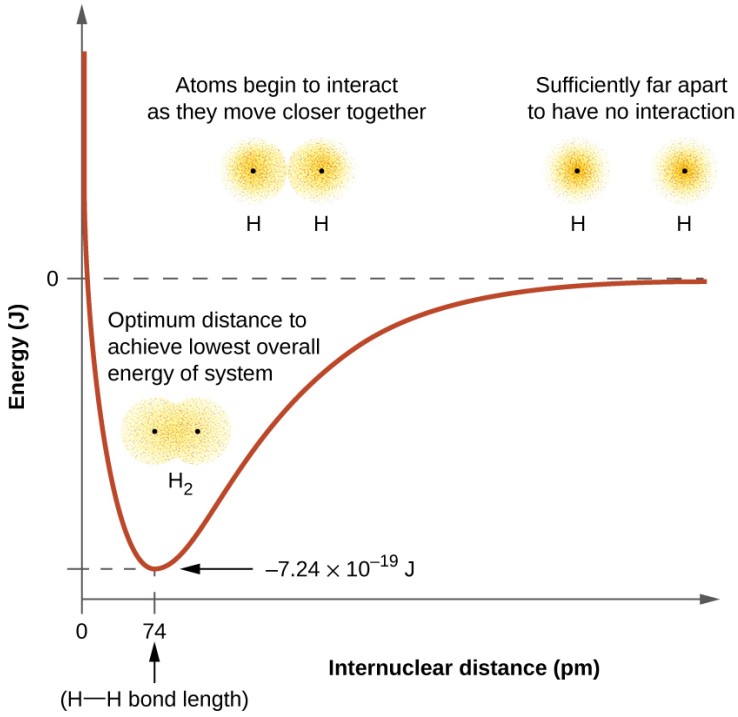


Figure 5.2.1: The interaction of two hydrogen atoms changes as a function of distance. The energy of the system changes as the atoms interact. The lowest (most stable) energy occurs at a distance of 74 pm, which is the bond length observed for the H_2 molecule.

A pair of diagrams are shown and labeled “a” and “b”. Diagram a shows three consecutive images. The first image depicts two separated blurry circles, each labeled with a positive sign and the term “H atom.” The phrase written under them reads, “Sufficiently far apart to have no interaction.” The second image shows the same two circles, but this time they are much closer together and are labeled, “Atoms begin to interact as they move closer together.” The third image shows the two circles overlapping, labeled, “H subscript 2,” and, “Optimum distance to achieve lowest overall energy of system.” Diagram b shows a graph on which the y-axis is labeled “Energy (J),” and the x-axis is labeled, “Internuclear distance (p m).” The midpoint of the y-axis is labeled as zero. The curve on the graph begins at zero p m and high on the y-axis. The graph slopes downward steeply to a point far below the zero joule line on the y-axis and the lowest point reads “0.74 p m” and “H bonded to H bond length.” It is also labeled “ negative 7.24 times 10 superscript negative 19 J.” The graph then rises again to zero J. The graph is accompanied by the same images from diagram a; the first image correlates to the point in the graph where it crosses the zero point on the y-axis, the third image where the graph is lowest.

The bond energy is the difference between the energy minimum (which occurs at the bond distance) and the energy of the two separated atoms. This is the quantity of energy released when the bond is formed. Conversely, the same amount of energy is required to break the bond. For the H_2 molecule shown in Figure 5.2.1, at the bond distance of 74 pm the system is $7.24 \times 10^{-19}\ J$ lower in energy than the two separated hydrogen atoms. This may seem like a small number. However, we know from our earlier description of thermochemistry that bond energies are often discussed on a per-mole basis. For example, it requires $7.24 \times 10^{-19}\ J$ to break one H–H bond, but it takes $4.36 \times 10^{5}\ J$ to break 1 mole of H–H bonds. A comparison of some bond lengths and energies is shown in Table 5.2.1. We can find many of these bonds in a variety of molecules, and this table provides average values. For example, breaking the first C–H bond in CH4 requires 439.3 kJ/mol, while breaking the first C–H bond in H– $CH_2C_6H_5$ (a common paint thinner) requires 375.5 kJ/mol.

Table 5.2.1: Representative Bond Energies and Lengths

Bond	Length (pm)	Energy (kJ/mol)	Bond	Length (pm)	Energy (kJ/mol)
H–H	74	436	C–O	140.1	358
H–C	106.8	413	C = O	119.7	745
H–N	101.5	391	C ≡ O	113.7	1072
H–O	97.5	467	H–Cl	127.5	431
C–C	150.6	347	H–Br	141.4	366

Bond	Length (pm)	Energy (kJ/mol)
C = C	133.5	614
C ≡ C	120.8	839
C–N	142.1	305
C = N	130.0	615
C ≡ N	116.1	891

Bond	Length (pm)	Energy (kJ/mol)
H–I	160.9	298
O–O	148	146
O = O	120.8	498
F–F	141.2	159
Cl–Cl	198.8	243

In addition to the distance between two orbitals, the orientation of orbitals also affects their overlap (other than for two *s* orbitals, which are spherically symmetric). Greater overlap is possible when orbitals are oriented such that they overlap on a direct line between the two nuclei. Figure 5.2.2 illustrates this for two *p* orbitals from different atoms; the overlap is greater when the orbitals overlap end to end rather than at an angle.

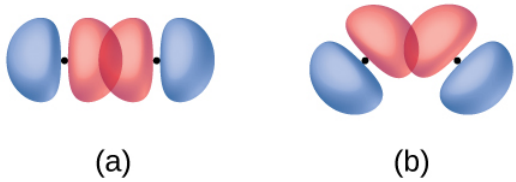


Figure 5.2.2: (a) The overlap of two p orbitals is greatest when the orbitals are directed end to end. (b) Any other arrangement results in less overlap. The dots indicate the locations of the nuclei.

The overlap of two *s* orbitals (as in H_2), the overlap of an *s* orbital and a *p* orbital (as in HCl), and the end-to-end overlap of two *p* orbitals (as in Cl_2) all produce sigma bonds (σ bonds), as illustrated in Figure 5.2.3. A σ bond is a covalent bond in which the electron density is concentrated in the region along the internuclear axis; that is, a line between the nuclei would pass through the center of the overlap region. Single bonds in Lewis structures are described as σ bonds in valence bond theory.

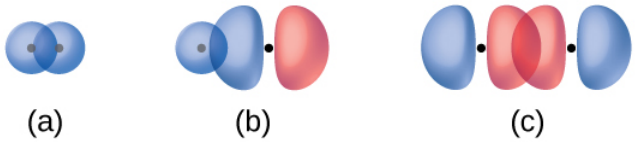


Figure 5.2.3: Sigma (σ) bonds form from the overlap of the following: (a) two s orbitals, (b) an s orbital and a p orbital, and (c) two p orbitals. The dots indicate the locations of the nuclei.

Three diagrams are shown and labeled “a,” “b,” and “c.” Diagram a shows two spherical orbitals lying side by side and overlapping. Diagram b shows one spherical and one peanut-shaped orbital lying near one another so that the spherical orbital overlaps with one end of the peanut-shaped orbital. Diagram c shows two peanut-shaped orbitals lying end to end so that one end of each orbital overlaps the other.

A pi bond (π bond) is a type of covalent bond that results from the side-by-side overlap of two *p* orbitals, as illustrated in Figure 5.2.4. In a π bond, the regions of orbital overlap lie on opposite sides of the internuclear axis. Along the axis itself, there is a node, that is, a plane with no probability of finding an electron.

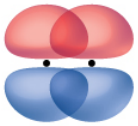
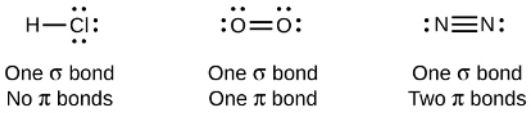


Figure 5.2.4: Pi (π) bonds form from the side-by-side overlap of two p orbitals. The dots indicate the location of the nuclei.

While all single bonds are σ bonds, multiple bonds consist of both σ and π bonds. As the Lewis structures suggest, O_2 contains a double bond, and N_2 contains a triple bond. The double bond consists of one σ bond and one π bond, and the triple bond consists of one σ bond and two π bonds. Between any two atoms, the first bond formed will always be a σ bond, but there can only be one σ bond in any one location. In any multiple bond, there will be one σ bond, and the remaining one or two bonds will be π bonds. These bonds are described in more detail later in this chapter.

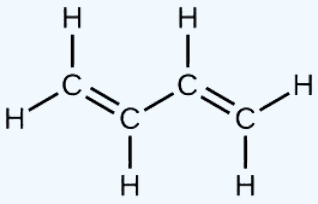


A diagram contains three Lewis structures. The left most structure shows an H atom bonded to a C l atom by a single bond. The C l atom has three lone pairs of electrons. The phrase “One sigma bond No pi bonds” is written below the drawing. The center structure shows two O atoms bonded by a double bond. The O atoms each have two lone pairs of electrons. The phrase “One sigma bond One pi bond” is written below the drawing. The right most structure shows two N atoms bonded by a triple bond. Each N atom has a lone pairs of electrons. The phrase “One sigma bond Two pi bonds” is written below the drawing.

As seen in Table 5.2.1, an average carbon-carbon single bond is 347 kJ/mol, while in a carbon-carbon double bond, the π bond increases the bond strength by 267 kJ/mol. Adding an additional π bond causes a further increase of 225 kJ/mol. We can see a similar pattern when we compare other σ and π bonds. Thus, each individual π bond is generally weaker than a corresponding σ bond between the same two atoms. In a σ bond, there is a greater degree of orbital overlap than in a π bond.

Example 5.2.1: Counting σ and π Bonds

Butadiene, C_4H_6, is used to make synthetic rubber. Identify the number of σ and π bonds contained in this molecule.



Butadiene

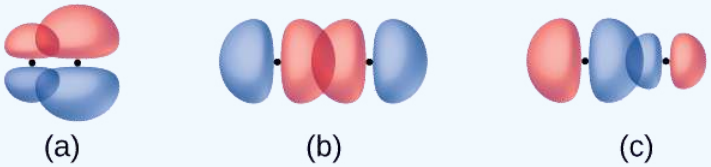
Solution

There are six σ C–H bonds and one σ C–C bond, for a total of seven from the single bonds. There are two double bonds that each have a π bond in addition to the σ bond. This gives a total nine σ and two π bonds overall.

Exercise 5.2.1

Identify each illustration as depicting a σ or π bond:

a. side-by-side overlap of a 4*p* and a 2*p* orbital
b. end-to-end overlap of a 4*p* and 4*p* orbital
c. end-to-end overlap of a 4*p* and a 2*p* orbital



Answer

(a) is a π bond with a node along the axis connecting the nuclei while (b) and (c) are σ bonds that overlap along the axis.

Summary

Valence bond theory describes bonding as a consequence of the overlap of two separate atomic orbitals on different atoms that creates a region with one pair of electrons shared between the two atoms. When the orbitals overlap along an axis containing the nuclei, they form a σ bond. When they overlap in a fashion that creates a node along this axis, they form a π bond.

Glossary

overlap
coexistence of orbitals from two different atoms sharing the same region of space, leading to the formation of a covalent bond

node
plane separating different lobes of orbitals, where the probability of finding an electron is zero

pi bond (π bond)
covalent bond formed by side-by-side overlap of atomic orbitals; the electron density is found on opposite sides of the internuclear axis

sigma bond (σ bond)
covalent bond formed by overlap of atomic orbitals along the internuclear axis

valence bond theory
description of bonding that involves atomic orbitals overlapping to form σ or π bonds, within which pairs of electrons are shared

---

This page titled 5.2: Valence Bond Theory is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **8.2: Valence Bond Theory** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

5.3: Hybrid Atomic Orbitals

Learning Objectives

- Explain the concept of atomic orbital hybridization
- Determine the hybrid orbitals associated with various molecular geometries

Thinking in terms of overlapping atomic orbitals is one way for us to explain how chemical bonds form in diatomic molecules. However, to understand how molecules with more than two atoms form stable bonds, we require a more detailed model. As an example, let us consider the water molecule, in which we have one oxygen atom bonding to two hydrogen atoms. Oxygen has the electron configuration $1s^2 2s^2 2p^4$, with two unpaired electrons (one in each of the two 2*p* orbitals). Valence bond theory would predict that the two O–H bonds form from the overlap of these two 2*p* orbitals with the 1*s* orbitals of the hydrogen atoms. If this were the case, the bond angle would be 90°, as shown in Figure 5.3.1, because *p* orbitals are perpendicular to each other. Experimental evidence shows that the bond angle is 104.5°, not 90°. The prediction of the valence bond theory model does not match the real-world observations of a water molecule; a different model is needed.

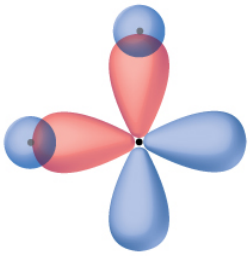


Figure 5.3.1: The hypothetical overlap of two of the 2p orbitals on an oxygen atom (red) with the 1s orbitals of two hydrogen atoms (blue) would produce a bond angle of 90°. This is not consistent with experimental evidence.[1]

Two peanut-shaped orbitals lie perpendicular to one another. They overlap with spherical orbitals to the left and top of the diagram.

Quantum-mechanical calculations suggest why the observed bond angles in H_2O differ from those predicted by the overlap of the 1*s* orbital of the hydrogen atoms with the 2*p* orbitals of the oxygen atom. The mathematical expression known as the wave function, ψ, contains information about each orbital and the wavelike properties of electrons in an isolated atom. When atoms are bound together in a molecule, the wave functions combine to produce new mathematical descriptions that have different shapes. This process of combining the wave functions for atomic orbitals is called hybridization and is mathematically accomplished by the *linear combination of atomic orbitals*, LCAO, (a technique that we will encounter again later). The new orbitals that result are called hybrid orbitals. The valence orbitals in an *isolated* oxygen atom are a 2*s* orbital and three 2*p* orbitals. The valence orbitals in an oxygen atom in a water molecule differ; they consist of four equivalent hybrid orbitals that point approximately toward the corners of a tetrahedron (Figure 5.3.2). Consequently, the overlap of the O and H orbitals should result in a tetrahedral bond angle (109.5°). The observed angle of 104.5° is experimental evidence for which quantum-mechanical calculations give a useful explanation: Valence bond theory must include a hybridization component to give accurate predictions.

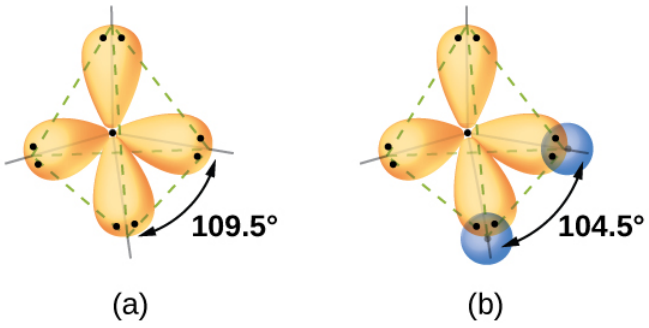


Figure 5.3.2: (a) A water molecule has four regions of electron density, so VSEPR theory predicts a tetrahedral arrangement of hybrid orbitals. (b) Two of the hybrid orbitals on oxygen contain lone pairs, and the other two overlap with the 1s orbitals of hydrogen atoms to form the O–H bonds in H_2O. This description is more consistent with the experimental structure.

Two diagrams are shown and labeled “a” and “b.” Diagram a shows two peanut-shaped orbitals lying in a tetrahedral arrangement around the letter “O.” Diagram b shows the same two orbitals, but they now overlap to the top and to the left with two spherical orbitals, each labeled “H.” A pair of electrons occupies each lobe of the peanut-shaped orbitals.

The following ideas are important in understanding hybridization:

1. Hybrid orbitals do not exist in isolated atoms. They are formed only in covalently bonded atoms.
2. Hybrid orbitals have shapes and orientations that are very different from those of the atomic orbitals in isolated atoms.
3. A set of hybrid orbitals is generated by combining atomic orbitals. The number of hybrid orbitals in a set is equal to the number of atomic orbitals that were combined to produce the set.
4. All orbitals in a set of hybrid orbitals are equivalent in shape and energy.
5. The type of hybrid orbitals formed in a bonded atom depends on its electron-pair geometry as predicted by the VSEPR theory.
6. Hybrid orbitals overlap to form σ bonds. Unhybridized orbitals overlap to form π bonds.

In the following sections, we shall discuss the common types of hybrid orbitals.

5.3.1: sp Hybridization

The beryllium atom in a gaseous $BeCl_2$ molecule is an example of a central atom with no lone pairs of electrons in a linear arrangement of three atoms. There are two regions of valence electron density in the $BeCl_2$ molecule that correspond to the two covalent Be–Cl bonds. To accommodate these two electron domains, two of the Be atom's four valence orbitals will mix to yield two hybrid orbitals. This hybridization process involves mixing of the valence *s* orbital with one of the valence *p* orbitals to yield two equivalent *sp* hybrid orbitals that are oriented in a linear geometry (Figure 5.3.3). In this figure, the set of *sp* orbitals appears similar in shape to the original *p* orbital, but there is an important difference. The number of atomic orbitals combined always equals the number of hybrid orbitals formed. The *p* orbital is one orbital that can hold up to two electrons. The *sp* set is two equivalent orbitals that point 180° from each other. The two electrons that were originally in the *s* orbital are now distributed to the two *sp* orbitals, which are half filled. In gaseous $BeCl_2$, these half-filled hybrid orbitals will overlap with orbitals from the chlorine atoms to form two identical σ bonds.

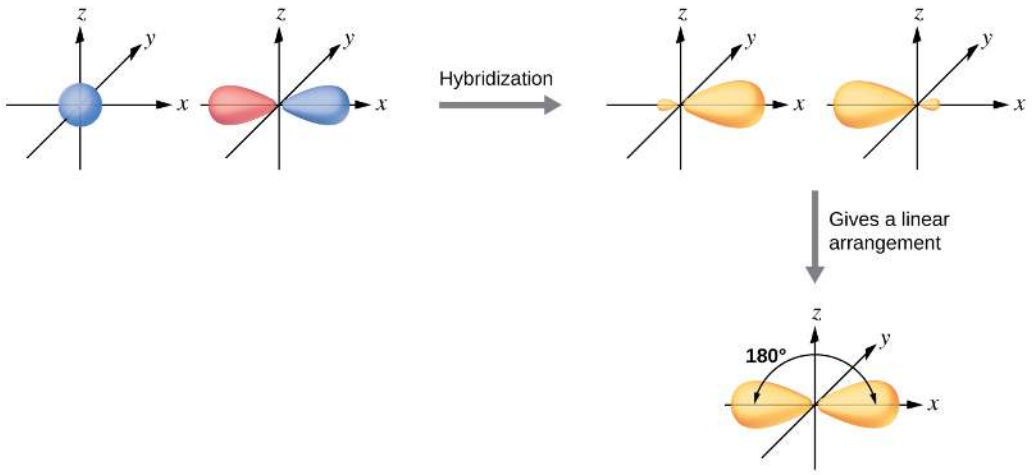


Figure 5.3.3: Hybridization of an s orbital (blue) and a p orbital (red) of the same atom produces two sp hybrid orbitals (yellow). Each hybrid orbital is oriented primarily in just one direction. Note that each sp orbital contains one lobe that is significantly larger than the other. The set of two sp orbitals are oriented at 180°, which is consistent with the geometry for two domains.

A series of three diagrams connected by a right-facing arrow that is labeled, "Hybridization," and a downward-facing arrow labeled, "Gives a linear arrangement," are shown. The first diagram shows a blue spherical orbital and a red, peanut-shaped orbital, each placed on an X, Y, Z axis system. The second diagram shows the same two orbitals, but they are now purple and have one enlarged lobe and one smaller lobe. Each lies along the x-axis in the drawing. The third diagram shows the same two orbitals, but their smaller lobes now overlap along the x-axis while their larger lobes are located at and labeled as "180 degrees" from one another.

We illustrate the electronic differences in an isolated Be atom and in the bonded Be atom in the orbital energy-level diagram in Figure 5.3.4. These diagrams represent each orbital by a horizontal line (indicating its energy) and each electron by an arrow. Energy increases toward the top of the diagram. We use one upward arrow to indicate one electron in an orbital and two arrows (up and down) to indicate two electrons of opposite spin.

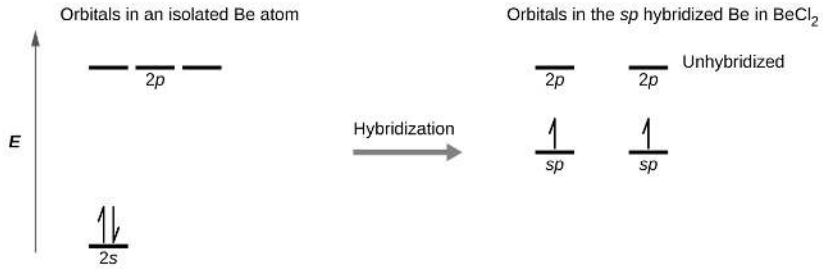


Figure 5.3.4: This orbital energy-level diagram shows the sp hybridized orbitals on Be in the linear $BeCl_2$ molecule. Each of the two sp hybrid orbitals holds one electron and is thus half filled and available for bonding via overlap with a Cl 3p orbital.

A diagram is shown in two parts, connected by a right facing arrow labeled, “Hybridization.” The left diagram shows an up-facing arrow labeled, “E.” To the lower right of the arrow is a short, horizontal line labeled, “2 s,” that has two vertical half-arrows facing up and down on it. To the upper right of the arrow are a series of three short, horizontal lines labeled, “2 p.” Above these two sets of lines is the phrase, “Orbitals in an isolated B e atom.” The right side of the diagram shows two short, horizontal lines placed halfway up the space and each labeled, “s p.” An upward-facing half arrow is drawn vertically on each line. Above these lines are two other short, horizontal lines, each labeled, “2 p.” Above these two sets of lines is the phrase, “Orbitals in the s p hybridized B e in B e C l subscript 2.”

When atomic orbitals hybridize, the valence electrons occupy the newly created orbitals. The Be atom had two valence electrons, so each of the *sp* orbitals gets one of these electrons. Each of these electrons pairs up with the unpaired electron on a chlorine atom when a hybrid orbital and a chlorine orbital overlap during the formation of the Be–Cl bonds. Any central atom surrounded by just two regions of valence electron density in a molecule will exhibit *sp* hybridization. Other examples include the mercury atom in the linear $HgCl_2$ molecule, the zinc atom in $Zn(CH_3)_2$, which contains a linear C–Zn–C arrangement, and the carbon atoms in HCCH and CO_2.

5.3.2: sp^2 Hybridization

The valence orbitals of a central atom surrounded by three regions of electron density consist of a set of three sp^2 hybrid orbitals and one unhybridized *p* orbital. This arrangement results from sp^2 hybridization, the mixing of one *s* orbital and two *p* orbitals to produce three identical hybrid orbitals oriented in a trigonal planar geometry (Figure 5.3.5).

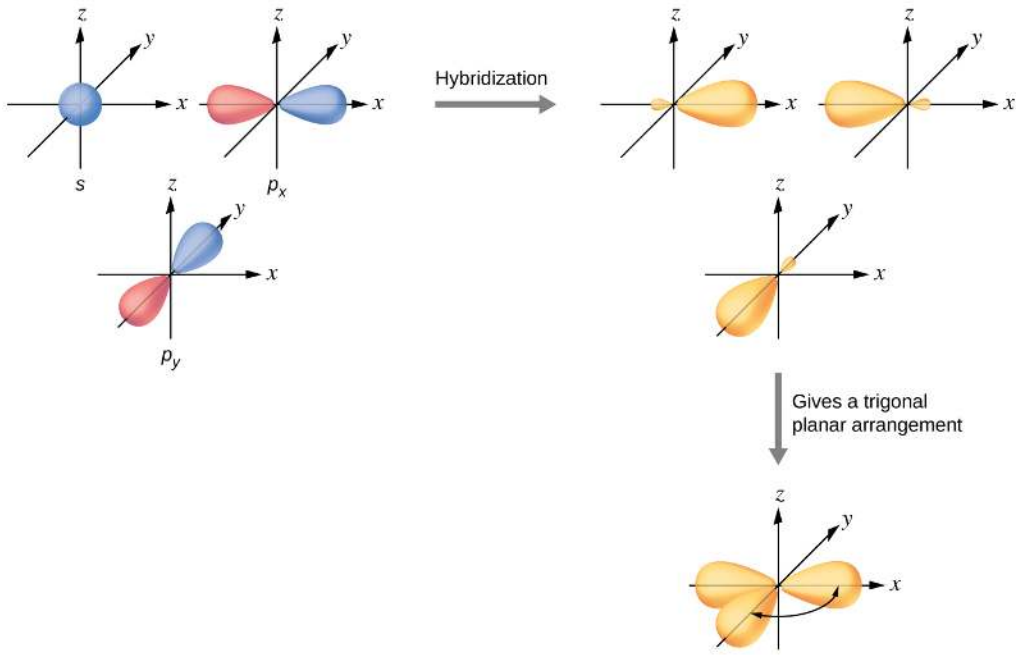


Figure 5.3.5: The hybridization of an s orbital (blue) and two p orbitals (red) produces three equivalent sp^2 hybridized orbitals (yellow) oriented at 120° with respect to each other. The remaining unhybridized p orbital is not shown here, but is located along the z axis.

A series of three diagrams connected by a right-facing arrow that is labeled, “Hybridization,” and a downward-facing arrow labeled, “Gives a trigonal planar arrangement,” are shown. The first diagram shows a blue spherical orbital and two red, peanut-shaped orbitals, each placed on an X, Y, Z axis system. The two red orbitals are located on the x and z axes, respectively. The second diagram shows the same three orbitals, but they are now purple and have one enlarged lobe and one smaller lobe. Each lies in a different axis in the drawing. The third diagram shows the same three orbitals, but their smaller lobes now overlap while their larger lobes are located at and labeled as “120 degrees” from one another.

Although quantum mechanics yields the “plump” orbital lobes as depicted in Figure 5.3.5, sometimes for clarity these orbitals are drawn thinner and without the minor lobes, as in Figure 5.3.6, to avoid obscuring other features of a given illustration. We will use these “thinner” representations whenever the true view is too crowded to easily visualize.

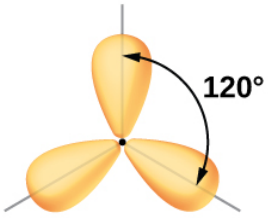


Figure 5.3.6: This alternate way of drawing the trigonal planar sp^2 hybrid orbitals is sometimes used in more crowded figures.

Three balloon-like orbitals are shown, and connect together near their narrower ends in one plane. The angle between a pair of lobes is labeled, “120 degrees.”

The observed structure of the borane molecule, BH_3, suggests sp^2 hybridization for boron in this compound. The molecule is trigonal planar, and the boron atom is involved in three bonds to hydrogen atoms (Figure 5.3.7).

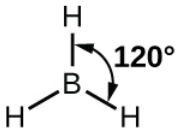


Figure 5.3.7: BH_3 is an electron-deficient molecule with a trigonal planar structure.

A boron atom is shown connected to three hydrogen atoms, which are arranged around it like a pyramid. The angle from one line connecting the boron atom to a hydrogen atom to another line connecting the boron atom to a hydrogen atom is labeled, “120 degrees.”

We can illustrate the comparison of orbitals and electron distribution in an isolated boron atom and in the bonded atom in BH_3 as shown in the orbital energy level diagram in Figure 5.3.8. We redistribute the three valence electrons of the boron atom in the three

sp^2 hybrid orbitals, and each boron electron pairs with a hydrogen electron when B–H bonds form.

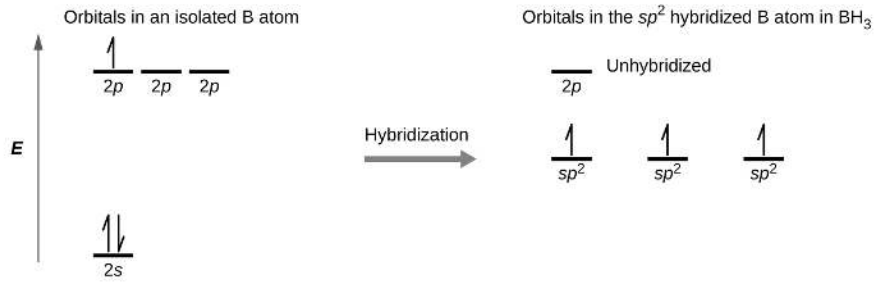


Figure 5.3.8: In an isolated B atom, there are one 2s and three 2p valence orbitals. When boron is in a molecule with three regions of electron density, three of the orbitals hybridize and create a set of three sp^2 orbitals and one unhybridized 2p orbital. The three half-filled hybrid orbitals each overlap with an orbital from a hydrogen atom to form three σ bonds in BH_3.

A diagram is shown in two parts, connected by a right facing arrow labeled, “Hybridization.” The left diagram shows an up-facing arrow labeled “E.” To the lower right of the arrow is a short, horizontal line labeled, “2 s,” that has two vertical half-arrows facing up and down on it. To the upper right of the arrow are a series of three short, horizontal lines labeled, “2 p.” Above both sets of these lines is the phrase, “Orbitals in an isolated B atom.” One of the lines has a vertical, up-facing arrow drawn on it. The right side of the diagram shows three short, horizontal lines placed halfway up the space and each labeled, “s p superscript 2.” An upward-facing half arrow is drawn vertically on each line. Above these lines is one other short, horizontal line, labeled, “2 p.” Above both sets of lines is the phrase, “Orbitals in the s p superscript 2 hybridized B atom in B H subscript 3.”

Any central atom surrounded by three regions of electron density will exhibit sp^2 hybridization. This includes molecules with a lone pair on the central atom, such as ClNO (Figure 5.3.9), or molecules with two single bonds and a double bond connected to the central atom, as in formaldehyde, CH_2O, and ethene, H_2CCH_2.

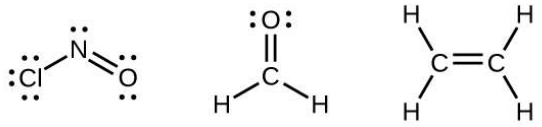


Figure 5.3.9: The central atom(s) in each of the structures shown contain three regions of electron density and are sp^2 hybridized. As we know from the discussion of VSEPR theory, a region of electron density contains all of the electrons that point in one direction. A lone pair, an unpaired electron, a single bond, or a multiple bond would each count as one region of electron density.

Three Lewis structures are shown. The left-hand structure shows a chlorine atom surrounded by three lone pairs of electrons single bonded to a nitrogen atom with one lone pair of electrons and double bonded to an oxygen atom with two lone pairs of electrons. The middle structure shows a carbon atom single bonded to two hydrogen atoms and double bonded to an oxygen atom that has two lone pairs of electrons. The right-hand structure shows two carbon atoms, double bonded to one another and each single bonded to two hydrogen atoms.

5.3.3: sp^3 Hybridization

The valence orbitals of an atom surrounded by a tetrahedral arrangement of bonding pairs and lone pairs consist of a set of four sp^3 hybrid orbitals. The hybrids result from the mixing of one *s* orbital and all three *p* orbitals that produces four identical sp^3 hybrid orbitals (Figure 5.3.10). Each of these hybrid orbitals points toward a different corner of a tetrahedron.

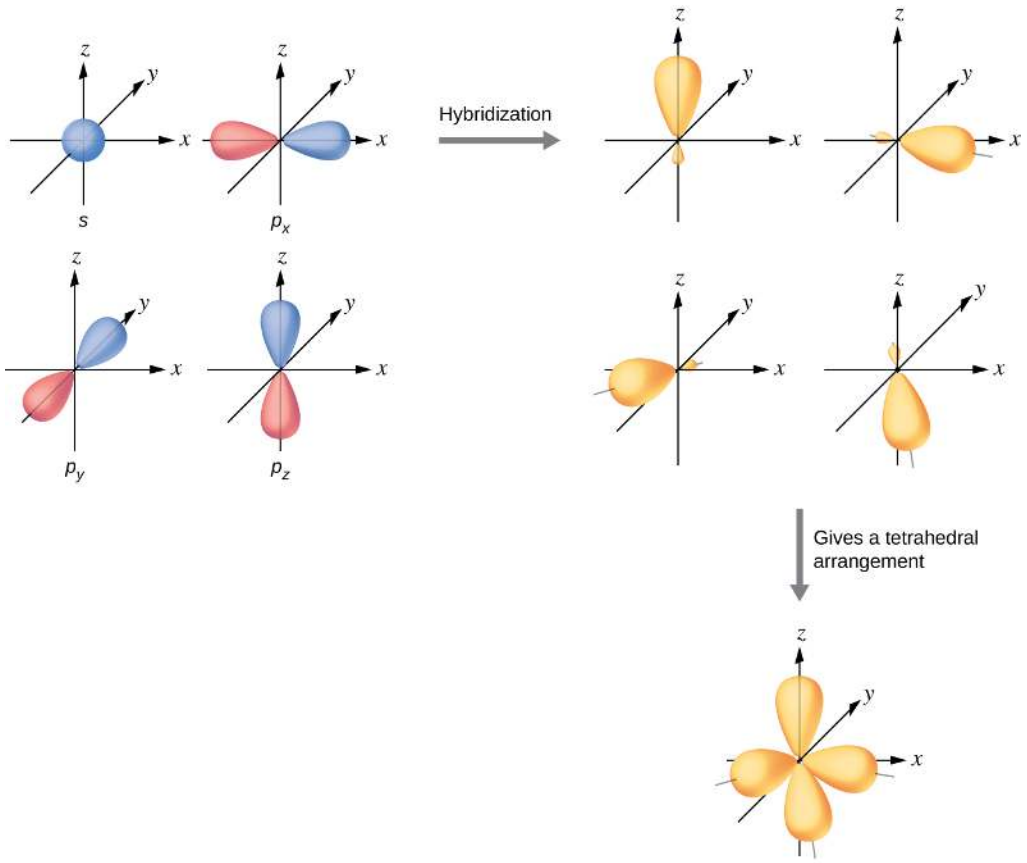


Figure 5.3.10: The hybridization of an s orbital (blue) and three p orbitals (red) produces four equivalent sp^3 hybridized orbitals (yellow) oriented at 109.5° with respect to each other.

A series of three diagrams connected by a right-facing arrow that is labeled, “Hybridization,” and a downward-facing arrow labeled, “Gives a tetrahedral arrangement,” are shown. The first diagram shows a blue spherical orbital and three red, peanut-shaped orbitals, each placed on an x, y, z axis system. The three red orbitals are located on the x , y and z axes, respectively. The second diagram shows the same four orbitals, but they are now purple and have one enlarged lobe and one smaller lobe. Each lies in a different axis in the drawing. The third diagram shows the same four orbitals, but their smaller lobes now overlap to form a tetrahedral structure.

A molecule of methane, CH_4, consists of a carbon atom surrounded by four hydrogen atoms at the corners of a tetrahedron. The carbon atom in methane exhibits sp^3 hybridization. We illustrate the orbitals and electron distribution in an isolated carbon atom and in the bonded atom in CH_4 in Figure 5.3.11. The four valence electrons of the carbon atom are distributed equally in the hybrid orbitals, and each carbon electron pairs with a hydrogen electron when the C–H bonds form.

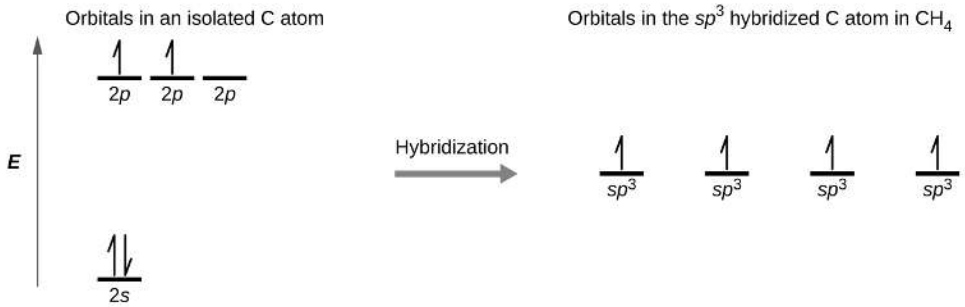


Figure 5.3.11: The four valence atomic orbitals from an isolated carbon atom all hybridize when the carbon bonds in a molecule like CH_4 with four regions of electron density. This creates four equivalent sp^3 hybridized orbitals. Overlap of each of the hybrid orbitals with a hydrogen orbital creates a C–H σ bond.

A diagram is shown in two parts, connected by a right facing arrow labeled, “Hybridization.” The left diagram shows an up-facing arrow labeled “E.” To the lower right of the arrow is a short, horizontal line labeled, “2 s,” that has two vertical half-arrows facing up and down on it. To the upper right of the arrow are a series of three short, horizontal lines labeled, “2 p.” Two of the lines have a vertical, up-facing arrow drawn on them. Above both sets of lines is the phrase, “Orbitals in an isolated C atom.” The right side of the diagram shows four short, horizontal lines placed halfway up the space and each labeled, “s p superscript 3.” An upward-facing half arrow is drawn vertically on each line. Above these lines is the phrase, “Orbitals in the s p superscript 3 hybridized C atom in C H subscript 4.”

In a methane molecule, the 1*s* orbital of each of the four hydrogen atoms overlaps with one of the four sp^3 orbitals of the carbon atom to form a sigma (σ) bond. This results in the formation of four strong, equivalent covalent bonds between the carbon atom and each of the hydrogen atoms to produce the methane molecule, CH_4.

The structure of ethane, C_2H_6, is similar to that of methane in that each carbon in ethane has four neighboring atoms arranged at the corners of a tetrahedron—three hydrogen atoms and one carbon atom (Figure 5.3.10). However, in ethane an sp^3 orbital of one carbon atom overlaps end to end with an sp^3 orbital of a second carbon atom to form a σ bond between the two carbon atoms. Each of the remaining sp^3 hybrid orbitals overlaps with an *s* orbital of a hydrogen atom to form carbon–hydrogen σ bonds. The structure and overall outline of the bonding orbitals of ethane are shown in Figure 5.3.12 The orientation of the two CH_3 groups is not fixed relative to each other. Experimental evidence shows that rotation around σ bonds occurs easily.

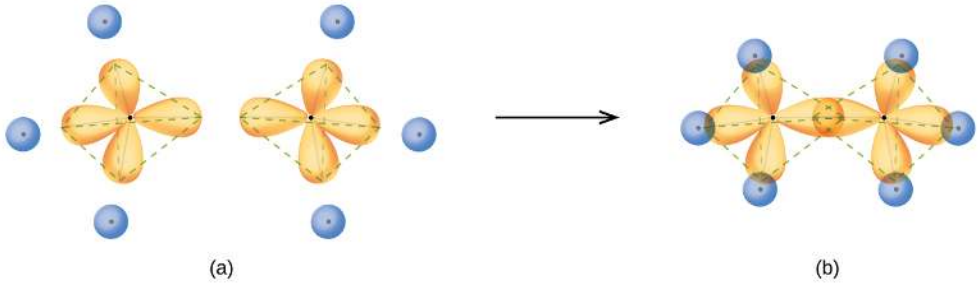


Figure 5.3.12: (a) In the ethane molecule, C_2H_6, each carbon has four sp^3 orbitals. (b) These four orbitals overlap to form seven σ bonds.

Two diagrams are shown and labeled “a” and “b.” Diagram a shows two carbon atoms, each surrounded by their four s p subscript three hybridized orbitals in a three dimensional arrangement. Each of the orbitals is shown overlapping with a spherical hydrogen atom. Diagram b shows the same general arrangement, but the hydrogen atoms are just represented by an, “H” and their spherical orbitals are not shown.

An sp^3 hybrid orbital can also hold a lone pair of electrons. For example, the nitrogen atom in ammonia is surrounded by three bonding pairs and a lone pair of electrons directed to the four corners of a tetrahedron. The nitrogen atom is sp^3 hybridized with one hybrid orbital occupied by the lone pair.

The molecular structure of water is consistent with a tetrahedral arrangement of two lone pairs and two bonding pairs of electrons. Thus we say that the oxygen atom is sp^3 hybridized, with two of the hybrid orbitals occupied by lone pairs and two by bonding pairs. Since lone pairs occupy more space than bonding pairs, structures that contain lone pairs have bond angles slightly distorted from the ideal. Perfect tetrahedra have angles of 109.5°, but the observed angles in ammonia (107.3°) and water (104.5°) are slightly smaller. Other examples of sp^3 hybridization include CCl_4, PCl_3, and NCl_3.

5.3.4: sp^3d and sp^3d^2 Hybridization

To describe the five bonding orbitals in a trigonal bipyramidal arrangement, we must use five of the valence shell atomic orbitals (the *s* orbital, the three *p* orbitals, and one of the *d* orbitals), which gives five sp^3d hybrid orbitals. With an octahedral arrangement of six hybrid orbitals, we must use six valence shell atomic orbitals (the *s* orbital, the three *p* orbitals, and two of the *d* orbitals in its valence shell), which gives six sp^3d^2 hybrid orbitals. These hybridizations are only possible for atoms that have *d* orbitals in their valence subshells (that is, not those in the first or second period).

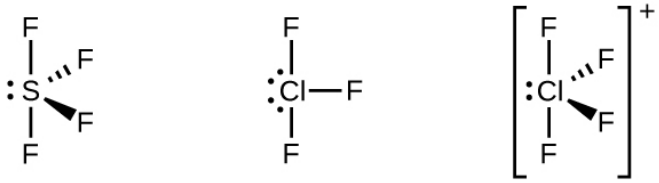


Figure 5.3.13: The three compounds pictured exhibit sp^3d hybridization in the central atom and a trigonal bipyramid form. SF_4 and ClF_4^+ *have one lone pair of electrons on the central atom, and* ClF_3 *has two lone pairs giving it the T-shape shown.*

Three Lewis structures are shown along with designations of molecular shape. The left image shows a sulfur atom singly bonded to four fluorine atoms. The sulfur atom has one lone pair of electrons while each fluorine has three. Two fluorine atoms are drawn vertically up and down from the sulfur while the other two are shown going into and out of the page. The second structure shows one chlorine atom singly bonded to three fluorine atoms. The chlorine has two lone pairs of electrons while each fluorine has three. Two fluorine atoms are drawn vertically up and down from the sulfur while the other is shown horizontally. The right structure shows a chlorine atom singly bonded to four fluorine atoms. The chlorine atom has one lone pair of electrons and a superscript plus sign, while each fluorine has three lone pairs of electrons. Two fluorine atoms are drawn vertically up and down from the sulfur while the other two are shown going into and out of the page.

In a molecule of phosphorus pentachloride, PCl_5, there are five P–Cl bonds (thus five pairs of valence electrons around the phosphorus atom) directed toward the corners of a trigonal bipyramid. We use the 3*s* orbital, the three 3*p* orbitals, and one of the 3*d* orbitals to form the set of five sp^3d hybrid orbitals (Figure 5.3.13) that are involved in the P–Cl bonds. Other atoms that exhibit sp^3d hybridization include the sulfur atom in SF_4 and the chlorine atoms in ClF_3 and in ClF_4^+. (The electrons on fluorine atoms are omitted for clarity.)

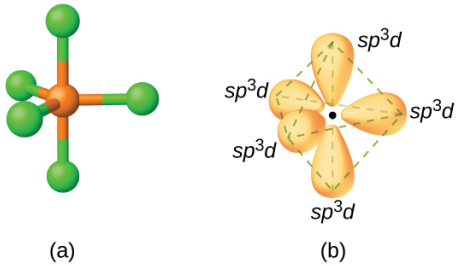


Figure 5.3.14: (a) The five regions of electron density around phosphorus in PCl_5 require five hybrid sp^3d orbitals. (b) These orbitals combine to form a trigonal bipyramidal structure with each large lobe of the hybrid orbital pointing at a vertex. As before, there are also small lobes pointing in the opposite direction for each orbital (not shown for clarity).

Two images are shown and labeled “a” and “b.” Image a depicts a ball-and-stick model in a trigonal bipyramidal arrangement. Image b depicts the hybrid orbitals in the same arrangement and each is labeled, “s p superscript three d.”

The sulfur atom in sulfur hexafluoride, SF_6, exhibits sp^3d^2 hybridization. A molecule of sulfur hexafluoride has six bonding pairs of electrons connecting six fluorine atoms to a single sulfur atom. There are no lone pairs of electrons on the central atom. To bond six fluorine atoms, the 3*s* orbital, the three 3*p* orbitals, and two of the 3*d* orbitals form six equivalent sp^3d^2 hybrid orbitals, each directed toward a different corner of an octahedron. Other atoms that exhibit sp^3d^2 hybridization include the phosphorus atom in PCl_6^-, the iodine atom in the interhalogens IF_6^+, IF_5, ICl_4^-, IF_4^- and the xenon atom in XeF_4.

https://chem.libretexts.org/@go/page/393236

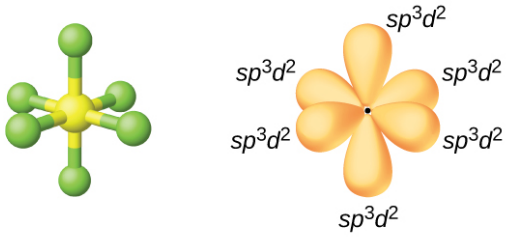


Figure 5.3.15: (a) Sulfur hexafluoride, SF_6, has an octahedral structure that requires sp^3d^2 hybridization. (b) The six sp^3d^2 orbitals form an octahedral structure around sulfur. Again, the minor lobe of each orbital is not shown for clarity.

Two images are shown and labeled “a” and “b.” Image a depicts a ball-and-stick model in an octahedral arrangement. Image b depicts the hybrid orbitals in the same arrangement and each is labeled, “s p superscript three d superscript two.”

5.3.5: Assignment of Hybrid Orbitals to Central Atoms

The hybridization of an atom is determined based on the number of regions of electron density that surround it. The geometrical arrangements characteristic of the various sets of hybrid orbitals are shown in Figure 5.3.16. These arrangements are identical to those of the electron-pair geometries predicted by VSEPR theory. VSEPR theory predicts the shapes of molecules, and hybrid orbital theory provides an explanation for how those shapes are formed. To find the hybridization of a central atom, we can use the following guidelines:

1. Determine the Lewis structure of the molecule.
2. Determine the number of regions of electron density around an atom using VSEPR theory, in which single bonds, multiple bonds, radicals, and lone pairs each count as one region.
3. Assign the set of hybridized orbitals from Figure 5.3.16 that corresponds to this geometry.

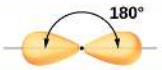
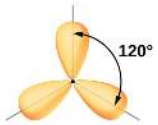
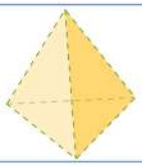
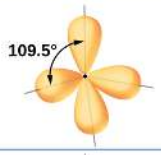
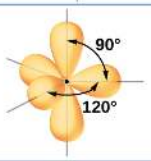
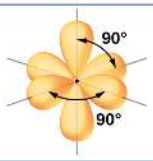
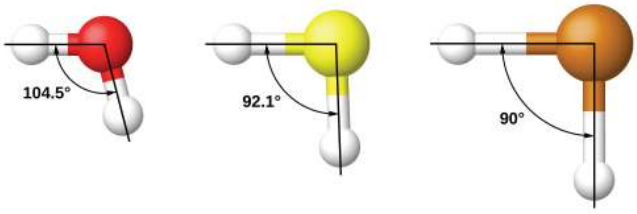
Regions of Electron Density	Arrangement		Hybridization	
2		linear	*sp*	
3		trigonal planar	sp^2	
4		tetrahedral	sp^3	
5		trigonal bipyramidal	sp^3d	
6		octahedral	sp^3d^2	

Figure 5.3.16: The shapes of hybridized orbital sets are consistent with the electron-pair geometries. For example, an atom surrounded by three regions of electron density is sp^2 hybridized, and the three sp^2 orbitals are arranged in a trigonal planar fashion.

A table is shown that is composed of five columns and six rows. The header row contains the phrases, “Regions of electron density,” “Arrangement,” (which has two columns below it), and “Hybridization,” (which has two columns below it). The first column contains the numbers “2,” “3,” “4,” “5,” and “6.” The second column contains images of a line, a triangle, a three sided pyramid, a trigonal bipyramid, and an eight-faced ocatahedron. The third column contains the terms, “Linear,” “Trigonal planar,” “Tetrahedral,” “Trigonal bipyramidal,” and “Octahedral.” The fourth column contains the terms “s p,” “s p superscript 2,” “s p superscript 3,” “s p superscript 3 d,” and “s p superscript 3 d superscript 2.” The last column contains drawings of the molecules beginning with a peanut-shaped structure marked with an angle of “180 degrees.” The second structure is made up of three equal-sized, rounded structures connected at one point with an angle of “120 degrees,” while the third structure is a three-dimensional arrangement of four equal-sized, rounded structures labeled as “109.5 degrees.” The fourth structure is made up of five equal-sized, rounded structures connected at “120 and 90 degrees,” while the fifth structure has six equal-sized, rounded structures connected at “90 degrees.”

> *It is important to remember that hybridization was devised to rationalize experimentally observed molecular geometries, not the other way around.*

The model works well for molecules containing small central atoms, in which the valence electron pairs are close together in space. However, for larger central atoms, the valence-shell electron pairs are farther from the nucleus, and there are fewer repulsions. Their compounds exhibit structures that are often not consistent with VSEPR theory, and hybridized orbitals are not necessary to explain the observed data.



Three Lewis structures are shown. The left structure shows an oxygen atom with two lone pairs of electrons single bonded to two hydrogen atoms. The middle structure is made up of a sulfur atom with two lone pairs of electrons single bonded to two hydrogen atoms. The right structure is made up of a tellurium atom with two lone pairs of electrons single bonded to two hydrogen atoms. From left to right, the bond angles of each molecule decrease.

For example, we have discussed the H–O–H bond angle in H_2O, 104.5°, which is more consistent with sp^3 hybrid orbitals (109.5°) on the central atom than with 2*p* orbitals (90°). Sulfur is in the same group as oxygen, and H_2S has a similar Lewis structure. However, it has a much smaller bond angle (92.1°), which indicates much less hybridization on sulfur than oxygen. Continuing down the group, tellurium is even larger than sulfur, and for H_2Te, the observed bond angle (90°) is consistent with overlap of the 5*p* orbitals, without invoking hybridization. We invoke hybridization where it is necessary to explain the observed structures.

Example 5.3.1: Assigning Hybridization

Ammonium sulfate is important as a fertilizer. What is the hybridization of the sulfur atom in the sulfate ion, SO_4^{2-}?

Solution

The Lewis structure of sulfate shows there are four regions of electron density.

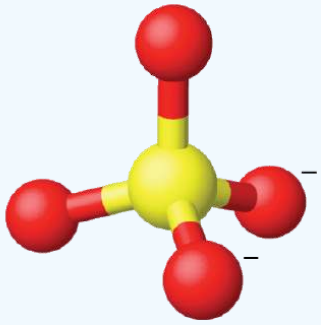


Figure 5.3.16).

A structure is shown in which a sulfur atom is bonded to four oxygen atoms in a tetrahedral arrangement. Two of the oxygen atoms have a negative charge.

Exercise 5.3.1

What is the hybridization of the selenium atom in SeF_4?



A Lewis structure is shown in which four fluorine atoms are each attached to one sulfur atom. Two of the attached fluorine atoms are vertically attached up and down, while two are attached into and out of the page to the right. The sulfur also has one lone pair of electrons attached to the left of the structure.

Answer

The selenium atom is sp^3d hybridized.

https://chem.libretexts.org/@go/page/393236

Example 5.3.2: Assigning Hybridization

Urea, $NH_2C(O)NH_2$, is sometimes used as a source of nitrogen in fertilizers. What is the hybridization of each nitrogen and carbon atom in urea?

Solution

The Lewis structure of urea is

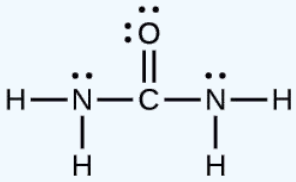


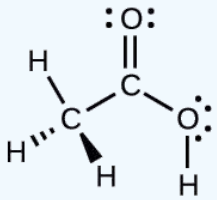
Figure 5.3.16). This is the hybridization of the nitrogen atoms in urea.

A Lewis structure is shown in which a carbon atom is double bonded to an oxygen atom that has two lone pairs of electrons. The carbon atom forms single bonds to two nitrogen atoms. Each nitrogen is single bonded to two hydrogen atoms, and each nitrogen atoms has one lone pair of electrons.

The carbon atom is surrounded by three regions of electron density, positioned in a trigonal planar arrangement. The hybridization in a trigonal planar electron pair geometry is sp^2 (Figure 5.3.16), which is the hybridization of the carbon atom in urea.

Exercise 5.3.1

Acetic acid, $H_3CC(O)OH$, is the molecule that gives vinegar its odor and sour taste. What is the hybridization of the two carbon atoms in acetic acid?



A Lewis structure is shown in which a carbon atom is double bonded to an oxygen atom that has two lone pairs of electrons and single bonded to another oxygen atom that is single boned to a hydrogen atom. This second oxygen atom has two lone pairs of electrons. The carbon is also single bonded to a carbon atom that is single bonded to three hydrogen atoms.

Answer

$H_3\underline{C}$, sp^3; $\underline{C}(O)OH$, sp^2

Summary

We can use hybrid orbitals, which are mathematical combinations of some or all of the valence atomic orbitals, to describe the electron density around covalently bonded atoms. These hybrid orbitals either form sigma (σ) bonds directed toward other atoms of the molecule or contain lone pairs of electrons. We can determine the type of hybridization around a central atom from the geometry of the regions of electron density about it. Two such regions imply *sp* hybridization; three, sp^2 hybridization; four, sp^3 hybridization; five, sp^3d hybridization; and six, sp^3d^2 hybridization. Pi (π) bonds are formed from unhybridized atomic orbitals (*p* or *d* orbitals).

5.3.5.1: Footnotes

1. Note that orbitals may sometimes be drawn in an elongated “balloon” shape rather than in a more realistic “plump” shape in order to make the geometry easier to visualize.

5.3.5.2: Glossary

hybrid orbital
orbital created by combining atomic orbitals on a central atom

hybridization
model that describes the changes in the atomic orbitals of an atom when it forms a covalent compound

***sp* hybrid orbital**
one of a set of two orbitals with a linear arrangement that results from combining one *s* and one *p* orbital

***sp*^{2} hybrid orbital**
one of a set of three orbitals with a trigonal planar arrangement that results from combining one *s* and two *p* orbitals

***sp*^{3} hybrid orbital**
one of a set of four orbitals with a tetrahedral arrangement that results from combining one *s* and three *p* orbitals

***sp*^{3}*d* hybrid orbital**
one of a set of five orbitals with a trigonal bipyramidal arrangement that results from combining one *s*, three *p*, and one *d* orbital

***sp*^{3}*d*^{2} hybrid orbital**
one of a set of six orbitals with an octahedral arrangement that results from combining one *s*, three *p*, and two *d* orbitals

---

This page titled 5.3: Hybrid Atomic Orbitals is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **8.3: Hybrid Atomic Orbitals** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

5.4: Multiple Bonds

Learning Objectives

- Describe multiple covalent bonding in terms of atomic orbital overlap
- Relate the concept of resonance to π-bonding and electron delocalization

The hybrid orbital model appears to account well for the geometry of molecules involving single covalent bonds. Is it also capable of describing molecules containing double and triple bonds? We have already discussed that multiple bonds consist of σ and π bonds. Next we can consider how we visualize these components and how they relate to hybrid orbitals. The Lewis structure of ethene, C_2H_4, shows us that each carbon atom is surrounded by one other carbon atom and two hydrogen atoms.

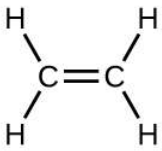


Figure 5.4.2).

A Lewis structure is shown in which two carbon atoms are bonded together by a double bond. Each carbon atom is bonded to two hydrogen atoms by a single bond.

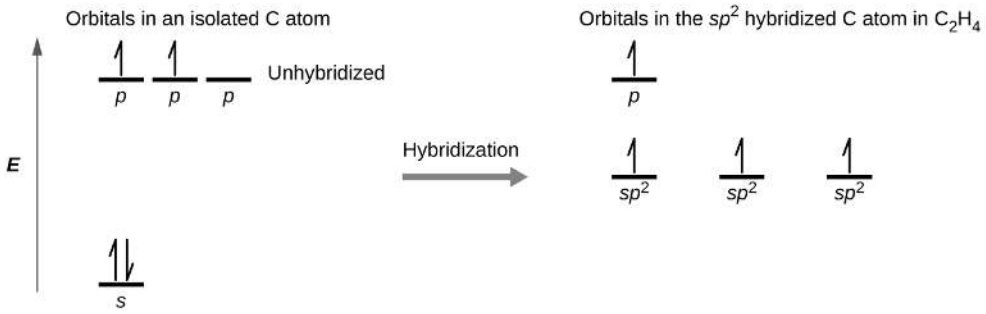


Figure 5.4.1: In ethene, each carbon atom is sp^2 hybridized, and the sp^2 orbitals and the p orbital are singly occupied. The hybrid orbitals overlap to form σ bonds, while the p orbitals on each carbon atom overlap to form a π bond.

A diagram is shown in two parts, connected by a right facing arrow labeled, “Hybridization.” The left diagram shows an up-facing arrow labeled, “E.” To the lower right of the arrow is a short, horizontal line labeled, “2 s,” that has two vertical half-arrows facing up and down on it. To the upper right of the arrow are a series of three short, horizontal lines labeled, “2 p.” Above both sets of lines is the phrase, “Orbitals in an isolated C atom.” Two of the lines have vertical, up-facing arrows drawn on them. The right side of the diagram shows three short, horizontal lines placed halfway up the space and each labeled, “s p superscript 2.” An upward-facing half arrow is drawn vertically on each line. Above these lines is one other short, horizontal line, labeled, “p.” Above both sets of lines is the phrase, “Orbitals in the s p superscript 2 hybridized C atom in C subscript 2 H subscript 4.”

The π bond in the C=C double bond results from the overlap of the third (remaining) 2p orbital on each carbon atom that is not involved in hybridization. This unhybridized p orbital (lobes shown in red and blue in Figure 5.4.2) is perpendicular to the plane of the sp^2 hybrid orbitals. Thus the unhybridized 2p orbitals overlap in a side-by-side fashion, above and below the internuclear axis and form a π bond.

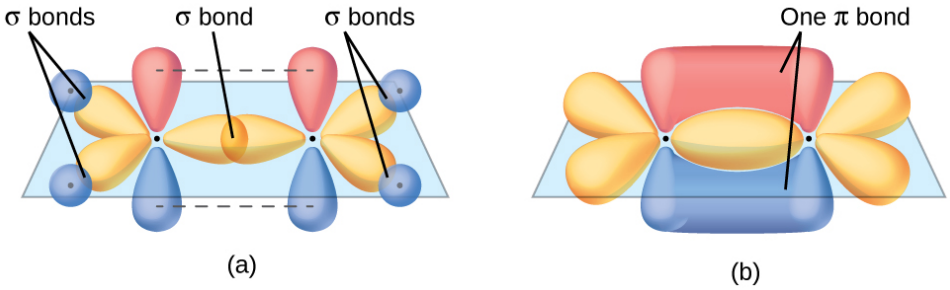
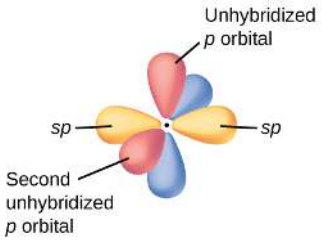


Figure 5.4.2: In the ethene molecule, C_2H_4, there are (a) five σ bonds. One C–C σ bond results from overlap of sp^2 hybrid orbitals on the carbon atom with one sp^2 hybrid orbital on the other carbon atom. Four C–H bonds result from the overlap between the C atoms' sp^2 orbitals with s orbitals on the hydrogen atoms. (b) The π bond is formed by the side-by-side overlap of the two unhybridized p orbitals in the two carbon atoms. The two lobes of the π bond are above and below the plane of the σ system.

Two diagrams are shown labeled, “a” and “b.” Diagram a shows two carbon atoms with three purple balloon-like orbitals arranged in a plane around them and two red balloon-like orbitals arranged vertically and perpendicularly to the plane. There is an overlap of two of the purple orbitals in between the two carbon atoms, and the other four purple orbitals that face the outside of the molecule are shown interacting with spherical blue orbitals from four hydrogen atoms. Diagram b depicts a similar image to diagram a, but the red, vertical orbitals are interacting above and below the plane of the molecule to form two areas labeled, “One pi bond.”

In an ethene molecule, the four hydrogen atoms and the two carbon atoms are all in the same plane. If the two planes of sp^2 hybrid orbitals tilted relative to each other, the *p* orbitals would not be oriented to overlap efficiently to create the π bond. The planar configuration for the ethene molecule occurs because it is the most stable bonding arrangement. This is a significant difference between σ and π bonds; rotation around single (σ) bonds occurs easily because the end-to-end orbital overlap does not depend on the relative orientation of the orbitals on each atom in the bond. In other words, rotation around the internuclear axis does not change the extent to which the σ bonding orbitals overlap because the bonding electron density is symmetric about the axis. Rotation about the internuclear axis is much more difficult for multiple bonds; however, this would drastically alter the off-axis overlap of the π bonding orbitals, essentially breaking the π bond.



A diagram of a carbon atom with two balloon-like purple orbitals labeled, “sp” arranged in a linear fashion around it is shown. Four red balloon-like orbitals are aligned in pairs in the y and z axes around the carbon and are labeled, “unhybridized p orbital,” and, “Second unhybridized p orbital.”

Figure 5.4.3: Diagram of the two linear sp hybrid orbitals of a carbon atom, which lie in a straight line, and the two unhybridized p orbitals at perpendicular angles.

In molecules with sp hybrid orbitals, two unhybridized p orbitals remain on the atom (Figure 5.4.3). We find this situation in acetylene, H−C≡C−H, which is a linear molecule. The sp hybrid orbitals of the two carbon atoms overlap end to end to form a σ bond between the carbon atoms (Figure 5.4.4). The remaining *sp* orbitals form σ bonds with hydrogen atoms. The two unhybridized *p* orbitals per carbon are positioned such that they overlap side by side and, hence, form two π bonds. The two carbon atoms of acetylene are thus bound together by one σ bond and two π bonds, giving a triple bond.

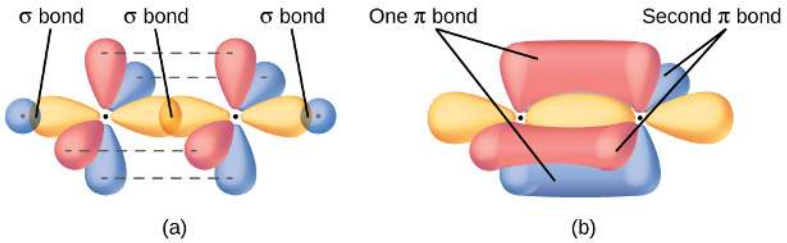
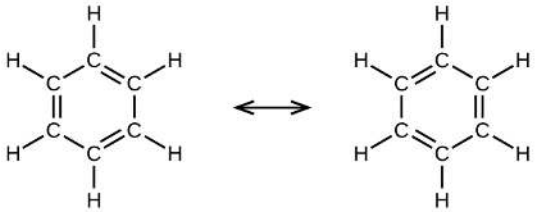


Figure 5.4.4: (a) In the acetylene molecule, C_2H_2, there are two C–H σ bonds and a C≡C triple bond involving one C–C σ bond and two C–C π bonds. The dashed lines, each connecting two lobes, indicate the side-by-side overlap of the four unhybridized p orbitals. (b) This shows the overall outline of the bonds in C_2H_2. The two lobes of each of the π bonds are positioned across from each other around the line of the C–C σ bond.

Two diagrams are shown and labeled, “a” and “b.” Diagram a shows two carbon atoms with two purple balloon-like orbitals arranged in a plane around each of them, and four red balloon-like orbitals arranged along the y and z axes perpendicular to the plane of the molecule. There is an overlap of two of the purple orbitals in between the two carbon atoms. The other two purple orbitals that face the outside of the molecule are shown interacting with spherical blue orbitals from two hydrogen atoms. Diagram b depicts a similar image to diagram a, but the red, vertical orbitals are interacting above and below and to the front and back of the plane of the molecule to form two areas labeled, “One pi bond,” and, “Second pi bond,” each respectively.

Hybridization involves only σ bonds, lone pairs of electrons, and single unpaired electrons (radicals). Structures that account for these features describe the correct hybridization of the atoms. However, many structures also include resonance forms. Remember that resonance forms occur when various arrangements of π bonds are possible. Since the arrangement of π bonds involves only the unhybridized orbitals, resonance does not influence the assignment of hybridization.

For example, molecule benzene has two resonance forms (Figure 5.4.5). We can use either of these forms to determine that each of the carbon atoms is bonded to three other atoms with no lone pairs, so the correct hybridization is sp^2. The electrons in the unhybridized *p* orbitals form π bonds. Neither resonance structure completely describes the electrons in the π bonds. They are not located in one position or the other, but in reality are delocalized throughout the ring. Valence bond theory does not easily address delocalization. Bonding in molecules with resonance forms is better described by molecular orbital theory.



A diagram is shown that is made up of two Lewis structures connected by a double ended arrow. The left image shows six carbon atoms bonded together with alternating double and single bonds to form a six-sided ring. Each carbon is also bonded to a hydrogen atom by a single bond. The right image shows the same structure, but the double and single bonds in between the carbon atoms have changed positions.

Figure 5.4.5: Each carbon atom in benzene, C_6H_6, is sp^2 hybridized, independently of which resonance form is considered. The electrons in the π bonds are not located in one set of p orbitals or the other, but rather delocalized throughout the molecule.

✔ Example 5.4.1: Assignment of Hybridization Involving Resonance

Some acid rain results from the reaction of sulfur dioxide with atmospheric water vapor, followed by the formation of sulfuric acid. Sulfur dioxide, SO_2, is a major component of volcanic gases as well as a product of the combustion of sulfur-containing coal. What is the hybridization of the *S* atom in SO_2?

Solution

The resonance structures of SO_2 are

https://chem.libretexts.org/@go/page/393237



Two Lewis structures connected by a double-ended arrow are shown. The left structure shows a sulfur atom with one lone pair of electrons and a positive sign which is single bonded on one side to an oxygen atom with three lone pairs of electrons and a negative sign. The sulfur atom is double bonded on the other side to another oxygen atom with two lone pairs of electrons. The right-hand structure is the same as the left except that the position of the double bonded oxygen atom is switched. In both structures the attached oxygen atoms form an acute angle in terms of the sulfur atom.

The sulfur atom is surrounded by two bonds and one lone pair of electrons in either resonance structure. Therefore, the electron-pair geometry is trigonal planar, and the hybridization of the sulfur atom is sp^2.

? Exercise 5.4.1

Another acid in acid rain is nitric acid, HNO_3, which is produced by the reaction of nitrogen dioxide, NO_2, with atmospheric water vapor. What is the hybridization of the nitrogen atom in NO_2? (Note: the lone electron on nitrogen occupies a hybridized orbital just as a lone pair would.)

Answer

sp^2

Summary

Multiple bonds consist of a σ bond located along the axis between two atoms and one or two π bonds. The σ bonds are usually formed by the overlap of hybridized atomic orbitals, while the π bonds are formed by the side-by-side overlap of unhybridized orbitals. Resonance occurs when there are multiple unhybridized orbitals with the appropriate alignment to overlap, so the placement of π bonds can vary.

This page titled 5.4: Multiple Bonds is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

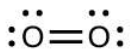
- **8.4: Multiple Bonds** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

5.5: Molecular Orbital Theory

Learning Objectives

- Outline the basic quantum-mechanical approach to deriving molecular orbitals from atomic orbitals
- Describe traits of bonding and antibonding molecular orbitals
- Calculate bond orders based on molecular electron configurations
- Write molecular electron configurations for first- and second-row diatomic molecules
- Relate these electron configurations to the molecules' stabilities and magnetic properties

For almost every covalent molecule that exists, we can now draw the Lewis structure, predict the electron-pair geometry, predict the molecular geometry, and come close to predicting bond angles. However, one of the most important molecules we know, the oxygen molecule O_2, presents a problem with respect to its Lewis structure. We would write the following Lewis structure for O_2:



A Lewis structure is shown. It is made up of two oxygen atoms, each with two lone pairs of electrons, bonded together with a double bond.

This electronic structure adheres to all the rules governing Lewis theory. There is an O=O double bond, and each oxygen atom has eight electrons around it. However, this picture is at odds with the magnetic behavior of oxygen. By itself, O_2 is not magnetic, but it is attracted to magnetic fields. Thus, when we pour liquid oxygen past a strong magnet, it collects between the poles of the magnet and defies gravity. Such attraction to a magnetic field is called paramagnetism, and it arises in molecules that have unpaired electrons. And yet, the Lewis structure of O_2 indicates that all electrons are paired. How do we account for this discrepancy?

Magnetic susceptibility measures the force experienced by a substance in a magnetic field. When we compare the weight of a sample to the weight measured in a magnetic field (Figure 5.5.1), paramagnetic samples that are attracted to the magnet will appear heavier because of the force exerted by the magnetic field. We can calculate the number of unpaired electrons based on the increase in weight.

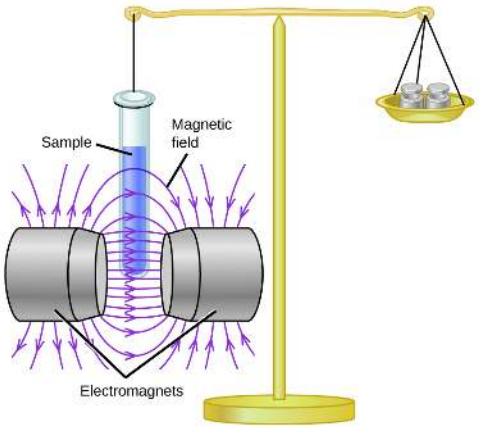


Figure 5.5.1: A Gouy balance compares the mass of a sample in the presence of a magnetic field with the mass with the electromagnet turned off to determine the number of unpaired electrons in a sample.

Experiments show that each O_2 molecule has two unpaired electrons. The Lewis-structure model does not predict the presence of these two unpaired electrons. Unlike oxygen, the apparent weight of most molecules decreases slightly in the presence of an inhomogeneous magnetic field. Materials in which all of the electrons are paired are diamagnetic and weakly repel a magnetic field. Paramagnetic and diamagnetic materials do not act as permanent magnets. Only in the presence of an applied magnetic field do they demonstrate attraction or repulsion.



Video 5.5.1: Water, like most molecules, contains all paired electrons. Living things contain a large percentage of water, so they demonstrate diamagnetic behavior. If you place a frog near a sufficiently large magnet, it will levitate. You can see videos of diamagnetic floating frogs, strawberries, and more (levitating frog [www.youtube.com])

Molecular orbital theory (MO theory) provides an explanation of chemical bonding that accounts for the paramagnetism of the oxygen molecule. It also explains the bonding in a number of other molecules, such as violations of the octet rule and more molecules with more complicated bonding (beyond the scope of this text) that are difficult to describe with Lewis structures. Additionally, it provides a model for describing the energies of electrons in a molecule and the probable location of these electrons. Unlike valence bond theory, which uses hybrid orbitals that are assigned to one specific atom, MO theory uses the combination of atomic orbitals to yield molecular orbitals that are delocalized over the entire molecule rather than being localized on its constituent atoms. MO theory also helps us understand why some substances are electrical conductors, others are semiconductors, and still others are insulators. Table 5.5.1 summarizes the main points of the two complementary bonding theories. Both theories provide different, useful ways of describing molecular structure.

Table \(\PageIndex{1}\): Comparison of Bonding Theories

Valence Bond Theory	Molecular Orbital Theory
considers bonds as localized between one pair of atoms	considers electrons delocalized throughout the entire molecule
creates bonds from overlap of atomic orbitals (*s*, *p*, *d*…) and hybrid orbitals (*sp*, sp^2, sp^3…)	combines atomic orbitals to form molecular orbitals (σ, σ*, π, π*)
forms σ or π bonds	creates bonding and antibonding interactions based on which orbitals are filled
predicts molecular shape based on the number of regions of electron density	predicts the arrangement of electrons in molecules
needs multiple structures to describe resonance	

Molecular orbital theory describes the distribution of electrons in molecules in much the same way that the distribution of electrons in atoms is described using atomic orbitals. Using quantum mechanics, the behavior of an electron in a molecule is still described by a wave function, Ψ, analogous to the behavior in an atom. Just like electrons around isolated atoms, electrons around atoms in molecules are limited to discrete (quantized) energies. The region of space in which a valence electron in a molecule is likely to be found is called a molecular orbital (Ψ^2). Like an atomic orbital, a molecular orbital is full when it contains two electrons with opposite spin.

We will consider the molecular orbitals in molecules composed of two identical atoms (H_2 or Cl_2, for example). Such molecules are called homonuclear diatomic molecules. In these diatomic molecules, several types of molecular orbitals occur.

The mathematical process of combining atomic orbitals to generate molecular orbitals is called the linear combination of atomic orbitals (LCAO). The wave function describes the wavelike properties of an electron. Molecular orbitals are combinations of atomic orbital wave functions. Combining waves can lead to constructive interference, in which peaks line up with peaks, or destructive interference, in which peaks line up with troughs (Figure 5.5.2). In orbitals, the waves are three dimensional, and they

combine with in-phase waves producing regions with a higher probability of electron density and out-of-phase waves producing nodes, or regions of no electron density.

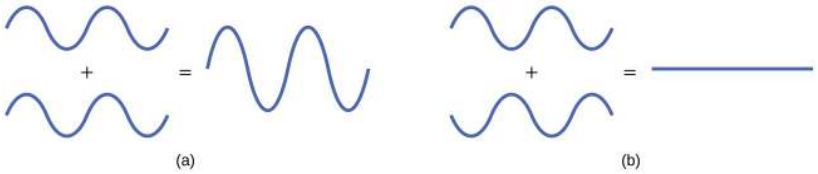


Figure 5.5.2: (a) When in-phase waves combine, constructive interference produces a wave with greater amplitude. (b) When out-of-phase waves combine, destructive interference produces a wave with less (or no) amplitude.

A pair of diagrams are shown and labeled, “a” and “b.” Diagram a shows two identical waves with two crests and two troughs. They are drawn one above the other with a plus sign in between and an equal sign to the right. To the right of the equal sign is a much taller wave with a same number of troughs and crests. Diagram b shows two waves with two crests and two troughs, but they are mirror images of one another rotated over a horizontal axis. They are drawn one above the other with a plus sign in between and an equal sign to the right. To the right of the equal sign is a flat line.

There are two types of molecular orbitals that can form from the overlap of two atomic *s* orbitals on adjacent atoms. The two types are illustrated in Figure 5.5.3. The in-phase combination produces a lower energy σ_s molecular orbital (read as "sigma-s") in which most of the electron density is directly between the nuclei. The out-of-phase addition (which can also be thought of as subtracting the wave functions) produces a higher energy σ_s^* molecular orbital (read as "sigma-s-star") molecular orbital in which there is a node between the nuclei. The asterisk signifies that the orbital is an antibonding orbital. Electrons in a σ_s orbital are attracted by both nuclei at the same time and are more stable (of lower energy) than they would be in the isolated atoms. Adding electrons to these orbitals creates a force that holds the two nuclei together, so we call these orbitals bonding orbitals. Electrons in the σ_s^* orbitals are located well away from the region between the two nuclei. The attractive force between the nuclei and these electrons pulls the two nuclei apart. Hence, these orbitals are called antibonding orbitals. Electrons fill the lower-energy bonding orbital before the higher-energy antibonding orbital, just as they fill lower-energy atomic orbitals before they fill higher-energy atomic orbitals.

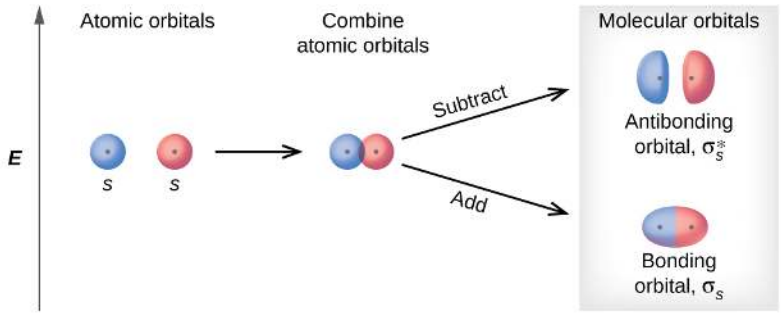
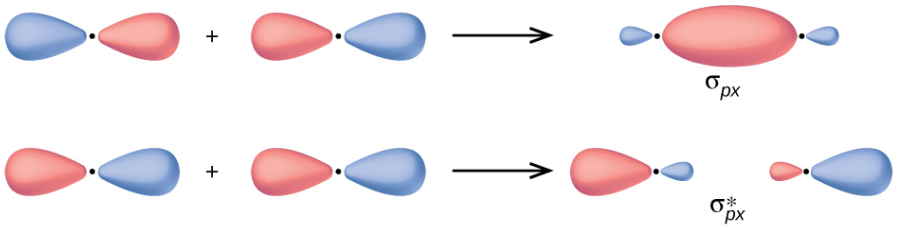


Figure 5.5.3: Sigma (σ) and sigma-star (σ*) molecular orbitals are formed by the combination of two s atomic orbitals. The plus (+) signs indicate the locations of nuclei.

A diagram is shown that depicts a vertical upward-facing arrow that lies to the left of all the other portions of the diagram and is labeled, “E.” To the immediate right of the midpoint of the arrow are two circles each labeled with a positive sign, the letter S, and the phrase, “Atomic orbitals.” These are followed by a right-facing horizontal arrow that points to the same two circles labeled with plus signs, but they are now touching and are labeled, “Combine atomic orbitals.” Two right-facing arrows lead to the last portion of the diagram, one facing upward and one facing downward. The upper arrow is labeled, “Subtract,” and points to two oblong ovals labeled with plus signs, and the phrase, “Antibonding orbitals sigma subscript s superscript asterisk.” The lower arrow is labeled, “Add,” and points to an elongated oval with two plus signs that is labeled, “Bonding orbital sigma subscript s.” The heading over the last section of the diagram are the words, “Molecular orbitals.”

In *p* orbitals, the wave function gives rise to two lobes with opposite phases, analogous to how a two-dimensional wave has both parts above and below the average. We indicate the phases by shading the orbital lobes different colors. When orbital lobes of the same phase overlap, constructive wave interference increases the electron density. When regions of opposite phase overlap, the destructive wave interference decreases electron density and creates nodes. When *p* orbitals overlap end to end, they create σ and σ* orbitals (Figure 5.5.4). If two atoms are located along the *x*-axis in a Cartesian coordinate system, the two p_x orbitals overlap end to end and form σ_{px} (bonding) and σ_{px}^* (antibonding) (read as "sigma-p-x" and "sigma-p-x star," respectively). Just as with *s*-orbital overlap, the asterisk indicates the orbital with a node between the nuclei, which is a higher-energy, antibonding orbital.



Two horizontal rows of diagrams are shown. The upper diagram shows two equally-sized peanut-shaped orbitals with a plus sign in between them connected to a merged orbital diagram by a right facing arrow. The merged diagram has a much larger oval at the center and much smaller ovular orbitals on the edge. It is labeled, “sigma subscript p x.” The lower diagram shows two equally-sized peanut-shaped orbitals with a plus sign in between them connected to a split orbital diagram by a right facing arrow. The split diagram has a much larger oval at the outer ends and much smaller ovular orbitals on the inner edges. It is labeled, “sigma subscript p x superscript asterisk”.

Figure 5.5.4: Combining wave functions of two p atomic orbitals along the internuclear axis creates two molecular orbitals, σp and σ_p^*.

The side-by-side overlap of two *p* orbitals gives rise to a pi (π) bonding molecular orbital and a \(π^*\) antibonding molecular orbital, as shown in Figure 5.5.5. In valence bond theory, we describe π bonds as containing a nodal plane containing the internuclear axis and perpendicular to the lobes of the *p* orbitals, with electron density on either side of the node. In molecular orbital theory, we describe the π orbital by this same shape, and a π bond exists when this orbital contains electrons. Electrons in this orbital interact with both nuclei and help hold the two atoms together, making it a bonding orbital. For the out-of-phase combination, there are two nodal planes created, one along the internuclear axis and a perpendicular one between the nuclei.

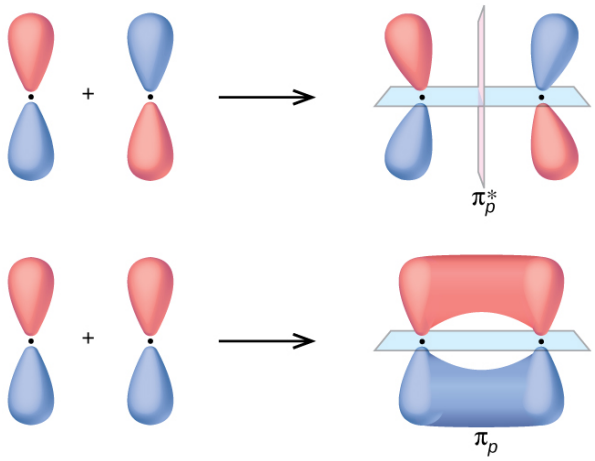


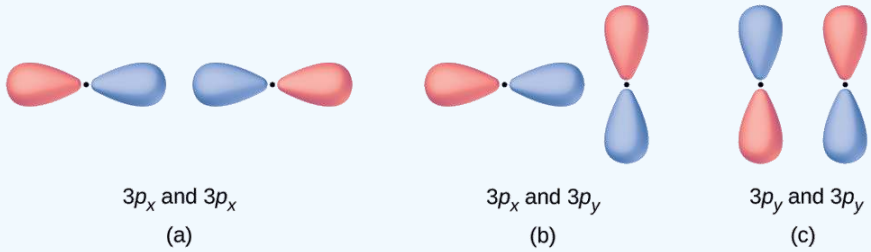
Figure 5.5.5: Side-by-side overlap of each two p orbitals results in the formation of two π molecular orbitals. Combining the out-of-phase orbitals results in an antibonding molecular orbital with two nodes. One contains the internuclear axis, and one is perpendicular to the axis. Combining the in-phase orbitals results in a bonding orbital. There is a node (blue plane) containing the internuclear axis with the two lobes of the orbital located above and below this node.

Two horizontal rows of diagrams are shown. The upper and lower diagrams both begin with two vertical peanut-shaped orbitals with a plus sign in between followed by a right-facing arrow. The upper diagram shows the same vertical peanut orbitals bending slightly away from one another and separated by a dotted line. It is labeled, “pi subscript p superscript asterisk.” The lower diagram shows the horizontal overlap of the two orbitals and is labeled, “pi subscript p.”

In the molecular orbitals of diatomic molecules, each atom also has two sets of *p* orbitals oriented side by side (p_y and p_z), so these four atomic orbitals combine pairwise to create two π orbitals and two π^* orbitals. The π_{py} and π_{py}^* orbitals are oriented at right angles to the π_{pz} and π_{pz}^* orbitals. Except for their orientation, the π_{py} and π_{pz} orbitals are identical and have the same energy; they are degenerate orbitals. The π_{py}^* and π_{pz}^* antibonding orbitals are also degenerate and identical except for their orientation. A total of six molecular orbitals results from the combination of the six atomic *p* orbitals in two atoms: σ_{px} and σ_{px}^*, π_{py} and π_{py}^*, π_{pz} and π_{pz}^*.

Example 5.5.1: Molecular Orbitals

Predict what type (if any) of molecular orbital would result from adding the wave functions so each pair of orbitals shown overlap. The orbitals are all similar in energy.



Three diagrams are shown and labeled “a,” “b,” and “c.” Diagram a shows two horizontal peanut-shaped orbitals laying side-by-side. They are labeled, “3 p subscript x and 3 p subscript x.” Diagram b shows one vertical and one horizontal peanut-shaped orbital which are at right angles to one another. They are labeled, “3 p subscript x and 3 p subscript y.” Diagram c shows two vertical peanut-shaped orbitals laying side-by-side and labeled, “3 p subscript y and 3 p subscript y.”

Solution

a. This is an in-phase combination, resulting in a σ_{3p} orbital
b. This will not result in a new orbital because the in-phase component (bottom) and out-of-phase component (top) cancel out. Only orbitals with the correct alignment can combine.
c. This is an out-of-phase combination, resulting in a π^*_{3p} orbital.

Exercise 5.5.1

Label the molecular orbital shown as σ or π, bonding or antibonding and indicate where the node occurs.



Two orbitals are shown lying end-to-end. Each has one enlarged and one small side. The small sides are facing one another

Answer

The orbital is located along the internuclear axis, so it is a σ orbital. There is a node bisecting the internuclear axis, so it is an antibonding orbital.



Two orbitals are shown lying end-to-end. Each has one enlarged and one small side. The small sides are facing one another and are separated by a vertical dotted line.

Application: Computational Chemistry in Drug Design

While the descriptions of bonding described in this chapter involve many theoretical concepts, they also have many practical, real-world applications. For example, drug design is an important field that uses our understanding of chemical bonding to develop pharmaceuticals. This interdisciplinary area of study uses biology (understanding diseases and how they operate) to identify specific targets, such as a binding site that is involved in a disease pathway. By modeling the structures of the binding site and potential drugs, computational chemists can predict which structures can fit together and how effectively they will bind (Figure 5.5.6). Thousands of potential candidates can be narrowed down to a few of the most promising candidates. These candidate molecules are then carefully tested to determine side effects, how effectively they can be transported through the

body, and other factors. Dozens of important new pharmaceuticals have been discovered with the aid of computational chemistry, and new research projects are underway.

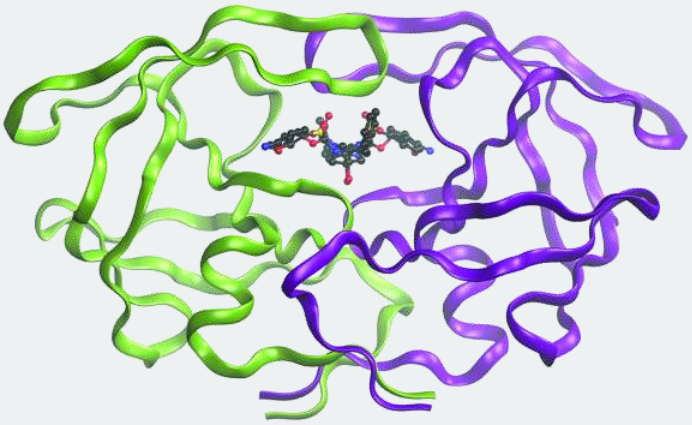


Figure 5.5.6: The molecule shown, HIV-1 protease, is an important target for pharmaceutical research. By designing molecules that bind to this protein, scientists are able to drastically inhibit the progress of the disease.

A diagram of a molecule is shown. The image shows a tangle of ribbon-like, intertwined, pink and green curling lines with a complex ball and stick model in the center.

5.5.1: Molecular Orbital Energy Diagrams

The relative energy levels of atomic and molecular orbitals are typically shown in a molecular orbital diagram (Figure 5.5.7). For a diatomic molecule, the atomic orbitals of one atom are shown on the left, and those of the other atom are shown on the right. Each horizontal line represents one orbital that can hold two electrons. The molecular orbitals formed by the combination of the atomic orbitals are shown in the center. Dashed lines show which of the atomic orbitals combine to form the molecular orbitals. For each pair of atomic orbitals that combine, one lower-energy (bonding) molecular orbital and one higher-energy (antibonding) orbital result. Thus we can see that combining the six 2*p* atomic orbitals results in three bonding orbitals (one σ and two π) and three antibonding orbitals (one σ* and two π*).

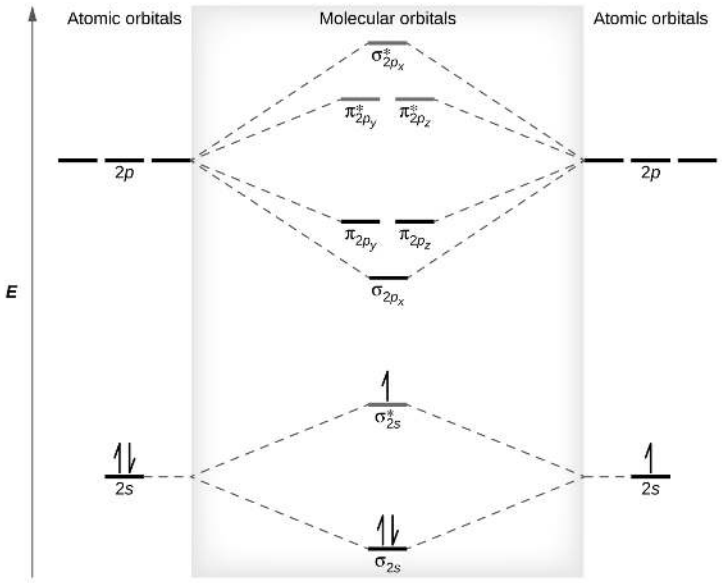


Figure 5.5.7: This is the molecular orbital diagram for the homonuclear diatomic Be_2^+, showing the molecular orbitals of the valence shell only. The molecular orbitals are filled in the same manner as atomic orbitals, using the Aufbau principle and Hund's rule.

A diagram is shown that has an upward-facing vertical arrow running along the left side labeled, "E." At the bottom center of the diagram is a horizontal line labeled, "sigma subscript 2 s," that has two vertical half arrows drawn on it, one facing up and one facing down. This line is connected to the right and left by upward-facing, dotted lines to two more horizontal lines, each labeled, "2 s." The line on the left has two vertical half arrows drawn on it, one facing up and one facing down while the line of the right has one half arrow facing up drawn on it. These two lines are connected by upward-facing dotted lines to another line in the center of the diagram, but further up from the first. It is labeled, "sigma subscript 2 s superscript asterisk." This horizontal line has one upward-facing vertical half-arrow drawn on it. Moving farther up the center of the diagram is a long horizontal line labeled, "sigma subscript 2 p subscript x," which lies below two horizontal lines. These two horizontal lines lie side-by-side, and labeled, "pi subscript 2 p subscript y," and, "pi subscript 2 p subscript z." Both the bottom and top lines are connected to the right and left by upward-facing, dotted lines to three more horizontal lines, each labeled, "2 p." These sets of lines are connected by upward-facing dotted lines to another single line and then pair of double lines in the center of the diagram, but farther up from the lower lines. They are labeled, "sigma subscript 2 p subscript x superscript asterisk," and, ""pi subscript 2 p subscript y superscript asterisk," and, "pi subscript 2 p subscript z superscript asterisk," respectively. The left and right sides of the diagram have headers that read, "Atomic orbitals," while the center is header reads "Molecular orbitals".

We predict the distribution of electrons in these molecular orbitals by filling the orbitals in the same way that we fill atomic orbitals, by the Aufbau principle. Lower-energy orbitals fill first, electrons spread out among degenerate orbitals before pairing, and each orbital can hold a maximum of two electrons with opposite spins (Figure 5.5.7). Just as we write electron configurations for atoms, we can write the molecular electronic configuration by listing the orbitals with superscripts indicating the number of electrons present. For clarity, we place parentheses around molecular orbitals with the same energy. In this case, each orbital is at a different energy, so parentheses separate each orbital. Thus we would expect a diatomic molecule or ion containing seven electrons (such as Be_2^+) would have the molecular electron configuration $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^1$. It is common to omit the core electrons from molecular orbital diagrams and configurations and include only the valence electrons.

5.5.2: Bond Order

The filled molecular orbital diagram shows the number of electrons in both bonding and antibonding molecular orbitals. The net contribution of the electrons to the bond strength of a molecule is identified by determining the bond order that results from the filling of the molecular orbitals by electrons.

When using Lewis structures to describe the distribution of electrons in molecules, we define bond order as the number of bonding pairs of electrons between two atoms. Thus a single bond has a bond order of 1, a double bond has a bond order of 2, and a triple bond has a bond order of 3. We define bond order differently when we use the molecular orbital description of the distribution of electrons, but the resulting bond order is usually the same. The MO technique is more accurate and can handle cases when the Lewis structure method fails, but both methods describe the same phenomenon.

In the molecular orbital model, an electron contributes to a bonding interaction if it occupies a bonding orbital and it contributes to an antibonding interaction if it occupies an antibonding orbital. The bond order is calculated by subtracting the destabilizing

(antibonding) electrons from the stabilizing (bonding) electrons. Since a bond consists of two electrons, we divide by two to get the bond order. We can determine bond order with the following equation:

$$\text{bond order} = \frac{(\text{number of bonding electrons}) - (\text{number of antibonding electrons})}{2}$$

The order of a covalent bond is a guide to its strength; a bond between two given atoms becomes stronger as the bond order increases. If the distribution of electrons in the molecular orbitals between two atoms is such that the resulting bond would have a bond order of zero, a stable bond does not form. We next look at some specific examples of MO diagrams and bond orders.

5.5.3: Bonding in Diatomic Molecules

A dihydrogen molecule (H_2) forms from two hydrogen atoms. When the atomic orbitals of the two atoms combine, the electrons occupy the molecular orbital of lowest energy, the σ_{1s} bonding orbital. A dihydrogen molecule, H_2, readily forms because the energy of a H_2 molecule is lower than that of two H atoms. The σ_{1s} orbital that contains both electrons is lower in energy than either of the two 1*s* atomic orbitals.

A molecular orbital can hold two electrons, so both electrons in the H_2 molecule are in the σ_{1s} bonding orbital; the electron configuration is $(\sigma_{1s})^2$. We represent this configuration by a molecular orbital energy diagram (Figure 5.5.8) in which a single upward arrow indicates one electron in an orbital, and two (upward and downward) arrows indicate two electrons of opposite spin.

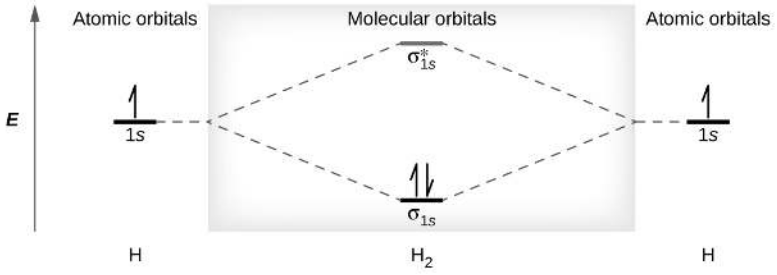


Figure 5.5.8: The molecular orbital energy diagram predicts that H_2 will be a stable molecule with lower energy than the separated atoms.

A diagram is shown that has an upward-facing vertical arrow running along the left side labeled “E.” At the bottom center of the diagram is a horizontal line labeled, “sigma subscript 1 s,” that has two vertical half arrows drawn on it, one facing up and one facing down. This line is connected to the right and left by upward-facing, dotted lines to two more horizontal lines, each labeled, “1 s,” and each with one vertical half-arrow facing up drawn on it. These two lines are connected by upward-facing dotted lines to another line in the center of the diagram, but farther up from the first, and labeled, “sigma subscript 1 s superscript asterisk.” The left and right sides of the diagram have headers that read, ”Atomic orbitals,” while the center header reads, “Molecular orbitals.” The bottom left and right are labeled “H” while the center is labeled “H subscript 2.”

A dihydrogen molecule contains two bonding electrons and no antibonding electrons so we have

$$\text{bond order in } H_2 = \frac{(2-0)}{2} = 1$$

Because the bond order for the H–H bond is equal to 1, the bond is a single bond.

A helium atom has two electrons, both of which are in its 1*s* orbital. Two helium atoms do not combine to form a dihelium molecule, He_2, with four electrons, because the stabilizing effect of the two electrons in the lower-energy bonding orbital would be offset by the destabilizing effect of the two electrons in the higher-energy antibonding molecular orbital. We would write the hypothetical electron configuration of He_2 as $(\sigma_{1s})^2(\sigma^*_{1s})^2$ as in Figure 5.5.9. The net energy change would be zero, so there is no driving force for helium atoms to form the diatomic molecule. In fact, helium exists as discrete atoms rather than as diatomic molecules. The bond order in a hypothetical dihelium molecule would be zero.

$$\text{bond order in } He_2 = \frac{(2-2)}{2} = 0$$

A bond order of zero indicates that no bond is formed between two atoms.

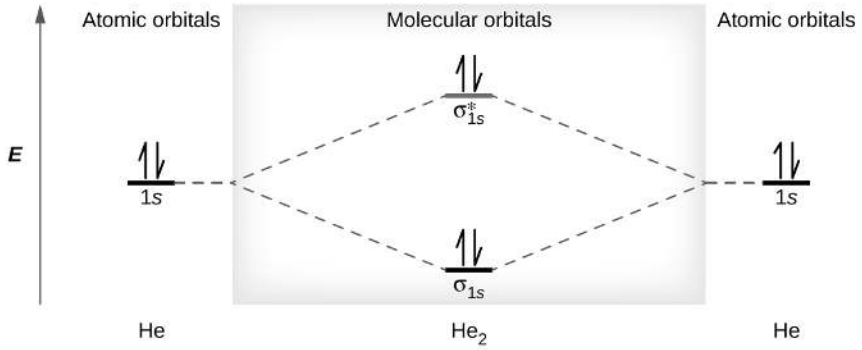


Figure 5.5.9: The molecular orbital energy diagram predicts that He_2 will not be a stable molecule, since it has equal numbers of bonding and antibonding electrons.

A diagram is shown that has an upward-facing vertical arrow running along the left side labeled, “E.” At the bottom center of the diagram is a horizontal line labeled, “sigma subscript 1 s,” that has two vertical half arrows drawn on it, one facing up and one facing down. This line is connected to the right and left by upward-facing, dotted lines to two more horizontal lines, each labeled, “1 s,” and each with one vertical half-arrow facing up and one facing down drawn on it. These two lines are connected by upward-facing dotted lines to another line in the center of the diagram, but farther up from the first, and labeled, “sigma subscript 1 s superscript asterisk.” This line has one upward-facing and one downward-facing vertical arrow drawn on it. The left and right sides of the diagram have headers that read, “Atomic orbitals,” while the center header reads, “Molecular orbitals.” The bottom left and right are labeled, “H e,” while the center is labeled, “H e subscript 2.”

5.5.4: The Diatomic Molecules of the Second Period

Eight possible homonuclear diatomic molecules might be formed by the atoms of the second period of the periodic table: Li_2, Be_2, B_2, C_2, N_2, O_2, F_2, and Ne_2. However, we can predict that the Be_2 molecule and the Ne_2 molecule would not be stable. We can see this by a consideration of the molecular electron configurations (Table 5.5.1).

Table 5.5.1: Electron Configuration and Bond Order for Molecular Orbitals in Homonuclear Diatomic Molecules of Period Two Elements

Molecule	Electron Configuration	Bond Order
Li_2	$(\sigma_{2s})^2$	1
Be_2 (unstable)	$(\sigma_{2s})^2(\sigma^*_{2s})^2$	0
B_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py},\ \pi_{2pz})^2$	1
C_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py},\ \pi_{2pz})^4$	2
N_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py},\ \pi_{2pz})^4(\sigma_{2px})^2$	3
O_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2px})^2(\pi_{2py},\ \pi_{2pz})^4(\pi^*_{2py}, \pi^*_{2pz})^2$	2
F_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2px})^2(\pi_{2py},\ \pi_{2pz})^4(\pi^*_{2py},\ \pi^*_{2pz})^4$	1
Ne_2 (unstable)	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2px})^2(\pi_{2py},\ \pi_{2pz})^4(\pi^*_{2py}, \pi^*_{2pz})^4(\sigma^*_{2px})^2$	0

We predict valence molecular orbital electron configurations just as we predict electron configurations of atoms. Valence electrons are assigned to valence molecular orbitals with the lowest possible energies. Consistent with Hund’s rule, whenever there are two or more degenerate molecular orbitals, electrons fill each orbital of that type singly before any pairing of electrons takes place.

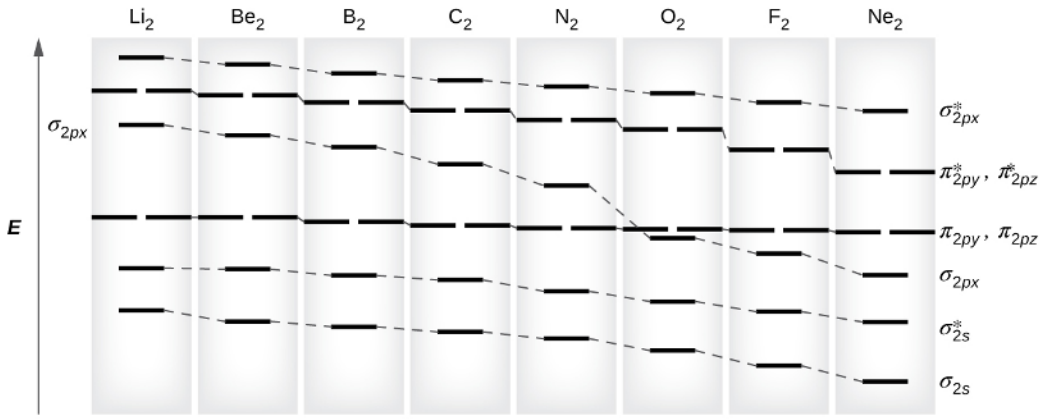


Figure 5.5.10: This shows the MO diagrams for each homonuclear diatomic molecule in the second period. The orbital energies decrease across the period as the effective nuclear charge increases and atomic radius decreases. Between N_2 and O_2, the order of the orbitals changes.

A graph is shown in which the y-axis is labeled, “E,” and appears as a vertical, upward-facing arrow. Across the top, the graph reads, “L i subscript 2,” “B e subscript 2,” “B subscript 2,” “C subscript 2,” “N subscript 2,” “O subscript 2,” “F subscript 2,” and “Ne subscript 2.” Directly below each of these element terms is a single pink line, and all lines are connected to one another by a dashed line, to create an overall line that decreases in height as it moves from left to right across the graph. This line is labeled, “sigma subscript 2 p x superscript asterisk”. Directly below each of these lines is a set of two pink lines, and all lines are connected to one another by a dashed line, to create an overall line that decreases in height as it moves from left to right across the graph. It is consistently lower than the first line. This line is labeled, “pi subscript 2 p y superscript asterisk,” and, “pi subscript 2 p z superscript asterisk.” Directly below each of these double lines is a single pink line, and all lines are connected to one another by a dashed line, to create an overall line that decreases in height as it moves from left to right across the graph. It has a distinctive drop at the label, “O subscript 2.” This line is labeled, “sigma subscript 2 p x.” Directly below each of these lines is a set of two pink lines, and all lines are connected to one another by a dashed line to create an overall line that decreases very slightly in height as it moves from left to right across the graph. It is consistently lower than the third line until it reaches the point labeled, “O subscript 2.” This line is labeled, “pi subscript 2 p y,” and, “pi subscript 2 p z.” Directly below each of these lines is a single blue line, and all lines are connected to one another by a dashed line to create an overall line that decreases in height as it moves from left to right across the graph. This line is labeled, “sigma subscript 2 s superscript asterisk.” Finally, directly below each of these lines is a single blue line, and all lines are connected to one another by a dashed line to create an overall line that decreases in height as it moves from left to right across the graph. This line is labeled. “sigma subscript 2 s.”

As we saw in valence bond theory, σ bonds are generally more stable than π bonds formed from degenerate atomic orbitals. Similarly, in molecular orbital theory, σ orbitals are usually more stable than π orbitals. However, this is not always the case. The MOs for the valence orbitals of the second period are shown in Figure 5.5.10. Looking at Ne_2 molecular orbitals, we see that the order is consistent with the generic diagram shown in the previous section. However, for atoms with three or fewer electrons in the *p* orbitals (Li through N) we observe a different pattern, in which the σ_p orbital is higher in energy than the π_p set. Obtain the molecular orbital diagram for a homonuclear diatomic ion by adding or subtracting electrons from the diagram for the neutral molecule.

This switch in orbital ordering occurs because of a phenomenon called s-p mixing. s-p mixing does not create new orbitals; it merely influences the energies of the existing molecular orbitals. The σ_s wavefunction mathematically combines with the σ_p wavefunction, with the result that the σ_s orbital becomes more stable, and the σ_p orbital becomes less stable (Figure 5.5.11). Similarly, the antibonding orbitals also undergo s-p mixing, with the σ_{s*} becoming more stable and the σ_{p*} becoming less stable.

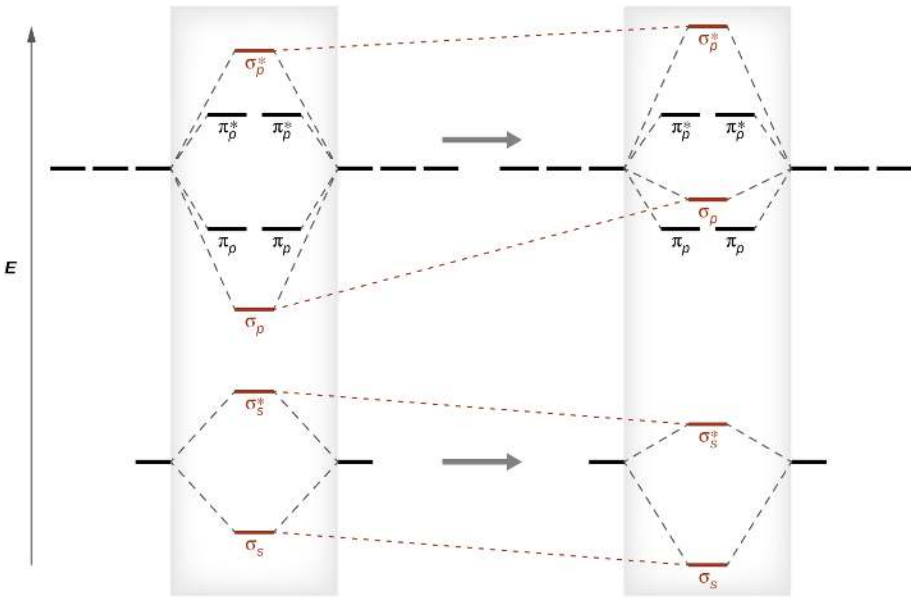


Figure 5.5.11: Without mixing, the MO pattern occurs as expected, with the σ_p orbital lower in energy than the σ_p orbitals. When s-p mixing occurs, the orbitals shift as shown, with the σ_p orbital higher in energy than the π_p orbitals.

A diagram is shown. At the bottom left of the diagram is a horizontal line that is connected to the right and left by upward-facing, dotted lines to two more horizontal lines. Those two lines are connected by upward-facing dotted lines to another line in the center of the diagram but farther up from the first. Each of the bottom two central lines has a vertical downward-facing arrow. Above this structure is a horizontal line that is connected to the right and left by upward-facing, dotted lines to two sets of three horizontal lines and those two lines are connected by upward-facing dotted lines to another line in the center of the diagram, but further up from the first. In between the horizontal lines of this structure are two pairs of horizontal lines that are above the first line but below the second and connected by dotted lines to the side horizontal lines. The bottom and top central lines each have an upward-facing vertical arrow. These two structures are redrawn on the right side of the diagram, but this time, the central lines of the bottom structure are moved downward in relation to the side lines. The upper portion of the structure has its central lines shifted upward in relation to the side lines. This structure also shows the bottom line appearing above the set of two lines.

s-p mixing occurs when the *s* and *p* orbitals have similar energies. The energy difference between 2*s* and 2*p* orbitals in O, F, and Ne is greater than that in Li, Be, B, C, and N. Because of this, O_2, F_2, and Ne exhibit negligible s-p mixing (not sufficient to change the energy ordering), and their MO diagrams follow the normal pattern, as shown in Figure 5.5.7. All of the other period 2 diatomic molecules do have s-p mixing, which leads to the pattern where the σ_p orbital is raised above the π_p set.

Using the MO diagrams shown in Figure 5.5.11, we can add in the electrons and determine the molecular electron configuration and bond order for each of the diatomic molecules. As shown in Table 5.5.1, Be_2 and Ne_2 molecules would have a bond order of 0, and these molecules do not exist.

The combination of two lithium atoms to form a lithium molecule, Li_2, is analogous to the formation of H_2, but the atomic orbitals involved are the valence 2*s* orbitals. Each of the two lithium atoms has one valence electron. Hence, we have two valence electrons available for the σ_{2s} bonding molecular orbital. Because both valence electrons would be in a bonding orbital, we would predict the Li_2 molecule to be stable. The molecule is, in fact, present in an appreciable concentration in lithium vapor at temperatures near the boiling point of the element. All of the other molecules in Table 5.5.1 with a bond order greater than zero are also known.

The O_2 molecule has enough electrons to half fill the $(\pi^*_{2py}, \pi^*_{2pz})$ level. We expect the two electrons that occupy these two degenerate orbitals to be unpaired, and this molecular electronic configuration for O_2 is in accord with the fact that the oxygen molecule has two unpaired electrons (Figure 5.5.10). The presence of two unpaired electrons has proved to be difficult to explain using Lewis structures, but the molecular orbital theory explains it quite well. In fact, the unpaired electrons of the oxygen molecule provide a strong piece of support for the molecular orbital theory.

Application: Band Theory in Extended Systems

When two identical atomic orbitals on different atoms combine, two molecular orbitals result (e.g., H_2 in Figure 5.5.8). The bonding orbital is lower in energy than the original atomic orbitals because the atomic orbitals are in-phase in the molecular orbital. The antibonding orbital is higher in energy than the original atomic orbitals because the atomic orbitals are out-of-phase.

In a solid, similar things happen, but on a much larger scale. Remember that even in a small sample there are a huge number of atoms (typically > 10^{23} atoms), and therefore a huge number of atomic orbitals that may be combined into molecular orbitals. When *N* valence atomic orbitals, all of the same energy and each containing one (1) electron, are combined, *N*/2 (filled) bonding orbitals and *N*/2 (empty) antibonding orbitals will result. Each bonding orbital will show an energy lowering as the atomic orbitals are *mostly* in-phase, but each of the bonding orbitals will be a little different and have slightly different energies. The antibonding orbitals will show an increase in energy as the atomic orbitals are *mostly* out-of-phase, but each of the antibonding orbitals will also be a little different and have slightly different energies. The allowed energy levels for all the bonding orbitals are so close together that they form a band, called the valence band. Likewise, all the antibonding orbitals are very close together and form a band, called the conduction band. Figure 5.5.12) shows the bands for three important classes of materials: insulators, semiconductors, and conductors.

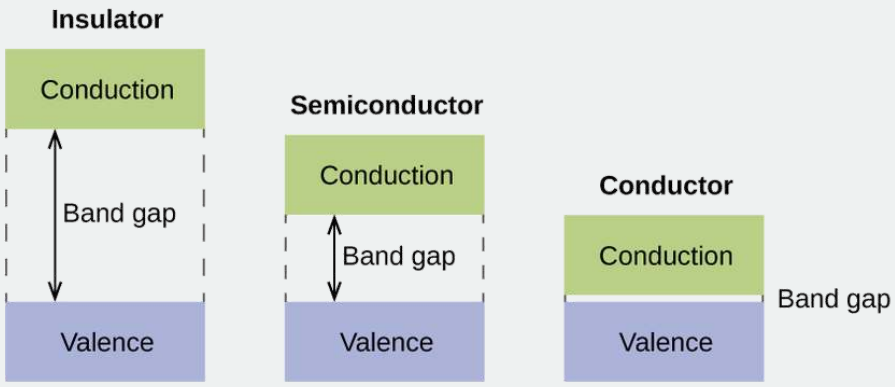


Figure 5.5.12: Molecular orbitals in solids are so closely spaced that they are described as bands. The valence band is lower in energy and the conduction band is higher in energy. The type of solid is determined by the size of the "band gap" between the valence and conduction bands. Only a very small amount of energy is required to move electrons from the valence band to the conduction band in a conductor, and so they conduct electricity well. In an insulator, the band gap is large, so that very few electrons move, and they are poor conductors of electricity. Semiconductors are in between: they conduct electricity better than insulators, but not as well as conductors.

This figure shows three diagrams. The first is labeled, "Insulator," and it consists of two boxes. The "conduction" box is above and the "valence" box is below. A large gap marked by 4 dashed lines contains a double-headed arrow. One head pointing towards the "conduction box" and the other towards the "valence" box. The arrow is labeled, "Band gap." The second diagram is similar to the first, but the band gap is about half as large. This diagram is labeled, "Semiconductor." The third diagram is similar to the other two, but the band gap is about a fifth that of the "Semiconductor" diagram. This diagram is labeled, "Conductor."

In order to conduct electricity, electrons must move from the filled valence band to the empty conduction band where they can move throughout the solid. The size of the band gap, or the energy difference between the top of the valence band and the bottom of the conduction band, determines how easy it is to move electrons between the bands. Only a small amount of energy is required in a conductor because the band gap is very small. This small energy difference is "easy" to overcome, so they are good conductors of electricity. In an insulator, the band gap is so "large" that very few electrons move into the conduction band; as a result, insulators are poor conductors of electricity. Semiconductors conduct electricity when "moderate" amounts of energy are provided to move electrons out of the valence band and into the conduction band. Semiconductors, such as silicon, are found in many electronics.

Semiconductors are used in devices such as computers, smartphones, and solar cells. Solar cells produce electricity when light provides the energy to move electrons out of the valence band. The electricity that is generated may then be used to power a light or tool, or it can be stored for later use by charging a battery. As of December 2014, up to 46% of the energy in sunlight could be converted into electricity using solar cells.

✔ Example 5.5.2: Molecular Orbital Diagrams, Bond Order, and Number of Unpaired Electrons

Draw the molecular orbital diagram for the oxygen molecule, O_2. From this diagram, calculate the bond order for O_2. How does this diagram account for the paramagnetism of O_2?

Solution

We draw a molecular orbital energy diagram similar to that shown in Figure 5.5.7. Each oxygen atom contributes six electrons, so the diagram appears as shown in Figure 5.5.7.

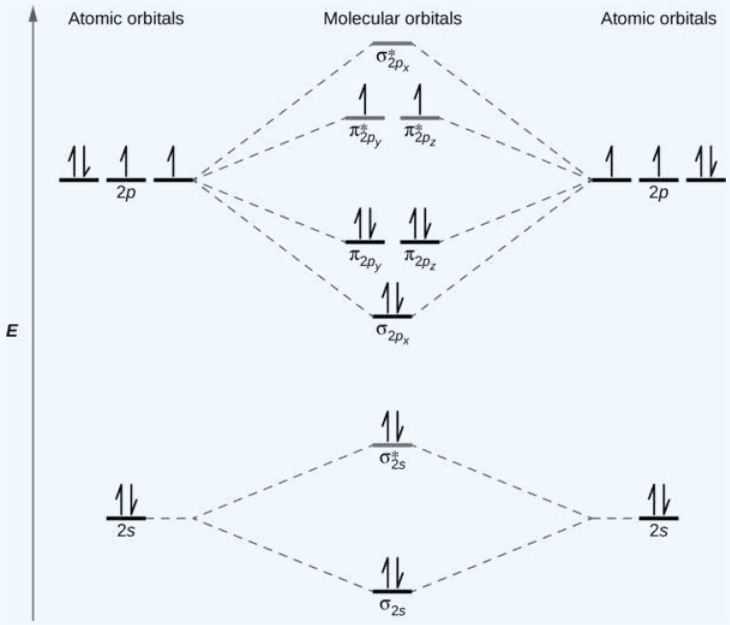


Figure 5.5.13: The molecular orbital energy diagram for O_2 predicts two unpaired electrons.

We calculate the bond order as

$$O_2 = \frac{(8-4)}{2} = 2$$

Oxygen's paramagnetism is explained by the presence of two unpaired electrons in the (π_{2py}, π_{2pz})* molecular orbitals.

Exercise 5.5.2

The main component of air is N_2. From the molecular orbital diagram of N_2, predict its bond order and whether it is diamagnetic or paramagnetic.

Answer

N_2 has a bond order of 3 and is diamagnetic.

Example 5.5.3: Ion Predictions with MO Diagrams

Give the molecular orbital configuration for the valence electrons in C_2^{2-}. Will this ion be stable?

Solution

Looking at the appropriate MO diagram, we see that the π orbitals are lower in energy than the σ_p orbital. The valence electron configuration for C_2 is

$$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py},\ \pi_{2pz})^4.$$

Adding two more electrons to generate the C_2^{2-} anion will give a valence electron configuration of

$$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py},\ \pi_{2pz})^4(\sigma_{2px})^2$$

Since this has six more bonding electrons than antibonding, the bond order will be 3, and the ion should be stable.

Exercise 5.5.3

How many unpaired electrons would be present on a Be_2^{2-} ion? Would it be paramagnetic or diamagnetic?

Answer

two, paramagnetic

5.5.5: Key Concepts and Summary

Molecular orbital (MO) theory describes the behavior of electrons in a molecule in terms of combinations of the atomic wave functions. The resulting molecular orbitals may extend over all the atoms in the molecule. Bonding molecular orbitals are formed by in-phase combinations of atomic wave functions, and electrons in these orbitals stabilize a molecule. Antibonding molecular orbitals result from out-of-phase combinations of atomic wave functions and electrons in these orbitals make a molecule less stable. Molecular orbitals located along an internuclear axis are called σ MOs. They can be formed from *s* orbitals or from *p* orbitals oriented in an end-to-end fashion. Molecular orbitals formed from *p* orbitals oriented in a side-by-side fashion have electron density on opposite sides of the internuclear axis and are called π orbitals.

We can describe the electronic structure of diatomic molecules by applying molecular orbital theory to the valence electrons of the atoms. Electrons fill molecular orbitals following the same rules that apply to filling atomic orbitals; Hund's rule and the Aufbau principle tell us that lower-energy orbitals will fill first, electrons will spread out before they pair up, and each orbital can hold a maximum of two electrons with opposite spins. Materials with unpaired electrons are paramagnetic and attracted to a magnetic field, while those with all-paired electrons are diamagnetic and repelled by a magnetic field. Correctly predicting the magnetic properties of molecules is in advantage of molecular orbital theory over Lewis structures and valence bond theory.

This page titled 5.5: Molecular Orbital Theory is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **8.5: Molecular Orbital Theory** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

5.E: Advanced Theories of Covalent Bonding (Exercises)

5.E.1: Molecular Structure and Polarity

Exercise 5.E.1

Explain why the HOH molecule is bent, whereas the HBeH molecule is linear.

Answer

The placement of the two sets of unpaired electrons in water forces the bonds to assume a tetrahedral arrangement, and the resulting HOH molecule is bent. The HBeH molecule (in which Be has only two electrons to bond with the two electrons from the hydrogens) must have the electron pairs as far from one another as possible and is therefore linear.

Exercise 5.E.2

What feature of a Lewis structure can be used to tell if a molecule's (or ion's) electron-pair geometry and molecular structure will be identical?

Answer

Add texts here. Do not delete this text first.

Exercise 5.E.3

Explain the difference between electron-pair geometry and molecular structure.

Answer

Space must be provided for each pair of electrons whether they are in a bond or are present as lone pairs. Electron-pair geometry considers the placement of all electrons. Molecular structure considers only the bonding-pair geometry.

Exercise 5.E.4

Why is the H–N–H angle in NH_3 smaller than the H–C–H bond angle in CH_4? Why is the H–N–H angle in NH_4^+ identical to the H–C–H bond angle in CH_4?

Answer

Add texts here. Do not delete this text first.

Exercise 5.E.5

Explain how a molecule that contains polar bonds can be nonpolar.

Answer

As long as the polar bonds are compensated (for example. two identical atoms are found directly across the central atom from one another), the molecule can be nonpolar.

Exercise 5.E.6

As a general rule, MX_n molecules (where M represents a central atom and X represents terminal atoms; n = 2 – 5) are polar if there is one or more lone pairs of electrons on M. NH_3 (M = N, X = H, n = 3) is an example. There are two molecular structures with lone pairs that are exceptions to this rule. What are they?

Answer

Add texts here. Do not delete this text first.

Exercise 5.E.7

Predict the electron pair geometry and the molecular structure of each of the following molecules or ions:

1. SF_6
2. PCl_5
3. BeH_2
4. CH_3^+

Answer

1. Both the electron geometry and the molecular structure are octahedral.
2. Both the electron geometry and the molecular structure are trigonal bipyramid.
3. Both the electron geometry and the molecular structure are linear.
4. Both the electron geometry and the molecular structure are trigonal planar.

Exercise 5.E.8

Identify the electron pair geometry and the molecular structure of each of the following molecules or ions:

1. IF_6^+
2. CF_4
3. BF_3
4. SiF_5^-
5. $BeCl_2$

Answer

Add texts here. Do not delete this text first.

Exercise 5.E.9

- What are the electron-pair geometry and the molecular structure of each of the following molecules or ions?

1. ClF_5
2. ClO_2^-
3. $TeCl_4^{2-}$
4. PCl_3
5. SeF_4
6. PH_2^-

Answer

1. electron-pair geometry: octahedral, molecular structure: square pyramidal
2. electron-pair geometry: tetrahedral, molecular structure: bent
3. electron-pair geometry: octahedral, molecular structure: square planar
4. electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal
5. electron-pair geometry: trigonal bypyramidal, molecular structure: seesaw
6. electron-pair geometry: tetrahedral, molecular structure: bent (109°)

Exercise 5.E.10

Predict the electron pair geometry and the molecular structure of each of the following ions:

1. H_3O^+
2. PCl_4^-
3. $SnCl_3^-$
4. $BrCl_4^-$
5. ICl_3
6. XeF_4
7. SF_2

Answer

Add texts here. Do not delete this text first.

Exercise 5.E.11

Identify the electron pair geometry and the molecular structure of each of the following molecules:

1. ClNO (N is the central atom)
2. CS_2
3. Cl_2CO (C is the central atom)
4. Cl_2SO (S is the central atom)
5. SO_2F_2 (S is the central atom)
6. XeO_2F_2 (Xe is the central atom)
7. $ClOF_2^+$ (Cl is the central atom)

Answer

1. electron-pair geometry: trigonal planar, molecular structure: bent (120°)
2. electron-pair geometry: linear, molecular structure: linear
3. electron-pair geometry: trigonal planar, molecular structure: trigonal planar
4. electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal
5. electron-pair geometry: tetrahedral, molecular structure: tetrahedral
6. electron-pair geometry: trigonal bipyramidal, molecular structure: seesaw
7. electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal

Exercise 5.E.12

Predict the electron pair geometry and the molecular structure of each of the following:

1. IOF_5 (I is the central atom)
2. $POCl_3$ (P is the central atom)
3. Cl_2SeO (Se is the central atom)
4. $ClSO^+$ (S is the central atom)
5. F_2SO (S is the central atom)
6. NO_2^-
7. SiO_4^{4-}

Answer

Add texts here. Do not delete this text first.

https://chem.libretexts.org/@go/page/393239

Exercise 5.E.13

- Which of the following molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?

1. ClF_5
2. ClO_2^-
3. $TeCl_4^{2-}$
4. PCl_3
5. SeF_4
6. PH_2^-
7. XeF_2

Answer

All of these molecules and ions contain polar bonds. Only ClF_5, ClO_2^-, PCl_3, SeF_4, and PH_2^- have dipole moments.

Exercise 5.E.14

Which of the molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?

1. H_3O^+
2. PCl_4^-
3. $SnCl_3^-$
4. $BrCl_4^-$
5. ICl_3
6. XeF_4
7. SF_2

Answer

Add texts here. Do not delete this text first.

Exercise 5.E.15

Which of the following molecules have dipole moments?

1. CS_2
2. SeS_2
3. CCl_2F_2
4. PCl_3 (P is the central atom)
5. ClNO (N is the central atom)

Answer

SeS_2, CCl_2F_2, PCl_3, and ClNO all have dipole moments.

Exercise 5.E.16

Identify the molecules with a dipole moment:

1. SF_4
2. CF_4
3. Cl_2CCBr_2
4. CH_3Cl
5. H_2CO

Answer

Add texts here. Do not delete this text first.

Exercise 5.E.17

The molecule XF_3 has a dipole moment. Is X boron or phosphorus?

Answer

P

Exercise 5.E.18

The molecule XCl_2 has a dipole moment. Is X beryllium or sulfur?

Answer

S

Exercise 5.E.19

Is the Cl_2BBCl_2 molecule polar or nonpolar?

Answer

nonpolar

Exercise 5.E.20

There are three possible structures for PCl_2F_3 with phosphorus as the central atom. Draw them and discuss how measurements of dipole moments could help distinguish among them.

Answer

Add texts here. Do not delete this text first.

Exercise 5.E.21

Describe the molecular structure around the indicated atom or atoms:

1. the sulfur atom in sulfuric acid, H_2SO_4 [$(HO)_2SO_2$]
2. the chlorine atom in chloric acid, $HClO_3$ [$HOClO_2$]
3. the oxygen atom in hydrogen peroxide, HOOH
4. the nitrogen atom in nitric acid, HNO_3 [$HONO_2$]
5. the oxygen atom in the OH group in nitric acid, HNO_3 [$HONO_2$]
6. the central oxygen atom in the ozone molecule, O_3
7. each of the carbon atoms in propyne, CH_3CCH
8. the carbon atom in Freon, CCl_2F_2
9. each of the carbon atoms in allene, H_2CCCH_2

Answer

1. tetrahedral
2. trigonal pyramidal
3. bent (109°)
4. trigonal planar
5. bent (109°)
6. bent (109°)

7. CH_3CCH tetrahedral, CH_3CCH linear
8. tetrahedral
9. H_2CCCH_2 linear, H_2CCCH_2 trigonal planar

Exercise 5.E.22

Draw the Lewis structures and predict the shape of each compound or ion:

1. CO_2
2. NO_2^-
3. SO_3
4. SO_3^{2-}

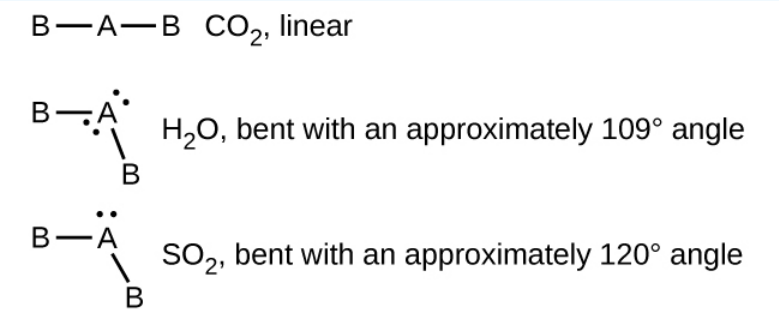
Answer

Add texts here. Do not delete this text first.

Exercise 5.E.23

A molecule with the formula AB_2, in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion for each shape.

Answer



Exercise 5.E.24

A molecule with the formula AB_3, in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion that has each shape.

Answer

Add texts here. Do not delete this text first.

Exercise 5.E.25

- Draw the Lewis electron dot structures for these molecules, including resonance structures where appropriate:

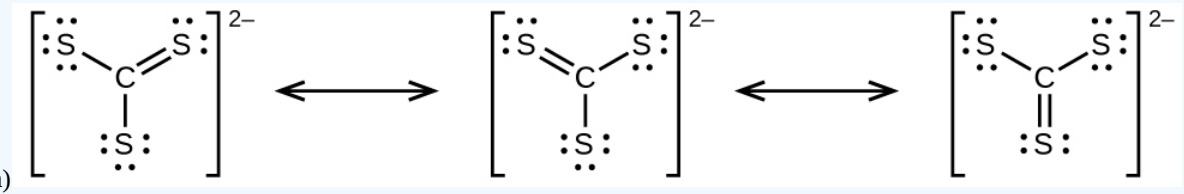
1. CS_3^{2-}
2. CS_2
3. CS

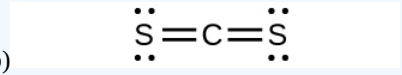
Answer

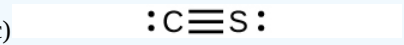
Add texts here. Do not delete this text first.

Exercise 5.E. 26

- predict the molecular shapes for CS_3^{2-} and CS_2 and explain how you arrived at your predictions

(a) 

(b) 

(c) 

Answer

CS_3^{2-} includes three regions of electron density (all are bonds with no lone pairs); the shape is trigonal planar;

CS_2 has only two regions of electron density (all bonds with no lone pairs);

the shape is linear

Exercise 5.E. 27

What is the molecular structure of the stable form of FNO_2? (N is the central atom.)

Answer

Add texts here. Do not delete this text first.

Exercise 5.E. 28

A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen. What is its molecular structure?

Answer

Add texts here. Do not delete this text first.

Use the simulation to perform the following exercises for a two-atom molecule:

1. Adjust the electronegativity value so the bond dipole is pointing toward B. Then determine what the electronegativity values must be to switch the dipole so that it points toward A.
2. With a partial positive charge on A, turn on the electric field and describe what happens.
3. With a small partial negative charge on A, turn on the electric field and describe what happens.
4. Reset all, and then with a large partial negative charge on A, turn on the electric field and describe what happens.

Exercise 5.E. 29

Use the simulation to perform the following exercises for a real molecule. You may need to rotate the molecules in three dimensions to see certain dipoles.

1. Sketch the bond dipoles and molecular dipole (if any) for O_3. Explain your observations.
2. Look at the bond dipoles for NH_3. Use these dipoles to predict whether N or H is more electronegative.
3. Predict whether there should be a molecular dipole for NH_3 and, if so, in which direction it will point. Check the molecular dipole box to test your hypothesis.

Answer

The molecular dipole points away from the hydrogen atoms.

Exercise 5.E.30

Use the Molecule Shape simulator to build a molecule. Starting with the central atom, click on the double bond to add one double bond. Then add one single bond and one lone pair. Rotate the molecule to observe the complete geometry. Name the electron group geometry and molecular structure and predict the bond angle.

Answer

Click the check boxes at the bottom and right of the simulator to check your answers.

Exercise 5.E.31

Use the Molecule Shape simulator to explore real molecules. On the Real Molecules tab, select H_2O. Switch between the "real" and "model" modes. Explain the difference observed.

Answer

The structures are very similar. In the model mode, each electron group occupies the same amount of space, so the bond angle is shown as 109.5°. In the "real" mode, the lone pairs are larger, causing the hydrogens to be compressed. This leads to the smaller angle of 104.5°.

Exercise 5.E.32

Use the Molecule Shape simulator to explore real molecules. On the Real Molecules tab, select "model" mode and S_2O. What is the model bond angle? Explain whether the "real" bond angle should be larger or smaller than the ideal model angle.

Answer

Add texts here. Do not delete this text first.

5.E.2: Valence Bond Theory

Exercise 5.E.33

Explain how σ and π bonds are similar and how they are different.

Answer

Similarities: Both types of bonds result from overlap of atomic orbitals on adjacent atoms and contain a maximum of two electrons. **Differences**: σ bonds are stronger and result from end-to-end overlap and all single bonds are σ bonds; π bonds between the same two atoms are weaker because they result from side-by-side overlap, and multiple bonds contain one or more π bonds (in addition to a σ bond).

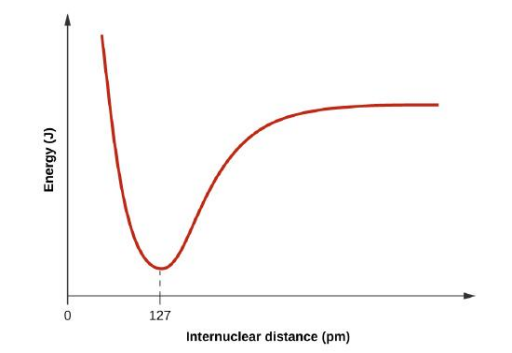
Exercise 5.E.34

Draw a curve that describes the energy of a system with H and Cl atoms at varying distances. Then, find the minimum energy of this curve two ways.

a. Use the bond energy found in Table 8.2.1 to calculate the energy for one single HCl bond (Hint: How many bonds are in a mole?)
b. Use the enthalpy of reaction and the bond energies for H_2 and Cl_2 to solve for the energy of one mole of HCl bonds.

$$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)} \quad \Delta H^{\circ}_{rxn} = -184.7\ kJ/mol \tag{5.E.1}$$

Answer



When H and Cl are separate (the x axis) the energy is at a particular value. As they approach, it decreases to a minimum at 127 pm (the bond distance), and then it increases sharply as you get closer.

a. (a) H–Cl431 kJ/mol 427kJmol×mol6.022×1023bonds×1000 JkJ=7.09×10−19
b. (b) We know Hess's law related to bond energies: ΔH°=ΣΔH∘BDE(broken)−ΣΔH∘BDE(formed) We are given the enthalpy of reaction

$$-184.7kJ/mol = (\Delta H \circ BDE(H-H) + \Delta H \circ BDE(Cl-Cl)) - (2\Delta H \circ BDE(H-Cl)) \tag{5.E.2}$$

$$H-His436kJ/molandCl-Clis243 \tag{5.E.3}$$

$$-184.7kJ/mol = (436+243)-2x = 679-2x \tag{5.E.4}$$

$$2x = 863.7kJ/mol \tag{5.E.5}$$

$$x = 432\ kJ/mol \tag{5.E.6}$$

This is very close to the value from part (a).

Exercise $5.E.35$

Explain why bonds occur at specific average bond distances instead of the atoms approaching each other infinitely close.

Answer

The specific average bond distance is the distance with the lowest energy. At distances less than the bond distance, the positive charges on the two nuclei repel each other, and the overall energy increases.

Exercise $5.E.36$

Use valence bond theory to explain the bonding in F_2, HF, and ClBr. Sketch the overlap of the atomic orbitals involved in the bonds.

Answer

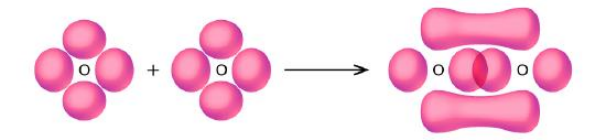
The single bond present in each molecule results from overlap of the relevant orbitals: F 2*p* orbitals in F_2, the H 1*s* and F 2*p* orbitals in HF, and the Cl 3*p* orbital and Br 4*p* orbital in ClBr.

Exercise $5.E.37$

Use valence bond theory to explain the bonding in O_2. Sketch the overlap of the atomic orbitals involved in the bonds in O_2.

Answer

Bonding: One σ bond and one π bond. The *s* orbitals are filled and do not overlap. The *p* orbitals overlap along the axis to form a σ bond and side by side to form the π bond.

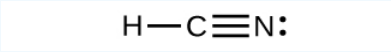


Exercise 5.E.38

How many σ and π bonds are present in the molecule HCN?

Answer

$H-C\equiv N$ has two σ (H–C and C–N) and two π (making the CN triple bond).

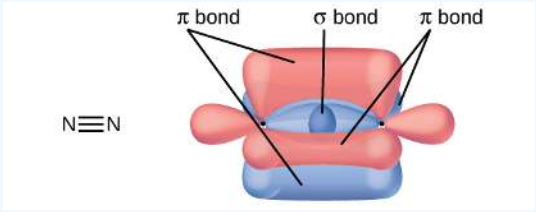


Exercise 5.E.39

A friend tells you N_2 has three π bonds due to overlap of the three *p*-orbitals on each N atom. Do you agree?

Answer

No, two of the *p* orbitals (one on each N) will be oriented end-to-end and will form a σ bond.



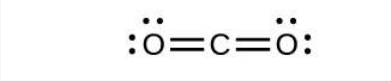
Exercise 5.E.40

Draw the Lewis structures for CO_2 and CO, and predict the number of σ and π bonds for each molecule.

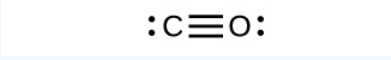
a. CO_2
b. CO

Answer

(a) 2 σ 2 π;



(b) 1 σ 2 π;



5.E.3: Hybrid Atomic Orbitals

https://chem.libretexts.org/@go/page/393239

Exercise 5.E.41

Why is the concept of hybridization required in valence bond theory?

Answer

Hybridization is introduced to explain the geometry of bonding orbitals in valance bond theory.Add texts here.

Exercise 5.E.42

Give the shape that describes each hybrid orbital set:

(a) sp^2

(b) sp^3d

(c) sp

(d) sp^3d^2

Answer

Add texts here. Do not delete this text first.

Exercise 5.E.43

Explain why a carbon atom cannot form five bonds using sp^3d hybrid orbitals.

Answer

There are no *d* orbitals in the valence shell of carbon.

Exercise 5.E.44

What is the hybridization of the central atom in each of the following?

(a) BeH_2

(b) SF_6

(c) PO_4^{3-}

(d) PCl_5

Answer

Add texts here. Do not delete this text first.

Exercise 5.E.45

A molecule with the formula AB_3 could have one of four different shapes. Give the shape and the hybridization of the central A atom for each.

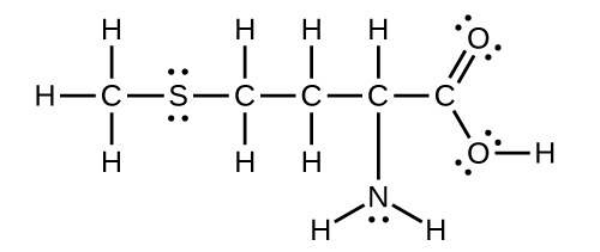
Answer

trigonal planar, sp^2; trigonal pyramidal (one lone pair on A) sp^3; T-shaped (two lone pairs on A sp^3d, or (three lone pairs on A) sp^3d^2

Exercise 5.E.46

Methionine, $CH_3SCH_2CH_2CH(NH_2)CO_2H$, is an amino acid found in proteins. Draw a Lewis structure of this compound. What is the hybridization type of each carbon, oxygen, the nitrogen, and the sulfur?

Answer



Exercise 5.E.47

Sulfuric acid is manufactured by a series of reactions represented by the following equations:

$S_8(s) + 8\,O_2(g) \longrightarrow 8\,SO_2(g)$

$2\,SO_2(g) + O_2(g) \longrightarrow 2\,SO_3(g)$

$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(l)$

Draw a Lewis structure, predict the molecular geometry by VSEPR, and determine the hybridization of sulfur for the following:

(a) circular S_8 molecule

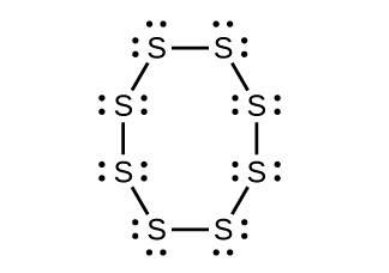
(b) SO_2 molecule

(c) SO_3 molecule

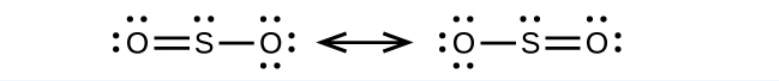
(d) H_2SO_4 molecule (the hydrogen atoms are bonded to oxygen atoms)

Answer

(a) Each S has a bent (109°) geometry, sp^3

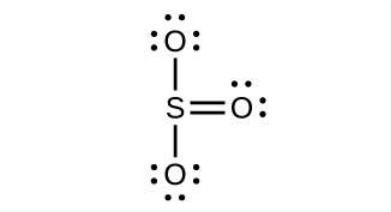


(b) Bent (120°), sp^2

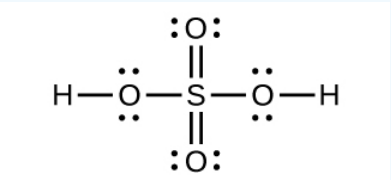


(c) Trigonal planar, sp^2

https://chem.libretexts.org/@go/page/393239



(d) Tetrahedral, sp^3



Exercise 5.E.48

Two important industrial chemicals, ethene, C_2H_4, and propene, C_3H_6, are produced by the steam (or thermal) cracking process:

$$2\,C_3H_8(g) \longrightarrow C_2H_4(g) + C_3H_6(g) + CH_4(g) + H_2(g)$$

For each of the four carbon compounds, do the following:

(a) Draw a Lewis structure.

(b) Predict the geometry about the carbon atom.

(c) Determine the hybridization of each type of carbon atom.

Answer

Add texts here. Do not delete this text first.

Exercise 5.E.49

For many years after they were discovered, it was believed that the noble gases could not form compounds. Now we know that belief to be incorrect. A mixture of xenon and fluorine gases, confined in a quartz bulb and placed on a windowsill, is found to slowly produce a white solid. Analysis of the compound indicates that it contains 77.55% Xe and 22.45% F by mass.

(a) What is the formula of the compound?

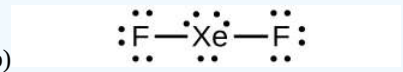
(b) Write a Lewis structure for the compound.

(c) Predict the shape of the molecules of the compound.

(d) What hybridization is consistent with the shape you predicted?

Answer

(a) XeF_2

(b) 

(c) linear

(d) sp^3d

https://chem.libretexts.org/@go/page/393239

Exercise 5.E.50

Consider nitrous acid, HNO_2 (HONO).

(a) Write a Lewis structure.

(b) What are the electron pair and molecular geometries of the internal oxygen and nitrogen atoms in the HNO_2 molecule?

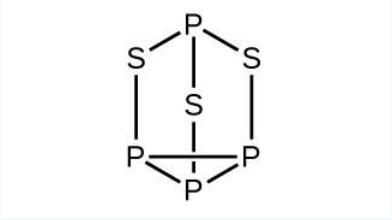
(c) What is the hybridization on the internal oxygen and nitrogen atoms in HNO_2?

Answer

Add texts here. Do not delete this text first.

Exercise 5.E.51

Strike-anywhere matches contain a layer of $KClO_3$ and a layer of P_4S_3. The heat produced by the friction of striking the match causes these two compounds to react vigorously, which sets fire to the wooden stem of the match. $KClO_3$ contains the ClO_3^- ion. P_4S_3 is an unusual molecule with the skeletal structure.



(a) Write Lewis structures for P_4S_3 and the ClO_3^- ion.

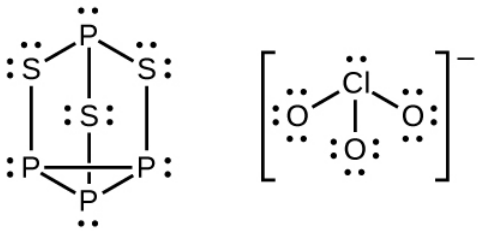
(b) Describe the geometry about the P atoms, the S atom, and the Cl atom in these species.

(c) Assign a hybridization to the P atoms, the S atom, and the Cl atom in these species.

(d) Determine the oxidation states and formal charge of the atoms in P_4S_3 and the ClO_3^- ion.

Answer

(a)



(b) P atoms, trigonal pyramidal; S atoms, bent, with two lone pairs; Cl atoms, trigonal pyramidal;

(c) Hybridization about P, S, and Cl is, in all cases, sp^3;

(d) Oxidation states P +1, S $-1\frac{1}{3}$, Cl +5, O –2. Formal charges: P 0; S 0; Cl +2: O –1

Exercise 5.E.52

Identify the hybridization of each carbon atom in the following molecule. (The arrangement of atoms is given; you need to determine how many bonds connect each pair of atoms.)



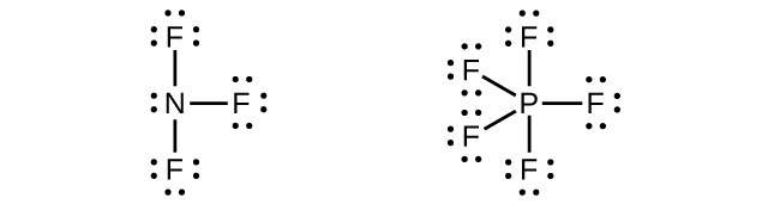
Answer

Add texts here. Do not delete this text first.

Exercise 5.E.53

Write Lewis structures for NF_3 and PF_5. On the basis of hybrid orbitals, explain the fact that NF_3, PF_3, and PF_5 are stable molecules, but NF_5 does not exist.

Answer



Phosphorus and nitrogen can form sp^3 hybrids to form three bonds and hold one lone pair in PF_3 and NF_3, respectively. However, nitrogen has no valence *d* orbitals, so it cannot form a set of sp^3d hybrid orbitals to bind five fluorine atoms in NF_5. Phosphorus has *d* orbitals and can bind five fluorine atoms with sp^3d hybrid orbitals in PF_5.

Exercise 5.E.54

In addition to NF_3, two other fluoro derivatives of nitrogen are known: N_2F_4 and N_2F_2. What shapes do you predict for these two molecules? What is the hybridization for the nitrogen in each molecule?

Answer

Add texts here. Do not delete this text first.

5.E.4: Multiple Bonds

Exercise 5.E.55

The bond energy of a C–C single bond averages 347 kJ mol^{-1}; that of a C≡C triple bond averages 839 kJ mol^{-1}. Explain why the triple bond is not three times as strong as a single bond.

Answer

Add texts here. Do not delete this text first.

Exercise 5.E.56

A triple bond consists of one σ bond and two π bonds. A σ bond is stronger than a π bond due to greater overlap.

For the carbonate ion, CO_3^{2-}, draw all of the resonance structures. Identify which orbitals overlap to create each bond.

Answer

Add texts here. Do not delete this text first.

Exercise 5.E.57

A useful solvent that will dissolve salts as well as organic compounds is the compound acetonitrile, H_3CCN. It is present in paint strippers.

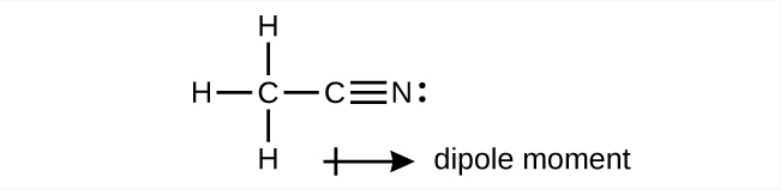
(a) Write the Lewis structure for acetonitrile, and indicate the direction of the dipole moment in the molecule.

(b) Identify the hybrid orbitals used by the carbon atoms in the molecule to form σ bonds.

(c) Describe the atomic orbitals that form the π bonds in the molecule. Note that it is not necessary to hybridize the nitrogen atom.

Answer

(a)



(b) The terminal carbon atom uses sp^3 hybrid orbitals, while the central carbon atom is *sp* hybridized.

(c) Each of the two π bonds is formed by overlap of a 2*p* orbital on carbon and a nitrogen 2*p* orbital.

Exercise 5.E.58

For the molecule allene, $H_2C=C=CH_2$, give the hybridization of each carbon atom. Will the hydrogen atoms be in the same plane or perpendicular planes?

Answer

Add texts here. Do not delete this text first.

Exercise 5.E.59

Identify the hybridization of the central atom in each of the following molecules and ions that contain multiple bonds:

(a) ClNO (N is the central atom)

(b) CS_2

(c) Cl_2CO (C is the central atom)

(d) Cl_2SO (S is the central atom)

(e) SO_2F_2 (S is the central atom)

(f) XeO_2F_2 (Xe is the central atom)

(g) $ClOF_2^+$ (Cl is the central atom)

Answer

https://chem.libretexts.org/@go/page/393239

(a) sp^2; (b) sp; (c) sp^2; (d) sp^3; (e) sp^3; (f) sp^3d; (g) sp^3

Exercise 5.E.60

Describe the molecular geometry and hybridization of the N, P, or S atoms in each of the following compounds.

(a) H_3PO_4, phosphoric acid, used in cola soft drinks

(b) NH_4NO_3, ammonium nitrate, a fertilizer and explosive

(c) S_2Cl_2, disulfur dichloride, used in vulcanizing rubber

(d) $K_4[O_3POPO_3]$, potassium pyrophosphate, an ingredient in some toothpastes

Answer

Add texts here. Do not delete this text first.

Exercise 5.E.61

For each of the following molecules, indicate the hybridization requested and whether or not the electrons will be delocalized:

(a) ozone (O_3) central O hybridization

(b) carbon dioxide (CO_2) central C hybridization

(c) nitrogen dioxide (NO_2) central N hybridization

(d) phosphate ion (PO_4^{3-}) central P hybridization

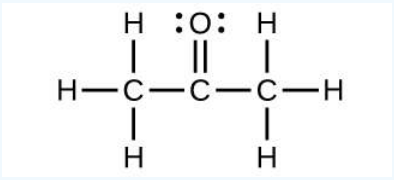
Answer

(a) sp^2, delocalized; (b) sp, localized; (c) sp^2, delocalized; (d) sp^3, delocalized

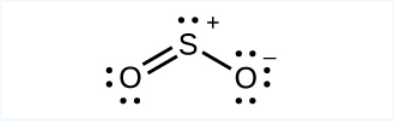
Exercise 5.E.62

For each of the following structures, determine the hybridization requested and whether the electrons will be delocalized:

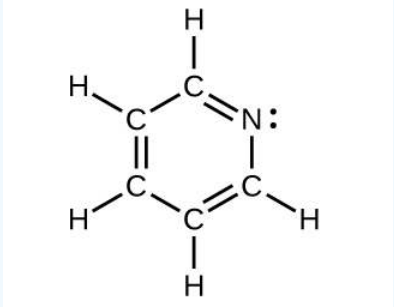
(a) Hybridization of each carbon



(b) Hybridization of sulfur



(c) All atoms



Answer

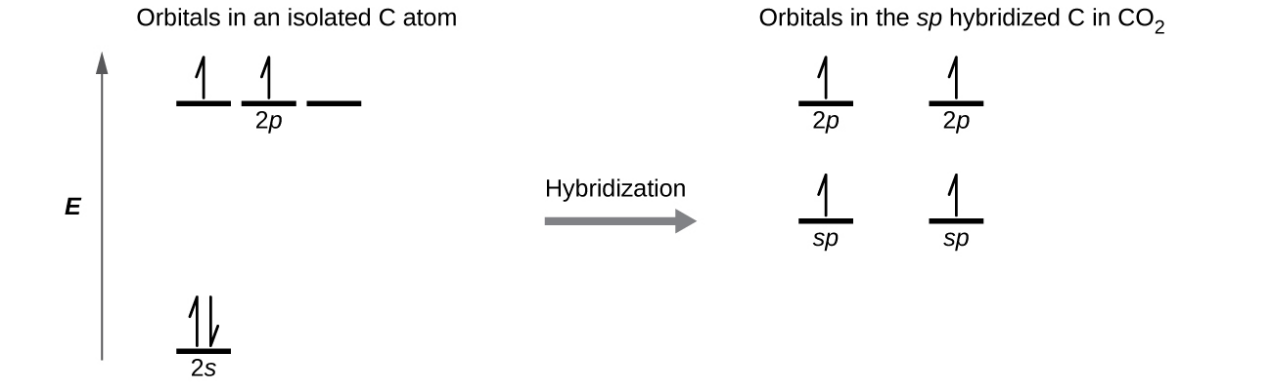
https://chem.libretexts.org/@go/page/393239

Add texts here. Do not delete this text first.

Exercise 5.E.63

Draw the orbital diagram for carbon in CO_2 showing how many carbon atom electrons are in each orbital.

Answer



Each of the four electrons is in a separate orbital and overlaps with an electron on an oxygen atom.

5.E.5: Molecular Orbital Theory

Exercise 5.E.64

Sketch the distribution of electron density in the bonding and antibonding molecular orbitals formed from two *s* orbitals and from two *p* orbitals.

How are the following similar, and how do they differ?

(a) σ molecular orbitals and π molecular orbitals

(b) ψ for an atomic orbital and ψ for a molecular orbital

(c) bonding orbitals and antibonding orbitals

Answer

(a) Similarities: Both are bonding orbitals that can contain a maximum of two electrons. Differences: σ orbitals are end-to-end combinations of atomic orbitals, whereas π orbitals are formed by side-by-side overlap of orbitals.

(b) Similarities: Both are quantum-mechanical constructs that represent the probability of finding the electron about the atom or the molecule. Differences: ψ for an atomic orbital describes the behavior of only one electron at a time based on the atom. For a molecule, ψ represents a mathematical combination of atomic orbitals.

(c) Similarities: Both are orbitals that can contain two electrons. Differences: Bonding orbitals result in holding two or more atoms together. Antibonding orbitals have the effect of destabilizing any bonding that has occurred.

Exercise 5.E.65

If molecular orbitals are created by combining five atomic orbitals from atom A and five atomic orbitals from atom B combine, how many molecular orbitals will result?

Answer

Add texts here. Do not delete this text first.

Exercise 5.E.66

Can a molecule with an odd number of electrons ever be diamagnetic? Explain why or why not.

Answer

An odd number of electrons can never be paired, regardless of the arrangement of the molecular orbitals. It will always be paramagnetic.

Exercise 5.E.67

Can a molecule with an even number of electrons ever be paramagnetic? Explain why or why not.

Answer

Add texts here. Do not delete this text first.

Exercise 5.E.68

Why are bonding molecular orbitals lower in energy than the parent atomic orbitals?

Answer

Bonding orbitals have electron density in close proximity to more than one nucleus. The interaction between the bonding positively charged nuclei and negatively charged electrons stabilizes the system.

Exercise 5.E.69

Calculate the bond order for an ion with this configuration:

$$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2px})^2(\pi_{2py},\ \pi_{2pz})^4(\pi^*_{2py},\ \pi^*_{2pz})^3$$

Answer

Add texts here. Do not delete this text first.

Exercise 5.E.70

Explain why an electron in the bonding molecular orbital in the H_2 molecule has a lower energy than an electron in the 1*s* atomic orbital of either of the separated hydrogen atoms.

Answer

The pairing of the two bonding electrons lowers the energy of the system relative to the energy of the nonbonded electrons.

Exercise 5.E.71

Predict the valence electron molecular orbital configurations for the following, and state whether they will be stable or unstable ions.

(a) Na_2^{2+}

(b) Mg_2^{2+}

(c) Al_2^{2+}

(d) Si_2^{2+}

(e) P_2^{2+}

(f) S_2^{2+}

(g) F_2^{2+}

(h) Ar_2^{2+}

Answer

Add texts here. Do not delete this text first.

Exercise 5.E.72

Determine the bond order of each member of the following groups, and determine which member of each group is predicted by the molecular orbital model to have the strongest bond.

(a) H_2, H_2^+, H_2^-

(b) O_2, O_2^{2+}, O_2^{2-}

(c) Li_2, Be_2^+, Be_2

(d) F_2, F_2^+, F_2^-

Answer

(a) H_2 bond order = 1, H_2^+ bond order = 0.5, H_2^- bond order = 0.5, strongest bond is H_2;

(b) O_2 bond order = 2, O_2^{2+} bond order = 3; O_2^{2-} bond order = 1, strongest bond is O_2^{2+};

(c) Li_2 bond order = 1, Be_2^+ bond order = 0.5, Be_2 bond order = 0, strongest bond is Li_2;

(d) F_2 bond order = 1, F_2^+ bond order = 1.5, F_2^- bond order = 0.5, strongest bond is F_2^+;

Exercise 5.E.73

For the first ionization energy for an N_2 molecule, what molecular orbital is the electron removed from?

Answer

Add texts here. Do not delete this text first.

Exercise 5.E.74

Compare the atomic and molecular orbital diagrams to identify the member of each of the following pairs that has the highest first ionization energy (the most tightly bound electron) in the gas phase:

(a) H and H_2

(b) N and N_2

(c) O and O_2

(d) C and C_2

(e) B and B_2

Answer

(a) H_2; (b) N_2; (c) O; (d) C_2; (e) B_2

Exercise 5.E.75

Which of the period 2 homonuclear diatomic molecules are predicted to be paramagnetic?

Answer

Add texts here. Do not delete this text first.

Exercise 5.E.76

A friend tells you that the 2*s* orbital for fluorine starts off at a much lower energy than the 2*s* orbital for lithium, so the resulting σ_{2s} molecular orbital in F_2 is more stable than in Li_2. Do you agree?

Answer

Yes, fluorine is a smaller atom than Li, so atoms in the 2*s* orbital are closer to the nucleus and more stable.

Exercise 5.E.77

True or false: Boron contains $2s^2 2p^1$ valence electrons, so only one *p* orbital is needed to form molecular orbitals.

Answer

Add texts here. Do not delete this text first.

Exercise 5.E.78

What charge would be needed on F_2 to generate an ion with a bond order of 2?

Answer

2+

Exercise 5.E.79

Predict whether the MO diagram for S_2 would show s-p mixing or not.

Answer

Add texts here. Do not delete this text first.

Exercise 5.E.80

Explain why N_2^{2+} is diamagnetic, while O_2^{4+}, which has the same number of valence electrons, is paramagnetic.

Answer

N_2 has s-p mixing, so the π orbitals are the last filled in N_2^{2+}. O_2 does not have s-p mixing, so the σ_p orbital fills before the π orbitals.

Exercise 5.E.81

Using the MO diagrams, predict the bond order for the stronger bond in each pair:

(a) F_2 or F_2^+

(b) O_2 or O_2^{2+}

Answer

Add texts here. Do not delete this text first.

This page titled 5.E: Advanced Theories of Covalent Bonding (Exercises) is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

5.S: Study Guide

5: Chemical Bonding II - Molecular Geometry and Hybridization of Atomic Orbitals

Key Topis for TRU students taking CHEM1500

- Molecular geometry
- dipole moment
- Valence Bond theory
- hybridization of atomic orbitals
- hybridization of molecules containing multiple bonds
- MO theory
- energy level diagrams for homonuclear diatomics

Key Learning Outcomes (Examples)

- determine and justify the hybrid orbital type for non-terminal atoms in molecules and polyatomic ions based on Valence Bond Theory
- predict molecular shapes based on Valence Shell Electron Pair Repulsion (VSEPR) Theory
- complete molecular orbital energy diagrams for simple homo-nuclear bi-atomic molecules and ions to predict bond-order and magnetic properties

5.S: Study Guide is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

6: Intermolecular Forces and Liquids and Solids

6.1: Intermolecular Forces

6.E: Intermolecular Forces and Liquids and Solids (Exercises)

6.S: Study Guide

6: Intermolecular Forces and Liquids and Solids is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

6.1: Intermolecular Forces

Learning Objectives

- Describe the types of intermolecular forces possible between atoms or molecules in condensed phases (dispersion forces, dipole-dipole attractions, and hydrogen bonding)
- Identify the types of intermolecular forces experienced by specific molecules based on their structures
- Explain the relation between the intermolecular forces present within a substance and the temperatures associated with changes in its physical state

As was the case for gaseous substances, the kinetic molecular theory may be used to explain the behavior of solids and liquids. In the following description, the term *particle* will be used to refer to an atom, molecule, or ion. Note that we will use the popular phrase "intermolecular attraction" to refer to attractive forces between the particles of a substance, regardless of whether these particles are molecules, atoms, or ions.

Consider these two aspects of the molecular-level environments in solid, liquid, and gaseous matter:

- Particles in a solid are tightly packed together and often arranged in a regular pattern; in a liquid, they are close together with no regular arrangement; in a gas, they are far apart with no regular arrangement.
- Particles in a solid vibrate about fixed positions and do not generally move in relation to one another; in a liquid, they move past each other but remain in essentially constant contact; in a gas, they move independently of one another except when they collide.

The differences in the properties of a solid, liquid, or gas reflect the strengths of the attractive forces between the atoms, molecules, or ions that make up each phase. The phase in which a substance exists depends on the relative extents of its intermolecular forces (IMFs) and the kinetic energies (KE) of its molecules. IMFs are the various forces of attraction that may exist between the atoms and molecules of a substance due to electrostatic phenomena, as will be detailed in this module. These forces serve to hold particles close together, whereas the particles' KE provides the energy required to overcome the attractive forces and thus increase the distance between particles. Figure 6.1.1 illustrates how changes in physical state may be induced by changing the temperature, hence, the average KE, of a given substance.

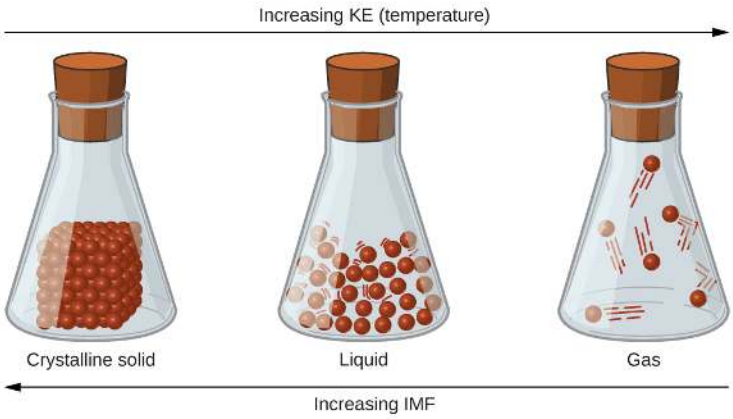


Figure 6.1.1: Transitions between solid, liquid, and gaseous states of a substance occur when conditions of temperature or pressure favor the associated changes in intermolecular forces. (Note: The space between particles in the gas phase is much greater than shown.)

As an example of the processes depicted in this figure, consider a sample of water. When gaseous water is cooled sufficiently, the attractions between H_2O molecules will be capable of holding them together when they come into contact with each other; the gas condenses, forming liquid H_2O. For example, liquid water forms on the outside of a cold glass as the water vapor in the air is cooled by the cold glass, as seen in Figure 6.1.2.



Figure 6.1.2: Condensation forms when water vapor in the air is cooled enough to form liquid water, such as (a) on the outside of a cold beverage glass or (b) in the form of fog. (credit a: modification of work by Jenny Downing; credit b: modification of work by Cory Zanker)

We can also liquefy many gases by compressing them, if the temperature is not too high. The increased pressure brings the molecules of a gas closer together, such that the attractions between the molecules become strong relative to their KE. Consequently, they form liquids. Butane, C_4H_{10}, is the fuel used in disposable lighters and is a gas at standard temperature and pressure. Inside the lighter's fuel compartment, the butane is compressed to a pressure that results in its condensation to the liquid state, as shown in Figure 6.1.3.



Figure 6.1.3: Gaseous butane is compressed within the storage compartment of a disposable lighter, resulting in its condensation to the liquid state. (credit: modification of work by "Sam-Cat"/Flickr)

Finally, if the temperature of a liquid becomes sufficiently low, or the pressure on the liquid becomes sufficiently high, the molecules of the liquid no longer have enough KE to overcome the IMF between them, and a solid forms. A more thorough discussion of these and other changes of state, or phase transitions, is provided in a later module of this chapter.

6.1.1: Forces between Molecules

Under appropriate conditions, the attractions between all gas molecules will cause them to form liquids or solids. This is due to intermolecular forces, not *intra*molecular forces. *Intra*molecular forces are those *within* the molecule that keep the molecule together, for example, the bonds between the atoms. *Inter*molecular forces are the attractions *between* molecules, which determine many of the physical properties of a substance. Figure 6.1.4 illustrates these different molecular forces. The strengths of these attractive forces vary widely, though usually the IMFs between small molecules are weak compared to the intramolecular forces that bond atoms together within a molecule. For example, to overcome the IMFs in one mole of liquid HCl and convert it into

gaseous HCl requires only about 17 kilojoules. However, to break the covalent bonds between the hydrogen and chlorine atoms in one mole of HCl requires about 25 times more energy—430 kilojoules.

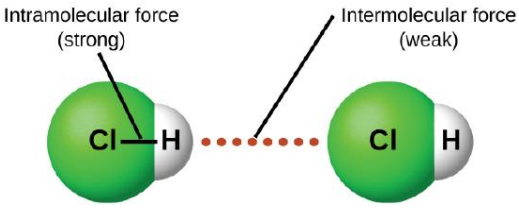


Figure 6.1.4: Intramolecular forces keep a molecule intact. Intermolecular forces hold multiple molecules together and determine many of a substance's properties.

All of the attractive forces between neutral atoms and molecules are known as van der Waals forces, although they are usually referred to more informally as intermolecular attraction. We will consider the various types of IMFs in the next three sections of this module.



Intermolecular Forces: https://youtu.be/nDUqGjcqQME

6.1.2: Dispersion Forces

One of the three van der Waals forces is present in all condensed phases, regardless of the nature of the atoms or molecules composing the substance. This attractive force is called the London dispersion force in honor of German-born American physicist Fritz London who, in 1928, first explained it. This force is often referred to as simply the dispersion force. Because the electrons of an atom or molecule are in constant motion (or, alternatively, the electron's location is subject to quantum-mechanical variability), at any moment in time, an atom or molecule can develop a temporary, instantaneous dipole if its electrons are distributed asymmetrically. The presence of this dipole can, in turn, distort the electrons of a neighboring atom or molecule, producing an induced dipole. These two rapidly fluctuating, temporary dipoles thus result in a relatively weak electrostatic attraction between the species—a so-called dispersion force like that illustrated in Figure 6.1.5.

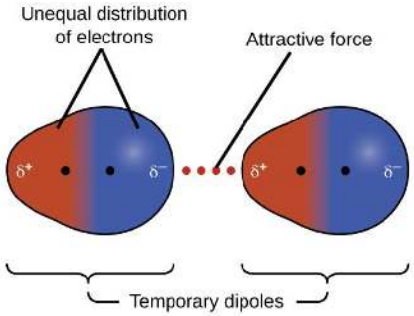


Figure 6.1.5: Dispersion forces result from the formation of temporary dipoles, as illustrated here for two nonpolar diatomic molecules.

Dispersion forces that develop between atoms in different molecules can attract the two molecules to each other. The forces are relatively weak, however, and become significant only when the molecules are very close. Larger and heavier atoms and molecules

exhibit stronger dispersion forces than do smaller and lighter atoms and molecules. F_2 and Cl_2 are gases at room temperature (reflecting weaker attractive forces); Br_2 is a liquid, and I_2 is a solid (reflecting stronger attractive forces). Trends in observed melting and boiling points for the halogens clearly demonstrate this effect, as seen in Table 6.1.1.

Table 6.1.1: Melting and Boiling Points of the Halogens

Halogen	Molar Mass	Atomic Radius	Melting Point	Boiling Point
fluorine, F_2	38 g/mol	72 pm	53 K	85 K
chlorine, Cl_2	71 g/mol	99 pm	172 K	238 K
bromine, Br_2	160 g/mol	114 pm	266 K	332 K
iodine, I_2	254 g/mol	133 pm	387 K	457 K
astatine, At_2	420 g/mol	150 pm	575 K	610 K

The increase in melting and boiling points with increasing atomic/molecular size may be rationalized by considering how the strength of dispersion forces is affected by the electronic structure of the atoms or molecules in the substance. In a larger atom, the valence electrons are, on average, farther from the nuclei than in a smaller atom. Thus, they are less tightly held and can more easily form the temporary dipoles that produce the attraction. The measure of how easy or difficult it is for another electrostatic charge (for example, a nearby ion or polar molecule) to distort a molecule's charge distribution (its electron cloud) is known as polarizability. A molecule that has a charge cloud that is easily distorted is said to be very polarizable and will have large dispersion forces; one with a charge cloud that is difficult to distort is not very polarizable and will have small dispersion forces.

Example 6.1.1: London Forces and Their Effects

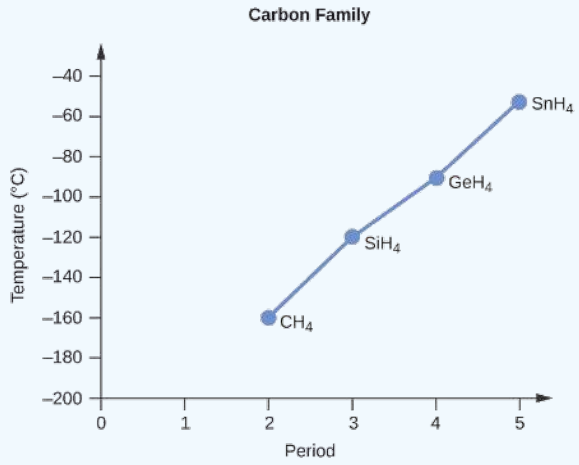
Order the following compounds of a group 14 element and hydrogen from lowest to highest boiling point: CH_4, SiH_4, GeH_4, and SnH_4. Explain your reasoning.

Solution

Applying the skills acquired in the chapter on chemical bonding and molecular geometry, all of these compounds are predicted to be nonpolar, so they may experience only dispersion forces: the smaller the molecule, the less polarizable and the weaker the dispersion forces; the larger the molecule, the larger the dispersion forces. The molar masses of CH_4, SiH_4, GeH_4, and SnH_4 are approximately 16 g/mol, 32 g/mol, 77 g/mol, and 123 g/mol, respectively. Therefore, CH_4 is expected to have the lowest boiling point and SnH_4 the highest boiling point. The ordering from lowest to highest boiling point is expected to be

$$CH_4 < SiH_4 < GeH_4 < SnH_4$$

A graph of the actual boiling points of these compounds versus the period of the group 14 elements shows this prediction to be correct:



https://chem.libretexts.org/@go/page/393241

Exercise 6.1.1

Order the following hydrocarbons from lowest to highest boiling point: C_2H_6, C_3H_8, and C_4H_{10}.

Answer

All of these compounds are nonpolar and only have London dispersion forces: the larger the molecule, the larger the dispersion forces and the higher the boiling point. The ordering from lowest to highest boiling point is therefore

$$C_2H_6 < C_3H_8 < C_4H_{10}.$$

The shapes of molecules also affect the magnitudes of the dispersion forces between them. For example, boiling points for the isomers *n*-pentane, isopentane, and neopentane (shown in Figure 6.1.6) are 36 °C, 27 °C, and 9.5 °C, respectively. Even though these compounds are composed of molecules with the same chemical formula, C_5H_{12}, the difference in boiling points suggests that dispersion forces in the liquid phase are different, being greatest for *n*-pentane and least for neopentane. The elongated shape of *n*-pentane provides a greater surface area available for contact between molecules, resulting in correspondingly stronger dispersion forces. The more compact shape of isopentane offers a smaller surface area available for intermolecular contact and, therefore, weaker dispersion forces. Neopentane molecules are the most compact of the three, offering the least available surface area for intermolecular contact and, hence, the weakest dispersion forces. This behavior is analogous to the connections that may be formed between strips of VELCRO brand fasteners: the greater the area of the strip's contact, the stronger the connection.

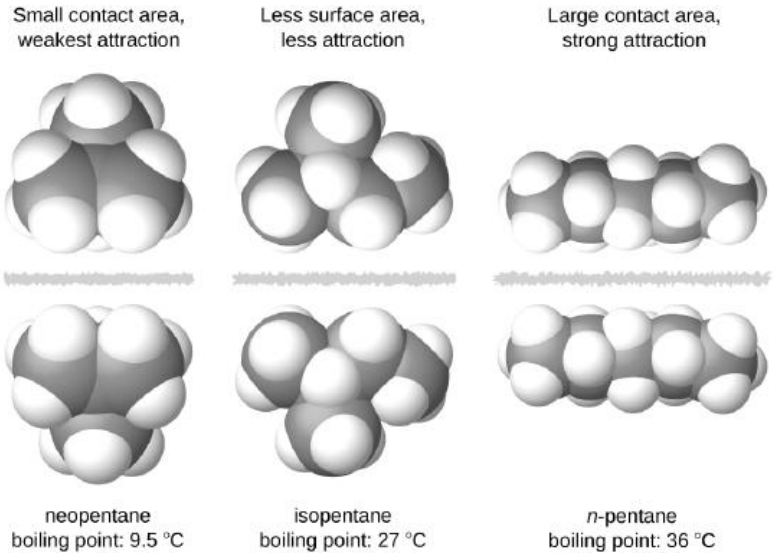


Figure 6.1.6: The strength of the dispersion forces increases with the contact area between molecules, as demonstrated by the boiling points of these pentane isomers.

Applications: Geckos and Intermolecular Forces

Geckos have an amazing ability to adhere to most surfaces. They can quickly run up smooth walls and across ceilings that have no toe-holds, and they do this without having suction cups or a sticky substance on their toes. And while a gecko can lift its feet easily as it walks along a surface, if you attempt to pick it up, it sticks to the surface. How are geckos (as well as spiders and some other insects) able to do this? Although this phenomenon has been investigated for hundreds of years, scientists only recently uncovered the details of the process that allows geckos' feet to behave this way.

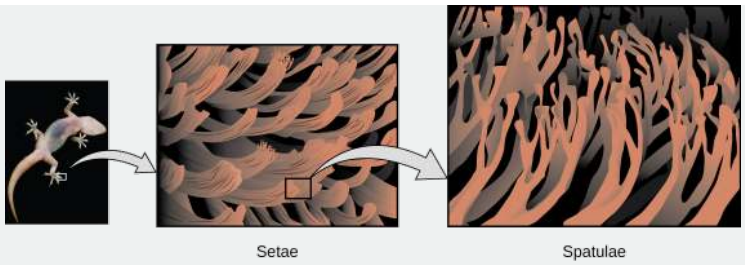


Figure 6.1.7: Geckos' toes contain large numbers of tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko's millions of spatulae. By changing how the spatulae contact the surface, geckos can turn their stickiness "on" and "off." (credit photo: modification of work by "JC*+A!"/Flickr)

Geckos' toes are covered with hundreds of thousands of tiny hairs known as *setae*, with each seta, in turn, branching into hundreds of tiny, flat, triangular tips called *spatulae*. The huge numbers of spatulae on its setae provide a gecko, shown in Figure 6.1.7, with a large total surface area for sticking to a surface. In 2000, Kellar Autumn, who leads a multi-institutional gecko research team, found that geckos adhered equally well to both polar silicon dioxide and nonpolar gallium arsenide. This proved that geckos stick to surfaces because of dispersion forces—weak intermolecular attractions arising from temporary, synchronized charge distributions between adjacent molecules. Although dispersion forces are very weak, the total attraction over millions of spatulae is large enough to support many times the gecko's weight.

In 2014, two scientists developed a model to explain how geckos can rapidly transition from "sticky" to "non-sticky." Alex Greaney and Congcong Hu at Oregon State University described how geckos can achieve this by changing the angle between their spatulae and the surface. Geckos' feet, which are normally nonsticky, become sticky when a small shear force is applied. By curling and uncurling their toes, geckos can alternate between sticking and unsticking from a surface, and thus easily move across it. Further investigations may eventually lead to the development of better adhesives and other applications.



Watch this video to learn more about Kellar Autumn's research that determined that van der Waals forces are responsible for a gecko's ability to cling and climb.



Dispersion Intermolecular Force: https://youtu.be/RCRTcIEQ-Hk

6.1.3: Dipole-Dipole Attractions

Recall from the chapter on chemical bonding and molecular geometry that *polar* molecules have a partial positive charge on one side and a partial negative charge on the other side of the molecule—a separation of charge called a *dipole*. Consider a polar molecule such as hydrogen chloride, HCl. In the HCl molecule, the more electronegative Cl atom bears the partial negative charge, whereas the less electronegative H atom bears the partial positive charge. An attractive force between HCl molecules results from the attraction between the positive end of one HCl molecule and the negative end of another. This attractive force is called a dipole-dipole attraction—the electrostatic force between the partially positive end of one polar molecule and the partially negative end of another, as illustrated in Figure 6.1.8.

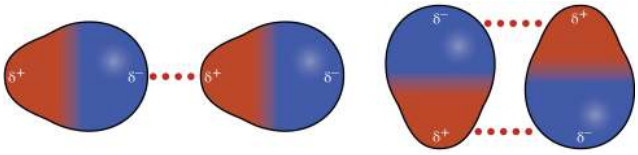


Figure 6.1.8: This image shows two arrangements of polar molecules, such as HCl, that allow an attraction between the partial negative end of one molecule and the partial positive end of another.

The effect of a dipole-dipole attraction is apparent when we compare the properties of HCl molecules to nonpolar F_2 molecules. Both HCl and F_2 consist of the same number of atoms and have approximately the same molecular mass. At a temperature of 150 K, molecules of both substances would have the same average KE. However, the dipole-dipole attractions between HCl molecules are sufficient to cause them to "stick together" to form a liquid, whereas the relatively weaker dispersion forces between nonpolar F_2 molecules are not, and so this substance is gaseous at this temperature. The higher normal boiling point of HCl (188 K) compared to F_2 (85 K) is a reflection of the greater strength of dipole-dipole attractions between HCl molecules, compared to the attractions between nonpolar F_2 molecules. We will often use values such as boiling or freezing points, or enthalpies of vaporization or fusion, as indicators of the relative strengths of IMFs of attraction present within different substances.

✔ Example 6.1.2: Dipole-Dipole Forces and Their Effects

Predict which will have the higher boiling point: N_2 or CO. Explain your reasoning.

Solution

CO and N_2 are both diatomic molecules with masses of about 28 amu, so they experience similar London dispersion forces. Because CO is a polar molecule, it experiences dipole-dipole attractions. Because N_2 is nonpolar, its molecules cannot exhibit dipole-dipole attractions. The dipole-dipole attractions between CO molecules are comparably stronger than the dispersion forces between nonpolar N_2 molecules, so CO is expected to have the higher boiling point.

A common method for preparing oxygen is the decomposition

Exercise 6.1.2

Predict which will have the higher boiling point: ICl or Br_2. Explain your reasoning.

Answer

ICl. ICl and Br_2 have similar masses (~160 amu) and therefore experience similar London dispersion forces. ICl is polar and thus also exhibits dipole-dipole attractions; Br_2 is nonpolar and does not. The relatively stronger dipole-dipole attractions require more energy to overcome, so ICl will have the higher boiling point.



Dipole Intermolecular Force: https://youtu.be/ACq_95SIBck

6.1.4: Hydrogen Bonding

Nitrosyl fluoride (ONF, molecular mass 49 amu) is a gas at room temperature. Water (H_2O, molecular mass 18 amu) is a liquid, even though it has a lower molecular mass. We clearly cannot attribute this difference between the two compounds to dispersion forces. Both molecules have about the same shape and ONF is the heavier and larger molecule. It is, therefore, expected to experience more significant dispersion forces. Additionally, we cannot attribute this difference in boiling points to differences in the dipole moments of the molecules. Both molecules are polar and exhibit comparable dipole moments. The large difference between the boiling points is due to a particularly strong dipole-dipole attraction that may occur when a molecule contains a hydrogen atom bonded to a fluorine, oxygen, or nitrogen atom (the three most electronegative elements). The very large difference in electronegativity between the H atom (2.1) and the atom to which it is bonded (4.0 for an F atom, 3.5 for an O atom, or 3.0 for a N atom), combined with the very small size of a H atom and the relatively small sizes of F, O, or N atoms, leads to *highly concentrated partial charges* with these atoms. Molecules with F-H, O-H, or N-H moieties are very strongly attracted to similar moieties in nearby molecules, a particularly strong type of dipole-dipole attraction called hydrogen bonding. Examples of hydrogen bonds include HF···HF, H_2O···HOH, and H_3N···HNH_2, in which the hydrogen bonds are denoted by dots. Figure 6.1.9 illustrates hydrogen bonding between water molecules.

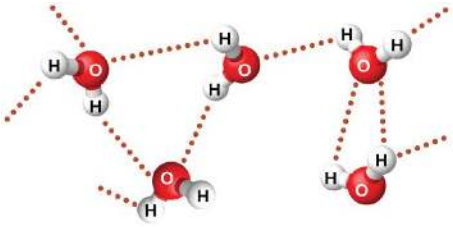


Figure 6.1.9: Water molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.

Despite use of the word “bond,” keep in mind that hydrogen bonds are *intermolecular* attractive forces, not *intramolecular* attractive forces (covalent bonds). Hydrogen bonds are much weaker than covalent bonds, only about 5 to 10% as strong, but are generally much stronger than other dipole-dipole attractions and dispersion forces.

Hydrogen bonds have a pronounced effect on the properties of condensed phases (liquids and solids). For example, consider the trends in boiling points for the binary hydrides of group 15 (NH_3, PH_3, AsH_3, and SbH_3), group 16 hydrides (H_2O, H_2S, H_2Se, and H_2Te), and group 17 hydrides (HF, HCl, HBr, and HI). The boiling points of the heaviest three hydrides for each group are plotted in Figure 6.1.10. As we progress down any of these groups, the polarities of the molecules decrease slightly, whereas the sizes of the molecules increase substantially. The effect of increasingly stronger dispersion forces dominates that of increasingly weaker dipole-dipole attractions, and the boiling points are observed to increase steadily. For the group 15, 16, and 17 hydrides, the boiling points for each class of compounds increase with increasing molecular mass for elements in periods 3, 4, and 5.

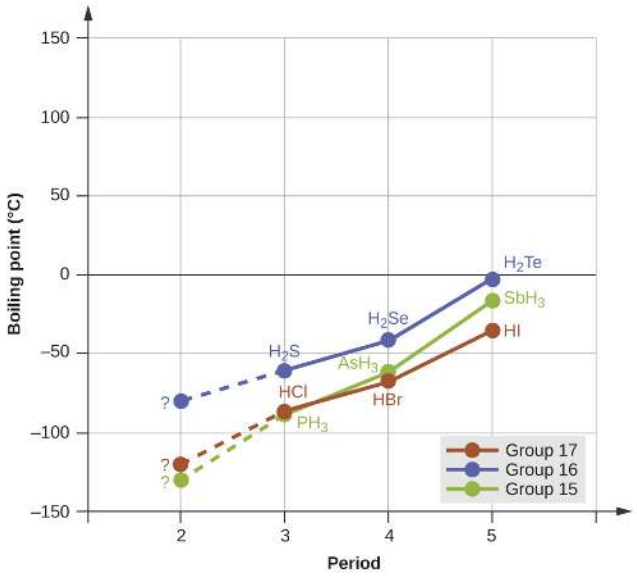


Figure 6.1.10: In comparison to periods 3−5, the binary hydrides of period 2 elements in groups 17, 16 and 15 (F, O and N, respectively) exhibit anomalously high boiling points due to hydrogen bonding.

If we use this trend to predict the boiling points for the lightest hydride for each group, we would expect NH_3 to boil at about −120 °C, H_2O to boil at about −80 °C, and HF to boil at about −110 °C. However, when we measure the boiling points for these compounds, we find that they are dramatically higher than the trends would predict, as shown in Figure 6.1.10. The stark contrast between our naïve predictions and reality provides compelling evidence for the strength of hydrogen bonding.

✔ Example 6.1.3: Effect of Hydrogen Bonding on Boiling Points

Consider the compounds dimethylether (CH_3OCH_3), ethanol (CH_3CH_2OH), and propane ($CH_3CH_2CH_3$). Their boiling points, not necessarily in order, are −42.1 °C, −24.8 °C, and 78.4 °C. Match each compound with its boiling point. Explain your reasoning.

Solution

The VSEPR-predicted shapes of CH_3OCH_3, CH_3CH_2OH, and $CH_3CH_2CH_3$ are similar, as are their molar masses (46 g/mol, 46 g/mol, and 44 g/mol, respectively), so they will exhibit similar dispersion forces. Since $CH_3CH_2CH_3$ is nonpolar, it may exhibit *only* dispersion forces. Because CH_3OCH_3 is polar, it will also experience dipole-dipole attractions. Finally, CH_3CH_2OH has an −OH group, and so it will experience the uniquely strong dipole-dipole attraction known as hydrogen bonding. So the ordering in terms of strength of IMFs, and thus boiling points, is $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CH_2OH$. The boiling point of propane is −42.1 °C, the boiling point of dimethylether is −24.8 °C, and the boiling point of ethanol is 78.5 °C.

? Exercise 6.1.3

Ethane (CH_3CH_3) has a melting point of −183 °C and a boiling point of −89 °C. Predict the melting and boiling points for methylamine (CH_3NH_2). Explain your reasoning.

Answer

The melting point and boiling point for methylamine are predicted to be significantly greater than those of ethane. CH_3CH_3 and CH_3NH_2 are similar in size and mass, but methylamine possesses an −NH group and therefore may exhibit hydrogen bonding. This greatly increases its IMFs, and therefore its melting and boiling points. It is difficult to predict values, but the known values are a melting point of −93 °C and a boiling point of −6 °C.

6.1.5: Hydrogen Bonding and DNA

Deoxyribonucleic acid (DNA) is found in every living organism and contains the genetic information that determines the organism's characteristics, provides the blueprint for making the proteins necessary for life, and serves as a template to pass this information on to the organism's offspring. A DNA molecule consists of two (anti-)parallel chains of repeating nucleotides, which form its well-known double helical structure, as shown in Figure 6.1.10.

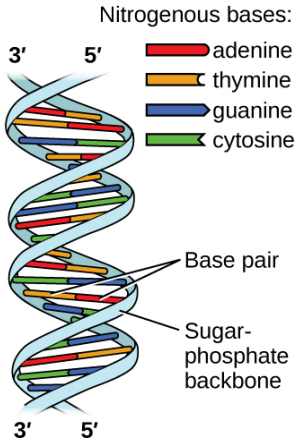


Figure 6.1.11: Two separate DNA molecules form a double-stranded helix in which the molecules are held together via hydrogen bonding. (credit: modification of work by Jerome Walker, Dennis Myts)

Each nucleotide contains a (deoxyribose) sugar bound to a phosphate group on one side, and one of four nitrogenous bases on the other. Two of the bases, cytosine (C) and thymine (T), are single-ringed structures known as pyrimidines. The other two, adenine (A) and guanine (G), are double-ringed structures called purines. These bases form complementary base pairs consisting of one purine and one pyrimidine, with adenine pairing with thymine, and cytosine with guanine. Each base pair is held together by hydrogen bonding. A and T share two hydrogen bonds, C and G share three, and both pairings have a similar shape and structure Figure 6.1.12

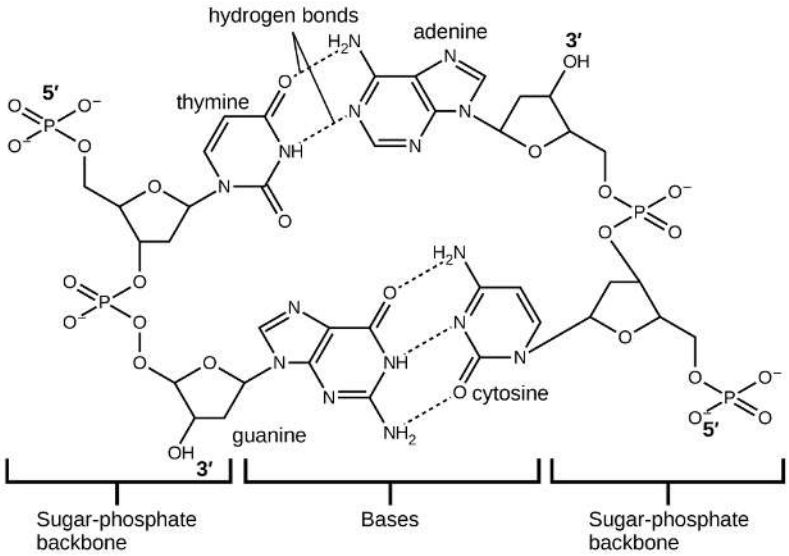


Figure 6.1.12: The geometries of the base molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called "complementary base pairs."

The cumulative effect of millions of hydrogen bonds effectively holds the two strands of DNA together. Importantly, the two strands of DNA can relatively easily “unzip” down the middle since hydrogen bonds are relatively weak compared to the covalent bonds that hold the atoms of the individual DNA molecules together. This allows both strands to function as a template for replication.



Hydrogen Bonding Intermolecular Force: https://youtu.be/92rbjSpHbr0

Summary

The physical properties of condensed matter (liquids and solids) can be explained in terms of the kinetic molecular theory. In a liquid, intermolecular attractive forces hold the molecules in contact, although they still have sufficient kinetic energy to move past each other. Intermolecular attractive forces, collectively referred to as van der Waals forces, are responsible for the behavior of liquids and solids and are electrostatic in nature. Dipole-dipole attractions result from the electrostatic attraction of the partial negative end of one dipolar molecule for the partial positive end of another. The temporary dipole that results from the motion of the electrons in an atom can induce a dipole in an adjacent atom and give rise to the London dispersion force. London forces increase with increasing molecular size. Hydrogen bonds are a special type of dipole-dipole attraction that results when hydrogen is bonded to one of the three most electronegative elements: F, O, or N.

Glossary

dipole-dipole attraction

intermolecular attraction between two permanent dipoles

dispersion force

(also, London dispersion force) attraction between two rapidly fluctuating, temporary dipoles; significant only when particles are very close together

hydrogen bonding

occurs when exceptionally strong dipoles attract; bonding that exists when hydrogen is bonded to one of the three most electronegative elements: F, O, or N

induced dipole

temporary dipole formed when the electrons of an atom or molecule are distorted by the instantaneous dipole of a neighboring atom or molecule

instantaneous dipole

temporary dipole that occurs for a brief moment in time when the electrons of an atom or molecule are distributed asymmetrically

intermolecular force

noncovalent attractive force between atoms, molecules, and/or ions

polarizability

measure of the ability of a charge to distort a molecule’s charge distribution (electron cloud)

van der Waals force

attractive or repulsive force between molecules, including dipole-dipole, dipole-induced dipole, and London dispersion forces; does not include forces due to covalent or ionic bonding, or the attraction between ions and molecules

---

This page titled 6.1: Intermolecular Forces is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **10.2: Intermolecular Forces** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

6.E: Intermolecular Forces and Liquids and Solids (Exercises)

6.E.1: Intermolecular Forces

Exercise 6.E.1

In terms of their bulk properties, how do liquids and solids differ? How are they similar?

Answer

Liquids and solids are similar in that they are matter composed of atoms, ions, or molecules. They are incompressible and have similar densities that are both much larger than those of gases. They are different in that liquids have no fixed shape, and solids are rigid.

Exercise 6.E.2

In terms of the kinetic molecular theory, in what ways are liquids similar to solids? In what ways are liquids different from solids?

Answer

Add texts here. Do not delete this text first.

Exercise 6.E.3

In terms of the kinetic molecular theory, in what ways are liquids similar to gases? In what ways are liquids different from gases?

Answer

They are similar in that the atoms or molecules are free to move from one position to another. They differ in that the particles of a liquid are confined to the shape of the vessel in which they are placed. In contrast, a gas will expand without limit to fill the space into which it is placed.

Exercise 6.E.4

Explain why liquids assume the shape of any container into which they are poured, whereas solids are rigid and retain their shape.

Answer

Add texts here. Do not delete this text first.

Exercise 6.E.5

What is the evidence that all neutral atoms and molecules exert attractive forces on each other?

Answer

All atoms and molecules will condense into a liquid or solid in which the attractive forces exceed the kinetic energy of the molecules, at sufficiently low temperature.

Exercise 6.E.6

Open the PhET States of Matter Simulation to answer the following questions:

1. Select the Solid, Liquid, Gas tab. Explore by selecting different substances, heating and cooling the systems, and changing the state. What similarities do you notice between the four substances for each phase (solid, liquid, gas)? What differences do you notice?
2. For each substance, select each of the states and record the given temperatures. How do the given temperatures for each state correlate with the strengths of their intermolecular attractions? Explain.
3. Select the Interaction Potential tab, and use the default neon atoms. Move the Ne atom on the right and observe how the potential energy changes. Select the Total Force button, and move the Ne atom as before. When is the total force on each atom attractive and large enough to matter? Then select the Component Forces button, and move the Ne atom. When do the attractive (van der Waals) and repulsive (electron overlap) forces balance? How does this relate to the potential energy versus the distance between atoms graph? Explain.

Answer

Add texts here. Do not delete this text first.

Exercise 6.E.7

Define the following and give an example of each:

1. dispersion force
2. dipole-dipole attraction
3. hydrogen bond

Answer

1. Dispersion forces occur as an atom develops a temporary dipole moment when its electrons are distributed asymmetrically about the nucleus. This structure is more prevalent in large atoms such as argon or radon. A second atom can then be distorted by the appearance of the dipole in the first atom. The electrons of the second atom are attracted toward the positive end of the first atom, which sets up a dipole in the second atom. The net result is rapidly fluctuating, temporary dipoles that attract one another (example: Ar).
2. A dipole-dipole attraction is a force that results from an electrostatic attraction of the positive end of one polar molecule for the negative end of another polar molecule (example: ICI molecules attract one another by dipole-dipole interaction).
3. Hydrogen bonds form whenever a hydrogen atom is bonded to one of the more electronegative atoms, such as a fluorine, oxygen, nitrogen, or chlorine atom. The electrostatic attraction between the partially positive hydrogen atom in one molecule and the partially negative atom in another molecule gives rise to a strong dipole-dipole interaction called a hydrogen bond (example: HF⋯HFHF⋯HF).

Exercise 6.E.8

The types of intermolecular forces in a substance are identical whether it is a solid, a liquid, or a gas. Why then does a substance change phase from a gas to a liquid or to a solid?

Answer

Add texts here. Do not delete this text first.

Exercise 6.E.9

Why do the boiling points of the noble gases increase in the order He < Ne < Ar < Kr < Xe?

Answer

The London forces typically increase as the number of electrons increase.

Exercise 6.E.10

Neon and HF have approximately the same molecular masses.

1. Explain why the boiling points of Neon and HF differ.
2. Compare the change in the boiling points of Ne, Ar, Kr, and Xe with the change of the boiling points of HF, HCl, HBr, and HI, and explain the difference between the changes with increasing atomic or molecular mass.

Answer

Add texts here. Do not delete this text first.

Exercise 6.E.11

Arrange each of the following sets of compounds in order of increasing boiling point temperature:

1. HCl, H_2O, SiH_4
2. F_2, Cl_2, Br_2
3. CH_4, C_2H_6, C_3H_8
4. O_2, NO, N_2

Answer

1. $SiH_4 < HCl < H_2O$;
2. $F_2 < Cl_2 < Br_2$;
3. $CH_4 < C_2H_6 < C_3H_8$;
4. $N_2 < O_2 < NO$

Exercise 6.E.12

The molecular mass of butanol, C_4H_9OH, is 74.14; that of ethylene glycol, $CH_2(OH)CH_2OH$, is 62.08, yet their boiling points are 117 °C and 197 °C, respectively. Explain the reason for the difference.

Answer

Add texts here. Do not delete this text first.

Exercise 6.E.13

On the basis of intermolecular attractions, explain the differences in the boiling points of *n*–butane (−1 °C) and chloroethane (12 °C), which have similar molar masses.

Answer

Only rather small dipole-dipole interactions from C-H bonds are available to hold *n*-butane in the liquid state. Chloroethane, however, has rather large dipole interactions because of the Cl-C bond; the interaction is therefore stronger, leading to a higher boiling point.Add texts here.

Exercise 6.E.14

On the basis of dipole moments and/or hydrogen bonding, explain in a qualitative way the differences in the boiling points of acetone (56.2 °C) and 1-propanol (97.4 °C), which have similar molar masses.

Answer

Add texts here. Do not delete this text first.

Exercise 6.E.15

The melting point of $H_2O(s)$ is 0 °C. Would you expect the melting point of $H_2S(s)$ to be −85 °C, 0 °C, or 185 °C? Explain your answer.

Answer

−85 °C. Water has stronger hydrogen bonds so it melts at a higher temperature.

Exercise 6.E.16

Silane (SiH_4), phosphine (PH_3), and hydrogen sulfide (H_2S) melt at −185 °C, −133 °C, and −85 °C, respectively. What does this suggest about the polar character and intermolecular attractions of the three compounds?

Answer

Add texts here. Do not delete this text first.

Exercise 6.E.17

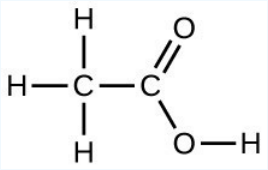
Explain why a hydrogen bond between two water molecules is weaker than a hydrogen bond between two hydrogen fluoride molecules.

Answer

The hydrogen bond between two hydrogen fluoride molecules is stronger than that between two water molecules because the electronegativity of F is greater than that of O. Consequently, the partial negative charge on F is greater than that on O. The hydrogen bond between the partially positive H and the larger partially negative F will be stronger than that formed between H and O.

Exercise 6.E.18

Under certain conditions, molecules of acetic acid, CH_3COOH, form “dimers,” pairs of acetic acid molecules held together by strong intermolecular attractions:



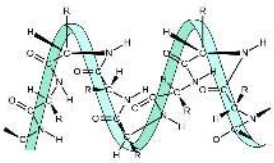
Draw a dimer of acetic acid, showing how two CH_3COOH molecules are held together, and stating the type of IMF that is responsible.

Answer

Add texts here. Do not delete this text first.

Exercise 6.E.19

Proteins are chains of amino acids that can form in a variety of arrangements, one of which is a helix. What kind of IMF is responsible for holding the protein strand in this shape? On the protein image, show the locations of the IMFs that hold the protein together:



Answer

H-bonding is the principle IMF holding the DNA strands together. The H-bonding is between the N−HN−H and C=OC=O.

Exercise 6.*E*. 20

The density of liquid NH_3 is 0.64 g/mL; the density of gaseous NH_3 at STP is 0.0007 g/mL. Explain the difference between the densities of these two phases.

Answer

Add texts here. Do not delete this text first.

Exercise 6.*E*. 21

Identify the intermolecular forces present in the following solids:

1. CH_3CH_2OH
2. $CH_3CH_2CH_3$
3. CH_3CH_2Cl

Answer

1. hydrogen bonding and dispersion forces;
2. dispersion forces;
3. dipole-dipole attraction and dispersion forces

This page titled 6.E: Intermolecular Forces and Liquids and Solids (Exercises) is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

6.S: Study Guide

6: Intermolecular Forces and Liquids and Solids

Key Topics for TRU students taking CHEM1500

- intermolecular forces (ionic, ion-dipole, hydrogen, dipole-dipole, dispersion)
- properties of liquids

Key Learning Outcomes (Examples)

- determine the type and relative strength of intermolecular forces in order to explain various physical properties such as solubility and boiling points

6.S: Study Guide is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

7: Organic Chemistry I - Bonding and Structure

7.1: Bonding and Structure I- Review of Bonding

7.1.1: Introduction to Organic Chemistry

7.1.2: Development of Chemical Bonding Theory

7.1.3: Describing Chemical Bonds - Valence Bond Theory

7.1.4: sp^3 Hybrid Orbitals and the Structure of Methane

7.1.5: sp^3 Hybrid Orbitals and the Structure of Ethane

7.1.6: sp^2 Hybrid Orbitals and the Structure of Ethylene

7.1.7: sp Hybrid Orbitals and the Structure of Acetylene

7.1.8: Hybridization of Nitrogen, Oxygen, Phosphorus and Sulfur

7.1.9: Describing Chemical Bonds- Molecular Orbital Theory

7.2: Drawing Chemical Structures

7.3: Functional Groups

7.4: Alkanes and Alkane Isomers

7.5: Naming of Alkanes and Cycloalkanes

7.5.1: Naming Alkanes

7.5.2: Naming Cycloalkanes

7.6: Study Guide

7: Organic Chemistry I - Bonding and Structure is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

SECTION OVERVIEW

7.1: Bonding and Structure I- Review of Bonding

Topic hierarchy

7.1.1: Introduction to Organic Chemistry

7.1.2: Development of Chemical Bonding Theory

7.1.3: Describing Chemical Bonds - Valence Bond Theory

7.1.4: sp^3 Hybrid Orbitals and the Structure of Methane

7.1.5: sp^3 Hybrid Orbitals and the Structure of Ethane

7.1.6: sp^2 Hybrid Orbitals and the Structure of Ethylene

7.1.7: sp Hybrid Orbitals and the Structure of Acetylene

7.1.8: Hybridization of Nitrogen, Oxygen, Phosphorus and Sulfur

7.1.9: Describing Chemical Bonds- Molecular Orbital Theory

7.1: Bonding and Structure I- Review of Bonding is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

7.1.1: Introduction to Organic Chemistry

Objectives

After completing this section, you should be able to

1. Define organic chemistry as the study of carbon-containing compounds.
2. Explain why the results of the experiments carried out by Chevreul and Wöhler contributed to the demise of the "vital force" theory.

Key Terms

Make certain that you can define, and use in context, the key term below.

- organic chemistry

All living things on earth are formed mostly of carbon compounds. The prevalence of carbon compounds in living things has led to the epithet "carbon-based" life. The truth is we know of no other kind of life. Early chemists regarded substances isolated from *organisms* (plants and animals) as a different type of matter that could not be synthesized artificially, and these substances were thus known as *organic compounds*.



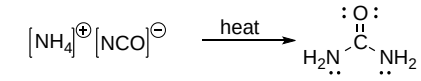
Figure 7.1.1.1: All organic compounds contain carbon and most are formed by living things, although they are also formed by geological and artificial processes. (credit left: modification of work by Jon Sullivan; credit left middle: modification of work by Deb Tremper; credit right middle: modification of work by "annszyp"/Wikimedia Commons; credit right: modification of work by George Shuklin)

Jöns Jacob Berzelius, a physician by trade, first coined the term "organic chemistry" in 1806 for the study of compounds derived from biological sources. Up through the early 19th century, naturalists and scientists observed critical differences between compounds that were derived from living things and those that were not.



Berzelius

In 1828, Friedrich Wöhler (widely regarded as a pioneer in organic chemistry) successfully completed an organic synthesis by heating ammonium cyanate and synthesizing of the biological compound urea (a component of urine in many animals) in what is now called "the Wöhler synthesis." Until this discovery it was widely believed by chemists that organic substances could only be formed under the influence of the "vital force" in the bodies of animals and plants. Wöhler's synthesis dramatically proved that view to be false.



ammonium cyanate **urea**

Urea synthesis was a critical discovery for biochemists because it showed that a compound known to be produced in nature only by biological organisms could be produced in a laboratory under controlled conditions from inanimate matter. This “in vitro” synthesis of organic matter disproved the common theory (vitalism) about the *vis vitalis*, a transcendent “life force” needed for producing organic compounds.

The ability to manipulate organic compounds includes fermentation to create wine and the making of soap, both of which have been a part of society so long their discovery has been lost in antiquity. Evidence has shown the Babylonians, as early as 2800 BC, were creating soap by mixing animal fat with wood ashes. It wasn't until the 19th century that the chemical nature of the creation of soap was discovered by Eugène Chevreul. In a reaction now call saponification, fats are heated in the presence of a strong base (KOH or NaOH) to produce fatty acid salts and glycerol. The fatty acid salts are the soap which improve water's ability to dissolve grease.

$$\text{animal fat} \xrightarrow[H_2O]{NaOH} \text{soap} + \text{glycerol}$$

Although originally defined as the chemistry of biological molecules, **organic chemistry** has since been redefined to refer specifically to carbon compounds — even those with non-biological origin. Some carbon molecules are not considered organic, with carbon dioxide being the most well known and most common inorganic carbon compound, but such molecules are the exception and not the rule. Organic chemistry focuses on carbon compounds and following movement of the electrons in carbon chains and rings, and also how electrons are shared with other carbon atoms and heteroatoms. Organic chemistry is primarily concerned with the properties of covalent bonds and non-metallic elements, though ions and metals do play critical roles in some reactions.

Why is carbon so special? The answer to this question involves carbon's special ability to bond with itself, which will be discussed in this chapter. Carbon is unique in its ability to form a wide variety of compounds from simple to complex. There are literally millions of organic compounds known to science from methane, which contains one carbon atom, to DNA which contains millions of carbons. More importantly, organic chemistry gives us the ability to make and alter the structure of organic compounds, which is the main topic in this book. The applications of organic chemistry are myriad, and include all sorts of plastics, dyes, flavorings, scents, detergents, explosives, fuels and many, many other products. Read the ingredient list for almost any kind of food that you eat — or even your shampoo bottle — and you will see the handiwork of organic chemists listed there.



The value to us of organic compounds ensures that organic chemistry is an important discipline within the general field of chemistry. In this chapter, we discuss why the element carbon gives rise to a vast number and variety of compounds, how those compounds are classified, and the role of organic compounds in representative biological and industrial settings. The field of organic chemistry is probably the most active and important field of chemistry at the moment, due to its extreme applicability to both biochemistry (especially in the pharmaceutical industry) and petrochemistry (especially in the energy industry). Organic chemistry has a relatively recent history, but it will have an enormously important future, affecting the lives of everyone around the world for many, many years to come

---

7.1.1: Introduction to Organic Chemistry is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Steven Farmer, Dietmar Kennepohl, Krista Cunningham, OpenStax, & OpenStax.

- **1.0: Introduction to Organic Chemistry** by Dietmar Kennepohl, Krista Cunningham, OpenStax, Steven Farmer is licensed CC BY-SA 4.0.

7.1.2: Development of Chemical Bonding Theory

Objectives

After completing this section, you should be able to

1. draw Lewis Dot Symbols for main group elements and ions.
2. describe the three-dimensional nature of molecules.
3. sketch a tetrahedral molecule, CX_4, using the “wedge-and-broken-line” method of representation.
4. make a ball-and-stick model of a simple tetrahedral molecule such as methane, CH_4.
5. draw Lewis Dot Structures for 2 electron group molecules.
6. draw Lewis Dot Structures for 3 electron group molecules.
7. draw Lewis Dot Structures for 4 electron group molecules.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- bond strength
- covalent bond
- ionic bond
- Lewis structure
- lone-pair electron
- non-bonding electron

Study Notes

To draw Lewis structures successfully, you need to know the number of valence electrons present in each of the atoms involved. Memorize the number of valence electrons possessed by each of the elements commonly encountered in organic chemistry: C, H, O, N, S, P and the halogens.

When drawing any organic structure, you must remember that a neutral carbon atom will almost always have four bonds. Similarly, hydrogen always has one bond; neutral oxygen atoms have two bonds; and neutral nitrogen atoms have three bonds. By committing these simple rules to memory, you can avoid making unnecessary mistakes later in the course.

The “wedge-and-broken-line” type of representation, which helps to convey the three-dimensional nature of organic compounds, will be used throughout the course.

Bonding Overview

Why are some substances chemically bonded molecules and others are an association of ions? The answer to this question depends upon the electronic structures of the atoms and nature of the chemical forces within the compounds. Although there are no sharply defined boundaries, chemical bonds are typically classified into three main types: ionic bonds, covalent bonds, and metallic bonds. In this chapter, each type of bond and the general properties found in typical substances in which the bond type occurs will be discussed.

1. Ionic bonds results from ***electrostatic forces that exist between ions of opposite charge***. These bonds typically involve a metal with a nonmetal
2. Covalent bonds ***result from the sharing of electrons between two atoms***. The bonds typically involve one nonmetallic element with another
3. Metallic bonds are found in solid metals (copper, iron, aluminum) with each metal atom bonded to several neighboring metal atoms and the bonding electrons are free to move throughout the 3-dimensional structure.

Each bond classification is discussed in detail in subsequent sections of the chapter. Let's look at the preferred arrangements of electrons in atoms when they form chemical compounds.

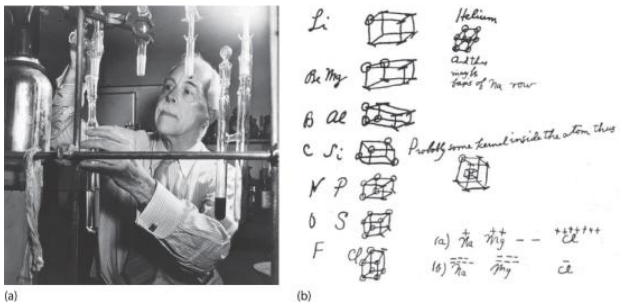


Figure 1.4.1: G. N. Lewis and the Octet Rule. (a) Lewis is working in the laboratory. (b) In Lewis's original sketch for the octet rule, he initially placed the electrons at the corners of a cube rather than placing them as we do now.

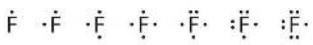
Lewis Symbols

At the beginning of the 20th century, the American 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 Dot symbols:

- provide a convenient representation of valence electrons
- allows you 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. Fluorine, for example, with the electron configuration $[He]2s^22p^5$, has seven valence electrons, so its Lewis dot symbol is constructed as follows:



Group	1	2	13	14	15	16	17	18
Electron Configuration	$[He]2s^1$	$[He]2s^2$	$[He]2s^22p^1$	$[He]2s^22p^2$	$[He]2s^22p^3$	$[He]2s^22p^4$	$[He]2s^22p^5$	$[He]2s^22p^6$
Lewis Dot Symbol	Li·	·Be·	·B·	·C·	·N·	:O·	:F·	:Ne:

Figure 7.1.2.2: Lewis Dot Symbols for the Elements in Period 2

Lewis used the unpaired dots to predict the number of bonds that an element will form in a compound. Consider the symbol for nitrogen in Figure 7.1.2.2 The Lewis dot symbol explains why nitrogen, with three unpaired valence electrons, tends to form compounds in which it shares the unpaired electrons to form three bonds. Boron, which also has three unpaired valence electrons in its Lewis dot symbol, also tends to form compounds with three bonds, whereas carbon, with four unpaired valence electrons in its Lewis dot symbol, tends to share all of its unpaired valence electrons by forming compounds in which it has four bonds. Lewis symbols are a tool to help draw structures. We will see why bonding in molecular compounds follow Lewis' theory in the next section.

Elements in the same group have the same number of valence electrons and similar Lewis symbols. For example, the electron configuration for atomic sulfur is $[Ne]3s^23p^4$, thus there are ***six*** valence electrons. Its Lewis symbol would therefore be similar to oxygen and look like:



The Octet Rule

Lewis's major contribution to bonding theory was to recognize that atoms tend to lose, gain, or share electrons to reach a total of eight valence electrons, called an *octet*. This so-called octet rule explains the stoichiometry of most compounds in the *s* and *p* blocks of the periodic table. We now know from quantum mechanics that the number eight corresponds to one *ns* and three *np* valence orbitals, which together can accommodate a total of eight electrons. Remarkably, though, Lewis's insight was made nearly a decade before Rutherford proposed the nuclear model of the atom. Common exceptions to the octet rule are helium, whose $1s^2$ electron configuration gives it a full $n = 1$ shell, and hydrogen, which tends to gain or share its one electron to achieve the electron configuration of helium.

Lewis's idea of an octet explains why noble gases rarely form compounds. They have the stable s^2p^6 configuration (full octet, no charge), so they have no reason to react and change their configuration. All other elements attempt to gain, lose, or share electrons to achieve a noble gas configuration. This explains why atom combine together to form compounds. By forming bond the makes the atoms more stable and lower in energy. Making bonds releases energy and represents a driving force for the formation of compounds.

Atoms often gain, lose, or share electrons to achieve the same number of electrons as the noble gas closest to them in the periodic table.

Lewis Structures

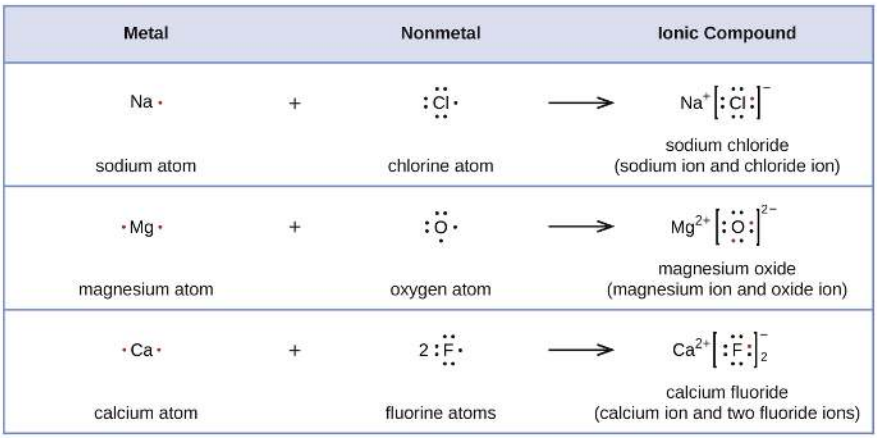
Lewis structures represent how Lewis symbols gain, lose, or share electrons to obtain an octet by forming compounds.

Lewis Structures of Ionic Compounds

Whenever there is a metal present in the structure of an organic compound, there is a high likelihood that at least one ionic bond is present. Ionic bonds are represented differently in Lewis structures than covalent bonds. Great care should be taken whenever drawing the Lewis structure of an organic compounds which contains and ionic bond. Ionic bonds typically are formed when a metal and a nonmetal are part of a compound. Some atoms achieve an octet by fully gaining or losing electrons to form ions. Ionic bonds form through the eletrostatic attraction of the created ions. The formula for table salt is NaCl. It is the result of Na^+ ions and Cl^- ions bonding together. If sodium metal and chlorine gas mix under the right conditions, they will form salt. The sodium loses an electron, and the chlorine gains that electron. In the process, a great amount of light and heat is released. The resulting salt is mostly unreactive — it is stable. It will not undergo any explosive reactions, unlike the sodium and chlorine that it is made of. Why? Referring to the octet rule, atoms attempt to get a noble gas electron configuration, which is eight valence electrons. Sodium ($1s^22s^22p^63s^1$) has one valence electron, so giving it up would result in the same electron configuration as neon ($1s^22s^22p^6$). Chlorine ($1s^22s^22p^63s^23p^7$)has seven valence electrons, so if it takes one it will have eight (an octet). Chlorine has the electron configuration of argon ($1s^22s^22p^63s^23p^8$) when it gains an electron.

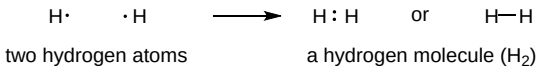
The Lewis structure of an ionic compound show the movement of electrons. For NaCl, sodium is in group 1 and has one valence electron and chlorine is in group 17 and has seven valence electrons. Sodium loses its sole valence electron thereby becomes positively charged. Chlorine gains this electron, gaining a full octet, and a negative charge. After the gain/loss of an electron the new Lewis structures of Na^+ and Cl^- are written next to each other representing the ionic bond in NaCl.

Examples of Lewis Structures of Ionic Compounds



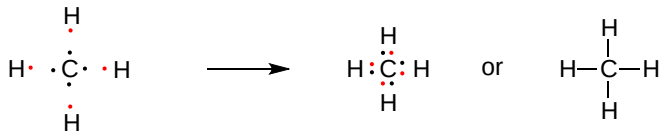
Covalent Bonds and the Lewis Structures of Molecular Compounds

While alkali metals (such as sodium and potassium), alkaline earth metals (such as magnesium and calcium), and halogens (such as fluorine and chlorine) often form ions in order to achieve a full octet, the principle elements of organic chemistry - carbon, hydrogen, nitrogen, and oxygen - instead tend to fill their octet by *sharing* electrons with other atoms, forming covalent bonds. Consider the simplest case of hydrogen gas. An isolated hydrogen atom has only one electron, located in the 1*s* orbital. If two hydrogen atoms come close enough so that their respective 1*s* orbitals overlap, the two electrons can be shared between the two nuclei, and a covalently bonded H_2 molecule is formed. In the Lewis structure of H_2, each pair of electrons that is shared between two atoms is drawn as a single line, designating a single covalent bond.

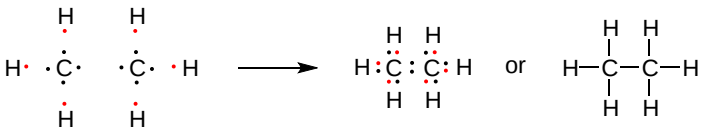


Hydrogen represents a special case, because a hydrogen atom cannot fulfill the octet rule; it needs only two electrons to have a full shell. This is often called the ‘doublet rule’ for hydrogen.

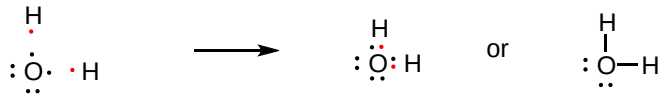
One of the simplest organic molecules is methane with the molecular formula CH_4. Methane is the ‘natural gas’ burned in home furnaces and hot water heaters, as well as in electrical power generating plants. To illustrate the covalent bonding in methane using a Lewis structure, we first must recognize that, although a carbon atom has a total of six electrons it's Lewis symbol has four unpaired electrons. Following Lewis' theory the carbon atom wants to form four covalent bonds to fill its octet. In a methane molecule, the central carbon atom shares its four valence electrons with four hydrogen atoms, thus forming four bonds and fulfilling the octet rule (for the carbon) and the ‘doublet rule’ (for each of the hydrogens).



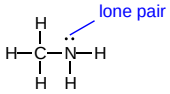
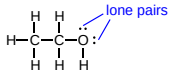
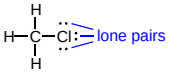
The next relatively simple organic molecule to consider is ethane, which has the molecular formula C_2H_6. If we draw each atom's Lewis symbol separately, we can see that the octet/doublet rule can be fulfilled for all of them by forming one carbon-carbon bond and six carbon-hydrogen bonds.



The same approach can be used for molecules in which there is no carbon atom. In a water molecule, the Lewis symbol of the oxygen atom has two unpaired electrons. These are paired with the single electron in the Lewis symbols of the hydrogens' two O-H covalent bonds. The remaining four non-bonding electrons on oxygen called ‘lone pairs’.

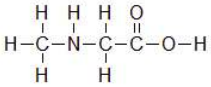


Since the lone pair electrons are often NOT shown in chemical structures, it is important to see mentally add the lone pairs. In the beginning, it can be helpful to physically add the lone pair electrons.

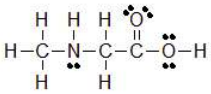
					
methylamine	ethanol	chloromethane			

Exercise

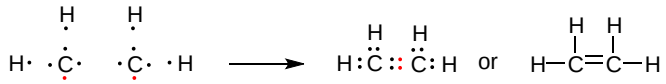
For the following structure, please fill in all of the missing lone pair electrons.



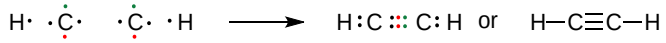
Answer



When two or more electrons are shared between atoms a multiple covalent bond is formed. The molecular formula for ethene (also known as ethylene, a compound found in fruits, such as apples, that signals them to ripen) is C_2H_4. Arranging Lewis symbols of the atoms, you can see that the octet/doublet rule can be fulfilled for all atoms only if the two carbons share *two* pairs of electrons between them. Ethene contains a carbon/carbon double bond.



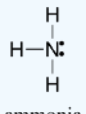
Following this pattern, the triple bond in ethyne molecular formula C_2H_2, (also known as acetylene, the fuel used in welding torches), is formed when the two carbon atoms share *three* pairs of electrons between them.



? Exercise 7.1.2.1

Draw the Lewis structure for ammonia, NH_3.

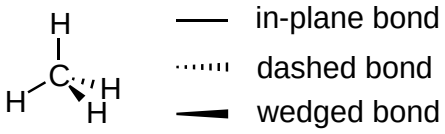
Answer



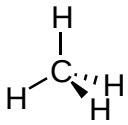
ammonia

Molecular Shape

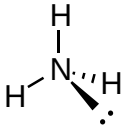
A stick and wedge drawing of methane shows the tetrahedral angles...(The wedge is coming out of the paper and the dashed line is going behind the paper. The solid lines are in the plane of the paper.)



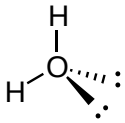
The following examples make use of this notation, and also illustrate the importance of including non-bonding valence shell electron pairs when viewing such configurations.



Methane



Water



Bonding configurations are readily predicted by valence-shell electron-pair repulsion theory, commonly referred to as **VSEPR** in most introductory chemistry texts. This simple model is based on the fact that electrons repel each other, and that it is reasonable to expect that the bonds and non-bonding valence electron pairs associated with a given atom will prefer to be as far apart as possible. The bonding configurations of carbon are easy to remember, since there are only three categories.

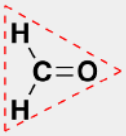
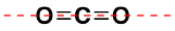
Configuration	Bonding Partners	Bond Angles	Example
Tetrahedral	4	109.5º	
Trigonal Planar	3	120º	
Linear	2	180º	

Figure 1.4.3

In the three examples shown above, the central atom (carbon) does not have any non-bonding valence electrons; consequently the configuration may be estimated from the number of bonding partners alone. However, for molecules of water and ammonia, the non-bonding electrons must be included in the calculation. In each case there are four regions of electron density associated with the valence shell so that a tetrahedral bond angle is expected. The measured bond angles of these compounds (H_2O 104.5º & NH_3 107.3º) show that they are closer to being tetrahedral than trigonal planar or linear. Of course, it is the configuration of atoms (not electrons) that defines the the shape of a molecule, and in this sense ammonia is said to be pyramidal (not tetrahedral). The compound boron trifluoride, BF_3, does not have non-bonding valence electrons and the configuration of its atoms is trigonal. Nice treatments of VSEPR theory have been provided by Oxford and Purdue. The best way to study the three-dimensional shapes of molecules is by using molecular models. Many kinds of model kits are available to students and professional chemists.

Two Electron Groups

Our first example is a molecule with two bonded atoms and no lone pairs of electrons, .

AX_2: BeH_2

1. The central atom, beryllium, contributes two valence electrons, and each hydrogen atom contributes one. The Lewis electron structure is



Figure 1.4.4: Lewis Structure for BeH_2

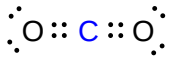
2. There are two electron groups around the central atom. We see from Figure 1.4.3 that the arrangement that minimizes repulsions places the groups 180° apart.

3. Both groups around the central atom are bonding pairs (BP). Thus BeH_2 is designated as AX_2.

4. From Figure 1.4.3 we see that with two bonding pairs, the molecular geometry that minimizes repulsions in BeH_2 is *linear*.

AX_2: CO_2

1. The central atom, carbon, contributes four valence electrons, and each oxygen atom contributes six. The Lewis electron structure is



2. The carbon atom forms two double bonds. Each double bond is a group, so there are two electron groups around the central atom. Like BeH_2, the arrangement that minimizes repulsions places the groups 180° apart.

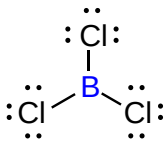
3. Once again, both groups around the central atom are bonding pairs (BP), so CO_2 is designated as AX_2.

4. VSEPR only recognizes groups around the *central* atom. Thus the lone pairs on the oxygen atoms do not influence the molecular geometry. With two bonding pairs on the central atom and no lone pairs, the molecular geometry of CO_2 is linear (Figure 1.4.3).

Three Electron Groups

AX_3: BCl_3

1. The central atom, boron, contributes three valence electrons, and each chlorine atom contributes seven valence electrons. The Lewis electron structure is



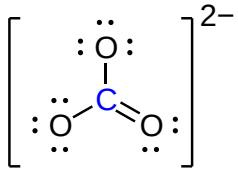
2. There are three electron groups around the central atom. To minimize repulsions, the groups are placed 120° apart (Figure 1.4.3).

3. All electron groups are bonding pairs (BP), so the structure is designated as AX_3.

4. From Figure 1.4.3 we see that with three bonding pairs around the central atom, the molecular geometry of BCl_3 is *trigonal planar*.

AX_3: CO_3^{2-}

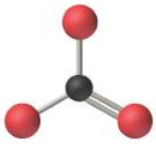
1. The central atom, carbon, has four valence electrons, and each oxygen atom has six valence electrons. As you learned previously, the Lewis electron structure of one of three resonance forms is represented as



2. The structure of CO_3^{2-} is a resonance hybrid. It has three identical bonds, each with a bond order of 4/3. We minimize repulsions by placing the three groups 120° apart (Figure 1.4.3).

3. All electron groups are bonding pairs (BP). With three bonding groups around the central atom, the structure is designated as AX_3.

4. We see from Figure 1.4.3 that the molecular geometry of CO_3^{2-} is trigonal planar.

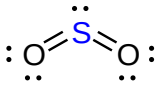


Molecular geometry
(trigonal planar)

In our next example we encounter the effects of lone pairs and multiple bonds on molecular geometry for the first time.

- AX_2E: SO_2

  1. The central atom, sulfur, has 6 valence electrons, as does each oxygen atom. With 18 valence electrons, the Lewis electron structure is shown below.



  2. There are three electron groups around the central atom, two double bonds and one lone pair. We initially place the groups in a trigonal planar arrangement to minimize repulsions (Figure 1.4.3).

  3. There are two bonding pairs and one lone pair, so the structure is designated as AX_2E. This designation has a total of three electron pairs, two X and one E. Because a lone pair is not shared by two nuclei, it occupies more space near the central atom than a bonding pair (Figure 1.4.4). Thus bonding pairs and lone pairs repel each other electrostatically in the order BP–BP < LP–BP < LP–LP. In SO_2, we have one BP–BP interaction and two LP–BP interactions.

  4. The molecular geometry is described only by the positions of the nuclei, *not* by the positions of the lone pairs. Thus with two nuclei and one lone pair the shape is *bent*, or *V shaped*, which can be viewed as a trigonal planar arrangement with a missing vertex (Figures 1.4.2.1 and 1.4.3).

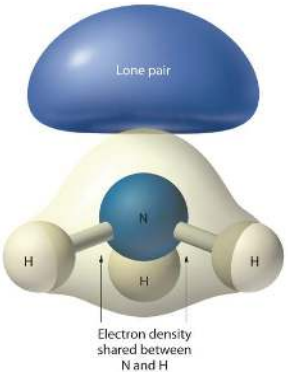
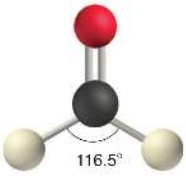


Figure 1.4.4: The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair

  As with SO_2, this composite model of electron distribution and negative electrostatic potential in ammonia shows that a lone pair of electrons occupies a larger region of space around the nitrogen atom than does a bonding pair of electrons that is shared with a hydrogen atom.

Like lone pairs of electrons, multiple bonds occupy more space around the central atom than a single bond, which can cause other bond angles to be somewhat smaller than expected. This is because a multiple bond has a higher electron density than a single bond, so its electrons occupy more space than those of a single bond. For example, in a molecule such as CH_2O (AX_3), whose structure is shown below, the double bond repels the single bonds more strongly than the single bonds repel each other. This causes a deviation from ideal geometry (an H–C–H bond angle of 116.5° rather than 120°).

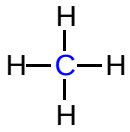


Four Electron Groups

One of the limitations of Lewis structures is that they depict molecules and ions in only two dimensions. With four electron groups, we must learn to show molecules and ions in three dimensions.

AX_4: CH_4

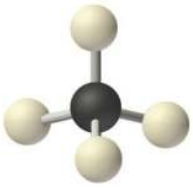
1. The central atom, carbon, contributes four valence electrons, and each hydrogen atom has one valence electron, so the full Lewis electron structure is



2. There are four electron groups around the central atom. As shown in Figure 1.4.2, repulsions are minimized by placing the groups in the corners of a tetrahedron with bond angles of 109.5°.

3. All electron groups are bonding pairs, so the structure is designated as AX_4.

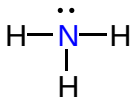
4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (Figure 1.4.3).



Molecular geometry (tetrahedral)

AX_3E: NH_3

1. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure



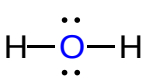
2. There are four electron groups around nitrogen, three bonding pairs and one lone pair. Repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

3. With three bonding pairs and one lone pair, the structure is designated as AX_3E. This designation has a total of four electron pairs, three X and one E. We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

4. There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*. In essence, this is a tetrahedron with a vertex missing (Figure 1.4.3). However, the H–N–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions.

AX_2E_2: H_2O

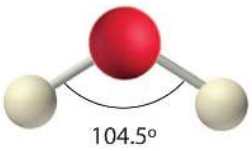
1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure



2. There are four groups around the central oxygen atom, two bonding pairs and two lone pairs. Repulsions are minimized by directing the bonding pairs and the lone pairs to the corners of a tetrahedron Figure 1.4.3.

3. With two bonding pairs and two lone pairs, the structure is designated as AX_2E_2 with a total of four electron pairs. Due to LP–LP, LP–BP, and BP–BP interactions, we expect a significant deviation from idealized tetrahedral angles.

4. With two hydrogen atoms and two lone pairs of electrons, the structure has significant lone pair interactions. There are two nuclei about the central atom, so the molecular shape is *bent*, or *V shaped*, with an H–O–H angle that is even less than the H–N–H angles in NH_3, as we would expect because of the presence of two lone pairs of electrons on the central atom rather than one.. This molecular shape is essentially a tetrahedron with two missing vertices.



7.1.2: Development of Chemical Bonding Theory is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Steven Farmer & Krista Cunningham.

- **1.4: Development of Chemical Bonding Theory** by Krista Cunningham, Steven Farmer is licensed CC BY-SA 4.0.

7.1.3: Describing Chemical Bonds - Valence Bond Theory

Objectives

After completing this section, you should be able to

1. explain how covalent bonds are formed as a result of the ability of atoms to share electrons.
2. describe the formation of covalent bonds in terms of the overlapping of atomic orbitals.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- bond strength
- covalent bond
- bond length
- sigma (σ) bond
- pi (π) bond
- valence bond theory

Valence Bond Theory

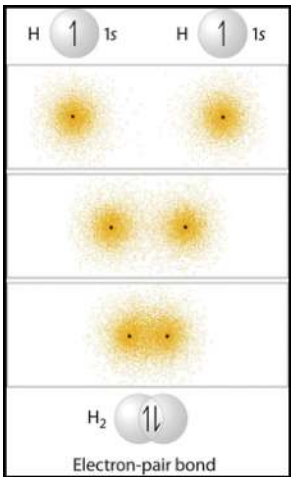
As we have been discussing how to use Lewis structures to depict the bonding in organic compounds, we have been very vague so far in our language about the actual nature of the chemical bonds themselves. We know that a covalent bond involves the 'sharing' of a pair of electrons between two atoms – but how does this happen, and how does it lead to the formation of a bond holding the two atoms together? Two main models have been developed to described how covalent bonds are formed: valence bond theory and molecularly orbital theory.

Valence bond theory is most often used to describe bonding in organic molecules. In this model, covalent bonds are considered to form from the overlap of two atomic orbitals on different atoms, each orbital containing a single electron. The electrons become paired in the orbital overlap bonding the atoms together.

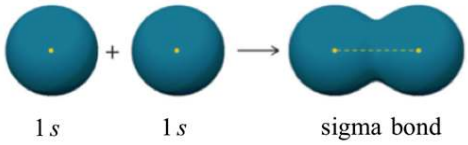
The simplest example valence bond theory can be demonstrated by the H_2 molecule. We can see from the periodic table that each hydrogen atom has a single valence electron. If 2 hydrogen atoms come together to form a bond, then each hydrogen atom effectively has a share in both electrons and thus each resembles the noble gas helium and is more stable. The 2 electrons shared in the orbital overlap are represented by a single dash between the atoms.



Valence bond theory describes a chemical bond as the overlap of atomic orbitals. In the case of the hydrogen molecule, the 1s orbital of one hydrogen atom overlaps with the 1s orbital of the second hydrogen atom to form a molecular orbital called a sigma bond which contains two electrons of opposite spin. The mutual attraction between this negatively charged electron pair and the two atoms' positively charged nuclei serves to physically link the two atoms through a force we define as a covalent bond. The strength of a covalent bond depends on the extent of overlap of the orbitals involved. Orbitals that overlap extensively form bonds that are stronger than those that have less overlap.



ne more characteristic of the covalent bond in H_2 is important to consider at this point. The two overlapping 1*s* orbitals can be visualized as two spherical balloons being pressed together. This means that the bond has **cylindrical symmetry**: if we were to take a cross-sectional plane of the bond at any point, it would form a circle. This type of bond is referred to as a **σ(sigma) bond**.



The energy of the system depends on how much the orbitals overlap. The energy diagram below illustrates how the sum of the energies of two hydrogen atoms (the colored curve) changes as they approach each other. When the atoms are far apart there is no overlap, and by convention we set the sum of the energies at zero. As the atoms move together, their orbitals begin to overlap. Each electron begins to feel the attraction of the nucleus in the other atom. In addition, the electrons begin to repel each other, as do the nuclei. While the atoms are still widely separated, the attractions are slightly stronger than the repulsions, and the energy of the system decreases. (A bond begins to form.) As the atoms move closer together, the overlap increases, so the attraction of the nuclei for the electrons continues to increase (as do the repulsions among electrons and between the nuclei). At some specific distance between the atoms, which varies depending on the atoms involved, the energy reaches its lowest (most stable) value. This optimum distance between the two bonded nuclei is called the the bond lengths between the two atoms. The bond is stable because at this point, the attractive and repulsive forces combine to create the lowest possible energy configuration.

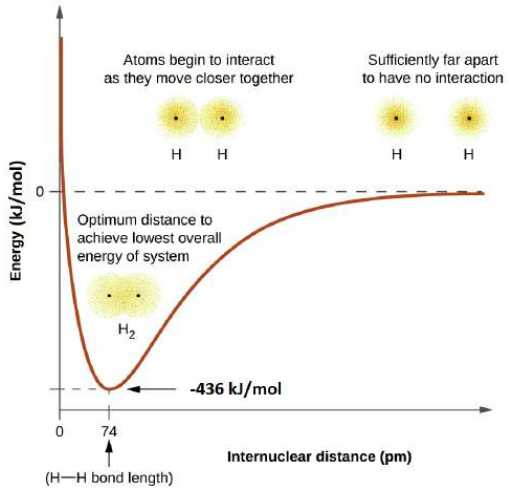


Figure 7.1.3.2: A Plot of Potential Energy versus Internuclear Distance for the Interaction between Two Gaseous Hydrogen **Atoms**

This optimal internuclear distance is the **bond length**. For the H_2 molecule, the distance is 74 pm (picometers, 10^{-12} meters). Likewise, the difference in potential energy between the lowest energy state (at the optimal internuclear distance) and the state where the two atoms are completely separated is called the **bond dissociation energy,** or, more simply**, bond strength**. For the

hydrogen molecule, the H-H bond strength is equal to about 435 kJ/mol. This means it would take 435 kJ to break one mole of H-H bonds.

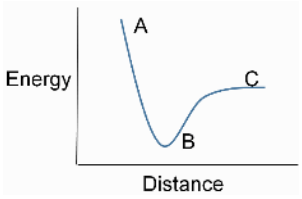
Every covalent bond in a given molecule has a characteristic length and strength. In general, the length of a typical carbon-carbon single bond in an organic molecule is about 150 pm, while carbon-carbon double bonds are about 130 pm, carbon-oxygen double bonds are about 120 pm, and carbon-hydrogen bonds are in the range of 100 to 110 pm. The strength of covalent bonds in organic molecules ranges from about 234 kJ/mol for a carbon-iodine bond (in thyroid hormone, for example), about 410 kJ/mole for a typical carbon-hydrogen bond, and up to over 800 kJ/mole for a carbon-carbon triple bond.

Table: Representative Bond Energies and Lengths

Bond	Length (pm)	Energy (kJ/mol)		Bond	Length (pm)	Energy (kJ/mol)
H-H	74	436		C-O	140.1	358
H-C	106.8	413		C=O	119.7	745
H-N	101.5	391		C≡O	113.7	1072
H-O	97.5	467		H-Cl	127.5	431
C-C	150.6	347		H-Br	141.4	366
C=C	133.5	614		H-I	160.9	298
C≡C	120.8	839		O-O	148	146
C-N	142.1	305		O=O	120.8	498
C=N	130.0	615		F-F	141.2	159
C≡N	116.1	891		Cl-Cl	198.8	243

Exercises

1) For the following energy diagram for energy vs. intermolecular distance is for a fluorine molecule (F_2). Please describe the importance for points A, B, & C on the graph.



Solutions

1)

A - Repulsive Forces are present, nuclei are too close to one another.

B - Optimal distance between the two orbitals to have a bond (the bond length)

C - Cannot form a bond, the orbitals are too far apart.

Exercises

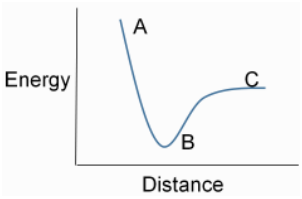
Questions

Q1.5.1

Draw an energy diagram for energy vs. intermolecular distance for a fluorine molecule (F_2) and describe the regions of the graph.

Solutions

S1.5.1



A - Repulsive Forces are present, p-orbitals are too close together

B - Optimal distance between the two p-orbitals to have a bond (the bond length)

C - Cannot form a bond, orbitals are too far away

7.1.3: Describing Chemical Bonds - Valence Bond Theory is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Steven Farmer & Dietmar Kennepohl.

- **1.5: Describing Chemical Bonds - Valence Bond Theory** by Dietmar Kennepohl, Steven Farmer is licensed CC BY-SA 4.0.

7.1.4: sp^3 Hybrid Orbitals and the Structure of Methane

Objective

After completing this section, you should be able to describe the structure of methane in terms of the sp^3 hybridization of the central carbon atom.

Key Terms

Make certain that you can define, and use in context, the key terms below.

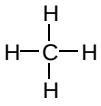
- bond angle
- hybridization
- sp^3 hybrid

Study Notes

The tetrahedral shape is a very important one in organic chemistry, as it is the basic shape of all compounds in which a carbon atom is bonded to four other atoms. Note that the tetrahedral bond angle of $\mathrm{H-C-H}$ is 109.5°.

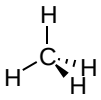
Valence Bond Theory

Valence bond theory's use of overlapping atomic orbitals to explain how chemical bonds form works well in simple diatomic molecules such as H_2. However, when molecules with more than two atoms form stable bonds, we require a more detailed model. A good example is methane (CH_4). According to valence bond theory, the structure of a covalent species can be depicted using a Lewis structure.



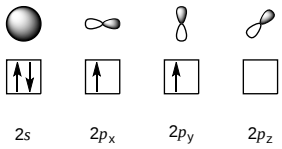
1

Experimentally, it has been shown that the four carbon-hydrogen bonds in the methane molecule are identical, meaning they have the same bond energy and the same bond length. Also, VSEPR theory suggests that the geometry at the carbon atom in the methane molecule is tetrahedral **(2)**, and there exists a large body of both theoretical and experimental evidence supporting this prediction.



2

According to valence bond theory, to form a covalent bond forms when an unpaired electron in one atom overlaps with an unpaired electron in a different atom. Now, consider the the electron configuration of the four valence electrons in carbon.



There is a serious mismatch between the electron configuration of carbon ($1s^2 2s^2 2p^2$) and the predicted structure of methane. The modern structure shows that there are only 2 unpaired electrons to share with hydrogens, instead of the 4 needed to create methane. Also, the p_x and p_y orbitals are at 90° to each other. They would form perpendicular bonds instead of the tetrahedral 109.5° bond angle predicted by VSEPR and experimental data. Lastly, there are two different orbitals, 2*s* and 2*p*, which would create different types of C-H bonds. As noted earlier, experimentally, the four carbon-hydrogen bonds in the methane molecule are identical.

Hybrid Orbitals

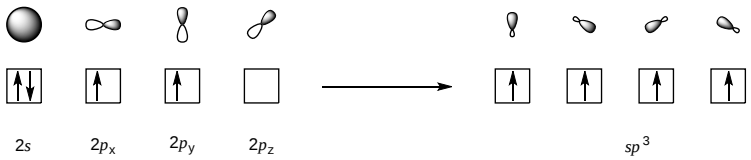
An answer to the problems posed above was offered in 1931 by Linus Pauling. He showed mathematically that an *s* orbital and three *p* orbitals on an atom can combine to form four equivalent hybrid atomic orbitals.

Important Ideals in Understanding Hybridization

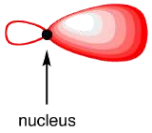
1. Hybrid orbitals do not exist in isolated atoms. They are formed only in covalently bonded atoms.
2. Hybrid orbitals have shapes and orientations that are very different from those of the atomic orbitals in isolated atoms.
3. A set of hybrid orbitals is generated by combining atomic orbitals. The number of hybrid orbitals in a set is equal to the number of atomic orbitals that were combined to produce the set.
4. All orbitals in a set of hybrid orbitals are equivalent in shape and energy.
5. The type of hybrid orbitals formed in a bonded atom create the molecular geometry as predicted by the VSEPR theory.
6. Hybrid orbitals overlap to form σ bonds.
7. Lone pair electrons are often contained in hybrid orbitals

sp^3 Hybridization in Methane

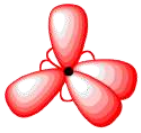
In order to explain this observation, valence bond theory relies on a concept called **orbital hybridization**. In this picture, the four valence orbitals of the carbon (one 2*s* and three 2*p* orbitals) combine mathematically (remember: orbitals are described by equations) to form four equivalent **hybrid orbitals**, which are named ***sp*^{3} orbitals** because they are formed from mixing one *s* and three *p* orbitals. In the new electron configuration, each of the four valence electrons on the carbon occupies a single sp^3 orbital creating four unpaired electrons.



The shape of an sp^3 hybridized orbital is a combination of *s* and *p* atomic orbitals.



Each sp^3-hybridized orbital bears an electron, and electrons repel each other. To minimize the repulsion between electrons, the four sp^3-hybridized orbitals arrange themselves around the carbon nucleus so that they are as far away as possible from each other, resulting in the tetrahedral arrangement predicted by VSPER. The carbon atom in methane is called an "sp^3-hybridized carbon atom." The larger lobes of the sp^3 hybrids are directed towards the four corners of a tetrahedron, meaning that the angle between any two orbitals is 109.5°.



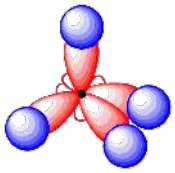
5

Bonding in Methane

Each C-H bond in methane, then, can be described as an overlap between a half-filled 1*s* orbital in four hydrogen atoms and the larger lobe of one of the four half-filled sp^3 hybrid orbitals form a four equivalent sigma (σ) bond. This orbital overlap is often described using the notation: sp^3(C)-1*s*(H). The formation of sp^3 hybrid orbitals successfully explains the tetrahedral structure of methane and the equivalency of the the four C-H bonds.

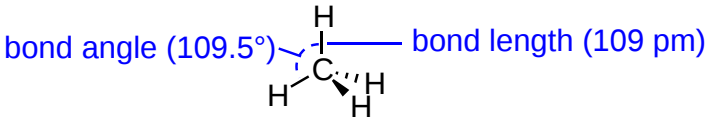
What remains is an explanation of why the sp^3 hybrid orbitals form. When the *s* and 3 *p* orbitals in carbon hybridize the resulting sp^3 hybrid orbital is unsymmetrical with one lobe larger than the other. This means the larger lobe can overlap more effectively

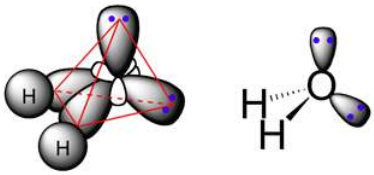
with orbitals from other bonds making them stronger. Hybridizing allows for the carbon to form stronger bonds than it would with unhybridized *s* or *p* orbitals.



6

The four carbon-hydrogen bonds in methane are equivalent and all have a bond length of 109 pm (1.09 x 10-10 m), bond strength of of 429 kJ/mol. All of the H-C-H bond angles are 109.5°.



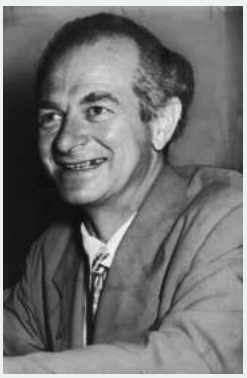


Looking Closer: Linus Pauling

Arguably the most influential chemist of the 20th century, Linus Pauling (1901–1994) is the only person to have won two individual (that is, unshared) Nobel Prizes. In the 1930s, Pauling used new mathematical theories to enunciate some fundamental principles of the chemical bond. His 1939 book *The Nature of the Chemical Bond* is one of the most significant books ever published in chemistry.

Pauling's big contribution to chemistry was valence bond theory, which combined his knowledge of quantum mechanical theory with his knowledge of basic chemical facts, like bond lengths and and bond strengths and shapes of molecules. Valence bond theory, like Lewis's bonding theory, provides a simple model that is useful for predicting and understanding the structures of molecules, especially for organic chemistry. .

By 1935, Pauling's interest turned to biological molecules, and he was awarded the 1954 Nobel Prize in Chemistry for his work on protein structure. (He was very close to discovering the double helix structure of DNA when James Watson and James Crick announced their own discovery of its structure in 1953.) He was later awarded the 1962 Nobel Peace Prize for his efforts to ban the testing of nuclear weapons.



Linus Pauling was one of the most influential chemists of the 20th century.

In his later years, Pauling became convinced that large doses of vitamin C would prevent disease, including the common cold. Most clinical research failed to show a connection, but Pauling continued to take large doses daily. He died in 1994, having spent a lifetime establishing a scientific legacy that few will ever equal

---

7.1.4: sp^3 Hybrid Orbitals and the Structure of Methane is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Steven Farmer, Dietmar Kennepohl, Krista Cunningham, Tim Soderberg, Gamini Gunawardena, & Gamini Gunawardena.

- **1.6: sp^3 Hybrid Orbitals and the Structure of Methane** by Dietmar Kennepohl, Gamini Gunawardena, Krista Cunningham, Steven Farmer, Tim Soderberg is licensed CC BY-SA 4.0.

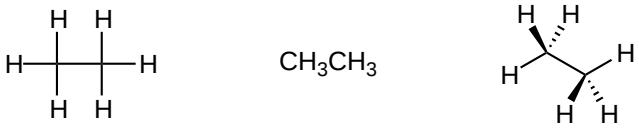
7.1.5: sp³ Hybrid Orbitals and the Structure of Ethane

Objective

After completing this section, you should be able to describe the structure of ethane in terms of the sp^3 hybridization of the two carbon atoms present in the molecule ethane.

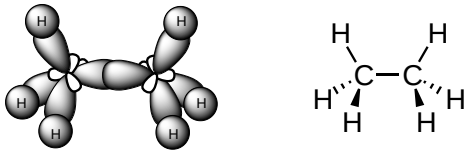
Bonding in Ethane

The simplest molecule with a carbon-carbon bond is ethane, C_2H_6.

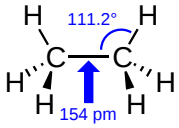


Representations of Ethane

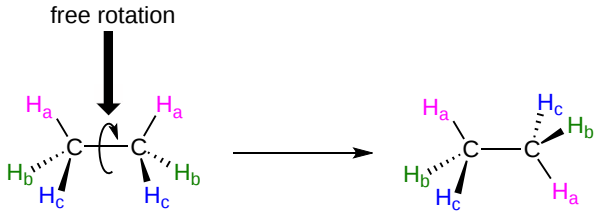
In ethane (CH_3CH_3), both carbons are sp^3-hybridized, meaning that both have four bonds with tetrahedral geometry. An sp^3 orbital of one carbon atom overlaps end to end with an sp^3 orbital of the second carbon atom to form a carbon-carbon σ bond. This orbital overlap is often described using the notation: sp^3(C)-sp^3(C). Each of the remaining sp^3 hybrid orbitals overlaps with the ***S*** orbital of a hydrogen atom to form carbon–hydrogen σ bonds.



The σ carbon-carbon bond has a bond length of 154 pm, and a bond strength of 377 kJ/mol. The carbon-hydrogen σ bonds are slightly weaker, 421 kJ/mol, than those of methane. The C-C-H bond angles in ethane are 111.2° which is close to the what is expected for tetrahedral molecules.



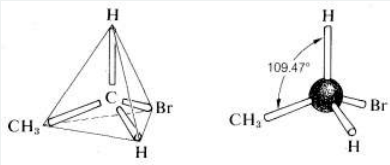
The orientation of the two CH_3 groups is not fixed relative to each other. Because they are formed from the end-on-end overlap of two orbitals, *sigma bonds are free to rotate*. This means, in the case of ethane molecule, that the two methyl (CH_3) groups can be pictured as two wheels on a hub, each one able to rotate freely with respect to the other. In Section 3.7 we will learn more about the implications of rotational freedom in sigma bonds, when we discuss the 'conformation' of organic molecules

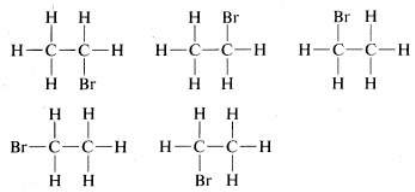


How did they know?

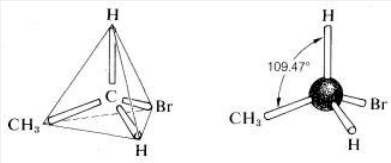
The tetrahedral geometry of carbon was predicted as far back as 1874. But how did they know? A question came up when looking at ethane with a bromine substituent (C_2H_5Br). When looking at the possible structures of the compound C_2H_5Br there are several possible structural formulas.here was a serious problem as to whether these formulas represent the same or different compounds. All that was known in the early days was that every purified sample of C_2H_5Br, no matter how prepared, had a boiling point of 38 °C and density of 1.460 gml^{-1}. Furthermore, all looked the same, all smelled the same, and all underwent

the same chemical reactions. There was no evidence that C_2H_5Br was a mixture or that more than one compound of this formula could be prepared. One might conclude, therefore, that all of the structural formulas above represent a single substance but how? A brilliant solution to the problem came when J. H. van 't Hoff proposed that all four bonds of carbon are equivalent and directed to the corners of a regular tetrahedron. If we redraw the structures for C_2H_5Br with both carbons having tetrahedral geometry, we see that there is only one possible arrangement. This theory hints at the idea of free rotation around sigma bonds which will be discussed later.





There was a serious problem as to whether these formulas represent the same or different compounds. All that was known in the early days was that every purified sample of C_2H_5Br, no matter how prepared, had a boiling point of 38 ºC and density of 1.460 gml^{-1}. Furthermore, all looked the same, all smelled the same, and all underwent the same chemical reactions. There was no evidence that C_2H_5Br was a mixture or that more than one compound of this formula could be prepared. One might conclude, therefore, that all of the structural formulas above represent a single substance but how? A brilliant solution to the problem came when J. H. van 't Hoff proposed that all four bonds of carbon are equivalent and directed to the corners of a regular tetrahedron. If we redraw the structures for C_2H_5Br with both carbons having tetrahedral geometry, we see that there is only one possible arrangement. This theory hints at the idea of free rotation around sigma bonds which will be discussed later.



Exercise

Questions

Q1.7.1

Draw pentane, $CH_3CH_2CH_2CH_2CH_3$, predict the bond angles within this molecule.

Solutions

S1.7.1

All the bond angles will be the same size.

7.1.5: sp³ Hybrid Orbitals and the Structure of Ethane is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Steven Farmer, Dietmar Kennepohl, Krista Cunningham, Tim Soderberg, William Reusch, & William Reusch.

- **1.7: sp³ Hybrid Orbitals and the Structure of Ethane** by Dietmar Kennepohl, Krista Cunningham, Steven Farmer, Tim Soderberg, William Reusch is licensed CC BY-SA 4.0.

7.1.6: sp² Hybrid Orbitals and the Structure of Ethylene

Objectives

After completing this section, you should be able to

1. account for the formation of carbon-carbon double bonds using the concept of sp^2 hybridization.
2. describe a carbon-carbon double bond as consisting of one σ bond and one π bond.
3. explain the difference between a σ bond and a π bond in terms of the way in which *p* orbitals overlap.

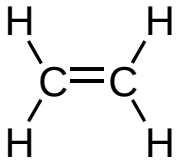
Key Terms

Make certain that you can define, and use in context, the key terms below.

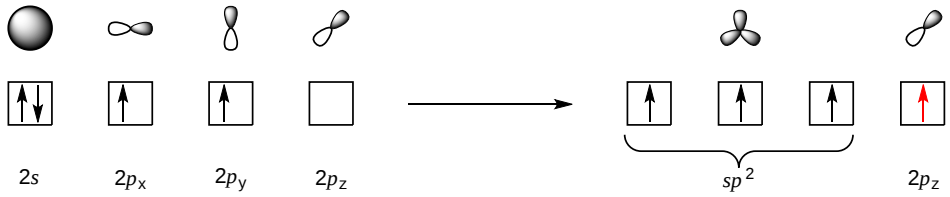
- pi (π) bond
- sp^2 hybrid

Bonding in Ethylene

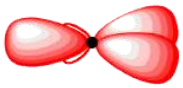
Thus far valence bond theory has been able to describe the bonding in molecules containing only single bonds. However, when molecules contain double or triple bonds the model requires more details. Ethylene (commonly knows as ethene), CH_2CH_2, is the simplest molecule which contains a carbon carbon double bond. The Lewis structure of ethylene indicates that there are one carbon-carbon double bond and four carbon-hydrogen single bonds. Experimentally, the four carbon-hydrogen bonds in the ethylene molecule have been shown to be identical. Because each carbon is surrounded by three electron groups, VSEPR theory says the molecule should have a trigonal planar geometry. Although each carbon has fulfilled its tetravalent requirement, one bond appears different. Clearly, a different type of orbital overlap is involved.



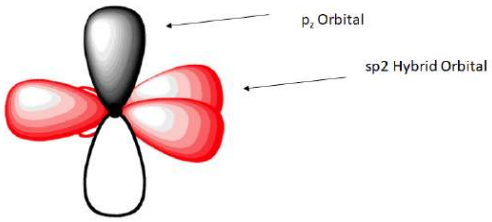
The sigma bonds formed in ethene is by the participation of a different kind of hybrid orbital. Three atomic orbitals on each carbon – the 2*s*, $2p_x$ and $2p_y$ – combine to form three sp^2 hybrids, leaving the $2p_z$ orbital unhybridized. Three of the four valence electrons on each carbon are distributed to the three sp^2 hybrid orbitals, while the remaining electron goes into the unhybridized p_z orbital. Each carbon in ethene is said to be a "sp^2-hybridized carbon." The electron configuration of the sp^2 hybridized carbon shows that there are four unpaired electrons to form bonds. However, the unpaired electrons are contained in two different types of orbitals so it is to be expected that two different types of bonds will form.



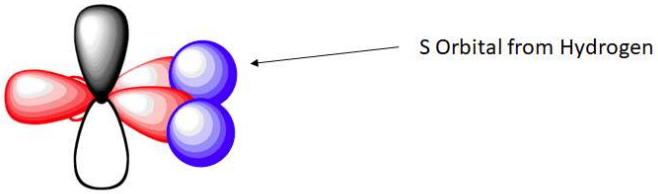
The shape of the sp^2-hybridized orbital has be mathematically shown to to be roughly the same as that of the sp^3-hybridized orbital. To minimize the repulsion between electrons, the three sp^2-hybridized orbitals are arranged with a trigonal planar geometry. Each orbital lobe is pointing to the three corners of an equilateral triangle, with angles of 120° between them. Again, geometry and hybrization can be tied together. Atoms surrounded by three electron groups can be said to have a trigonal planar geometry and sp^2 hybridization.



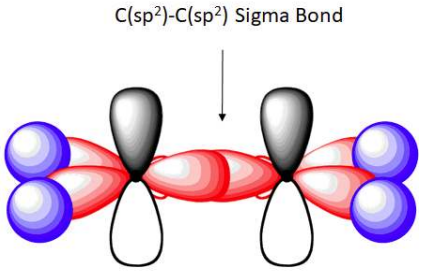
The unhybridized $2p_z$ orbital is *perpendicular* to the plane of the trigonal planar sp^2 hybrid orbtals.



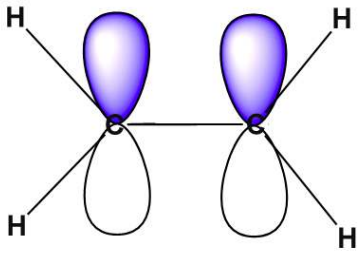
In the ethylene molecule, each carbon atom is bonded to two hydrogen atoms. Thus, overlap two sp^2-hybridized orbitals with the 1s orbitals of two hydrogen atoms for the C-H sigma bonds in ethylene (sp^2(C)-1s(H). Consequently, consistent with the observations, the four carbon-hydrogen bonds in ethylene are identical.



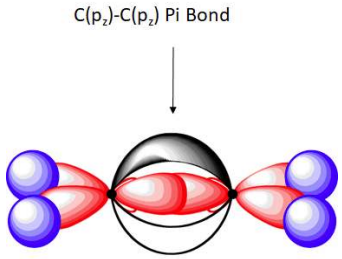
The C-C sigma bond in ethylene is formed by the overlap of an sp^2 hybrid orbital from each carbon.



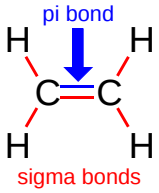
The overlap of hybrid orbitals or a hybrid orbital and a 1s orbtial from hydrogen creates the sigma bond framework of the ethylene molecule. However the unhybridized p_z orbital on each carbon remains.



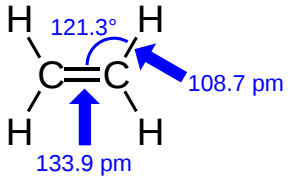
The unhybridized pz orbitals on each carbon overlap to a π bond (pi). The orbital overlap is commonly written as p_z(C)-1p_z(C). In general multiple bonds in molecular compound are formed by the overlap of unhybridized p orbitals. It should be noted that the carbon-carbon double bond in ethlene is made up of two different types of bond, a sigma and a pi.



Overall, ethylene is said to contain five sigma bonds and one pi bond. Pi bonds tend to be weaker than sigma bonds because the side-by-side overlap the p orbitals give a less effective orbital overlap when compared to the end-to-end orbital overlap of a sigma bond. This makes the pi much easier to break which is one of the most important ideas in organic chemistry reactions as we will see in Chapter 7 and subsequent chapters.

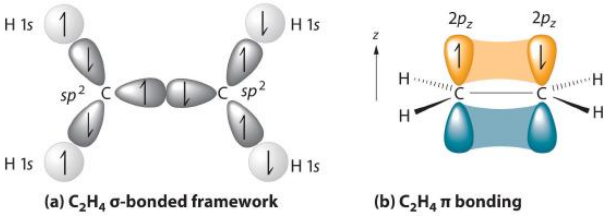


An ethylene molecule is said to be made up of five sigma bonds and one pi bond. The three sp^2 hybrid orbitals on each carbon orient to create the basic trigonal planer geometry. The H-C-C bond angle in ethylene is 121.3º which is very close to the 120º predicted by VSEPR. The four C-H sigma bonds in ethylene . The carbon-carbon double bond in ethylene is both shorter (133.9 pm) and almost twice as strong (728 kJ/mol) than the carbon- carbon single bond in ethylene (154 pm & 377 kJ/mol). Each of the four carbon-hydrogen bond in ethylene are equivalent has have a length of 108.7 pm



Rigidity in Ethene

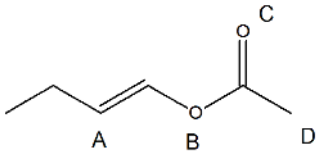
Because they are the result of side-by-side overlap (rather then end-to-end overlap like a sigma bond), *pi bonds are not free to rotate.* If rotation about this bond were to occur, it would involve disrupting the side-by-side overlap between the two $2p_z$ orbitals that make up the pi bond. If free rotation were to occur the p-orbitals would have to go through a phase where they are 90° from each other, which would break the pi bond because there would be no overlap. Since the pi bond is essential to the structure of ethene it must not break, so there can be not free rotation about the carbon-carbon sigma bond. The presence of the pi bond thus 'locks' the six atoms of ethene into the same plane.



(a) C_2H_4 σ-bonded framework (b) C_2H_4 π bonding

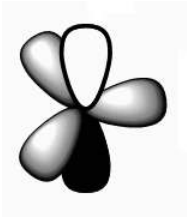
Exercise

1) Consider the following molecule:



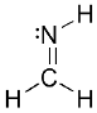
At each atom, what is the hybridization and the bond angle and the bond angle predicted by VSPER?

2) Please identify the types of orbitals shown in the following diagram:



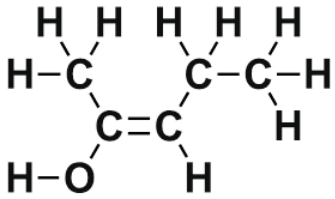
3)

a: Describe the orbitals which overlap to the carbon-nitrogen sigma bond and pie bond in the molecule below:



b: What kind of orbital holds the nitrogen lone pair?

4) For the following molecule please indicate with atoms are being held in the same plane by the carbon-carbon double bond:



Solutions

1)

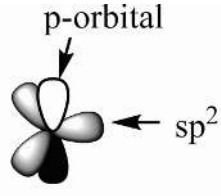
A - sp^2, 120°

B - sp^3, 109°

C - sp^2, 120° (with the lone pairs present)

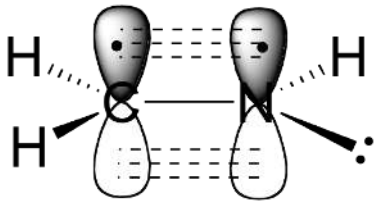
D - sp^3, 109°

2)



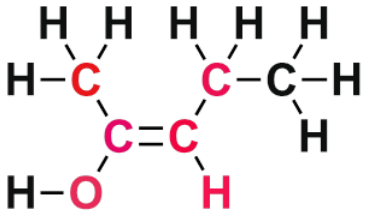
3)

a) The carbon and nitrogen atoms are both sp^2 hybridized. The carbon-nitrogen double bond is composed of a sigma bond formed from two sp^2 orbitals, and a pi bond formed from the side-by-side overlap of two unhybridized *2p* orbitals.



b) As shown in the figure above, the nitrogen lone pair electrons occupy one of the three sp^2 hybrid orbitals.

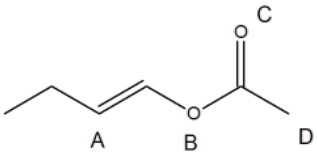
4)



Questions

Q1.8.1

Consider the following molecule:



At each atom, what is the hybridization and the bond angle? At atom A draw the molecular orbital.

Solutions

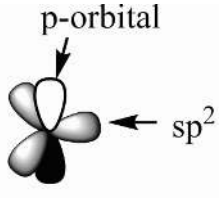
S1.8.1

A - sp^2, 120°

B - sp^3, 109°

C - sp^2, 120° (with the lone pairs present)

D - sp^3, 109°



7.1.6: sp² Hybrid Orbitals and the Structure of Ethylene is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Steven Farmer, Dietmar Kennepohl, Krista Cunningham, Tim Soderberg, William Reusch, & William Reusch.

- **1.8: sp² Hybrid Orbitals and the Structure of Ethylene** by Dietmar Kennepohl, Krista Cunningham, Steven Farmer, Tim Soderberg, William Reusch is licensed CC BY-SA 4.0.

7.1.7: sp Hybrid Orbitals and the Structure of Acetylene

Objectives

After completing this section, you should be able to

1. use the concept of *sp* hybridization to account for the formation of carbon-carbon triple bonds, and describe a carbon-carbon triple bond as consisting of one σ bond and two π bonds.
2. list the approximate bond lengths associated with typical carbon-carbon single bonds, double bonds and triple bonds. [You may need to review Sections 1.7 and 1.8.]
3. list the approximate bond angles associated with sp^3-, sp^2- and *sp*-hybridized carbon atoms and predict the bond angles to be expected in given organic compounds. [If necessary, review Sections 1.6, 1.7 and 1.8.]
4. account for the differences in bond length, bond strength and bond angles found in compounds containing sp^3-, sp^2- and sp-hybridized carbon atoms, such as ethane, ethylene and acetylene.

Key Terms

Make certain that you can define, and use in context, the key term below.

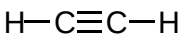
- *sp* hybrid orbital

Study Notes

The bond angles associated with sp^3-, sp^2- and *sp*-hybridized carbon atoms are approximately 109.5°, 120° and 180°, respectively.

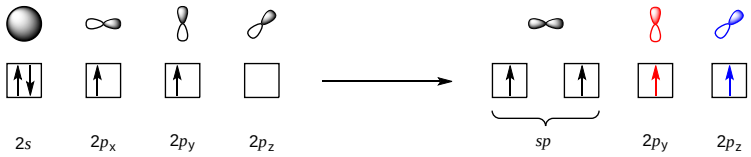
Bonding in acetylene

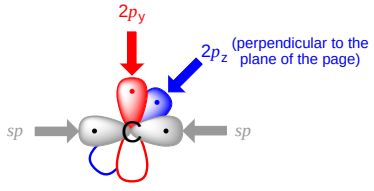
Finally, the hybrid orbital concept applies well to triple-bonded groups, such as alkynes and nitriles. Consider, for example, the structure of ethyne (another common name is acetylene), the simplest alkyne.



ethyne
(acetylene)

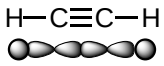
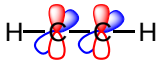
This molecule is linear: all four atoms lie in a straight line. The carbon-carbon triple bond is only 1.20Å long. In the hybrid orbital picture of acetylene, both carbons are ***sp*-hybridized**. In an *sp*-hybridized carbon, the 2*s* orbital combines with the $2p_x$ orbital to form two *sp* hybrid orbitals that are oriented at an angle of 180°with respect to each other (eg. along the x axis). The $2p_y$ and $2p_z$ orbitals remain non-hybridized, and are oriented perpendicularly along the y and z axes, respectively.



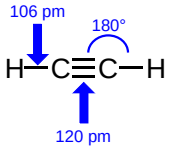


The C-C sigma bond is formed by the overlap of one *sp* orbital from each of the carbons, while the two C-H sigma bonds are formed by the overlap of the second *sp* orbital on each carbon with a 1*s* orbital on a hydrogen. Each carbon atom still has two half-filled $2p_y$ and $2p_z$ orbitals, which are perpendicular both to each other and to the line formed by the sigma bonds. These two

perpendicular pairs of *p* orbitals form two pi bonds between the carbons, resulting in a triple bond overall (one sigma bond plus two pi bonds).

	
sigma bonding in ethylene	pi bonding in ethylene

Acetylene is said to have three sigma bonds and two pi bonds. The carbon-carbon triple bond in acetylene is the shortest (120 pm) and the strongest (965 kJ/mol) of the carbon-carbon bond types. Because each carbon in acetylene has two electron groups, VSEPR predicts a linear geometry and and H-C-C bond angle of 180º.

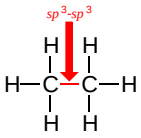
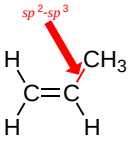
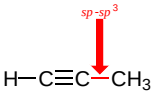


Comparison of C-C bonds Ethane, Ethylene, and Acetylene

Molecule	Bond	Bond Strength (kJ/mol)	Bond Length (pm)
Ethane, CH_3CH_3	(sp^3) C-C (sp^3)	376	154
Ethylene, $H_2C{=}CH_2$	(sp^2) C=C (sp^2)	728	134
Acetylene, HC≡CH	(*sp*) C≡C (*sp*)	965	120

Notice that as the bond order increases the bond length decreases and the bond strength increases.

The hybrid orbital concept nicely explains another experimental observation: single bonds adjacent to double and triple bonds are progressively shorter and stronger than 'normal' single bonds, such as the one in a simple alkane. The carbon-carbon bond in ethane (structure A below) results from the overlap of two sp^3 orbitals.

		
A	B	C

In propene (B), however, the carbon-carbon single bond is the result of overlap between an sp^2 orbital and an sp^3 orbital, while in propyne (C) the carbon-carbon single bond is the result of overlap between an sp orbital and an sp^3 orbital. These are all single bonds, but the single bond in molecule C is shorter and stronger than the one in B, which is in turn shorter and stronger than the one in A.

The explanation here is relatively straightforward. An sp orbital is composed of one *s* orbital and one *p* orbital, and thus it has 50% *s* character and 50% *p* character. sp^2 orbitals, by comparison, have 33% *s* character and 67% *p* character, while sp^3 orbitals have 25% *s* character and 75% *p* character. Because of their spherical shape, 2*s* orbitals are smaller, and hold electrons closer and 'tighter' to the nucleus, compared to 2*p* orbitals. Consequently, bonds involving sp + sp^3 overlap (as in alkyne C) are shorter and stronger than bonds involving sp^2 + sp^3 overlap (as in alkene B). Bonds involving sp^3-sp^3overlap (as in alkane A) are the longest and weakest of the group, because of the 75% '*p*' character of the hybrids.

Hybridization Summary

- A single bond is a sigma bond.
- A double bond is made up of a sigma bond and a pi bond.
- A triple bond is made up of a sigma bond and two pi bonds.
- Sigma bonds are made by the overlap of two hybrid orbitals or the overlap of a hybrid orbital and a s orbital from hydrogen.

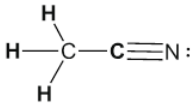
- Pi bonds are made by the overlap of two unhybridized p orbitals.
- Lone pair electrons are usually contained in hybrid orbitals.

The hybrid orbitals used (and hence the hybridization) depends on how many electron groups are around the atom in question. An electron group can mean either a bonded atom or a lone pair. Molecular geometry is also decided by the number of electron groups so it is directly linked to hybridization.

# of Electron Groups	Hybrid Orbital Used	Example	Basic Geometry	Basic Bond Angle
2	sp		Linear	180^o
3	sp^2		Trigonal Planar	120^o
4	sp^3		Tetrahedral	109.5^o

Exercises

1) For the molecule acetonitrile:



Acetonitrile

a) How many sigma and pi bonds does it have?

b) What orbitals overlap to form the C-H sigma bonds?

c) What orbitals overlap to form the C-C sigma bond?

d) What orbitals overlap to form the C-N sigma bond?

e) What orbitals overlap to the form the C-N pi bonds?

f) What orbital contains the lone pair electrons on nitrogen?

Solutions

1)

a) 5 sigma and 2 pi

b) An sp^3 hybrid orbital from carbon and an a s orbital from hydrogen.

c) An sp^3 hybrid orbital from one carbon and an sp orbital from the other carbon.

d) An sp hybrid orbital from carbon and an a sp orbital from nitrogen.

e) An p_y and p_z orbital from carbon and an p_y and p_z orbital from nitrogen.

f) An sp hybrid orbital.

1.9: sp Hybrid Orbitals and the Structure of Acetylene

1.9 Exercises

Questions

Q1.9.1

1-Cyclohexyne is a very strained molecule. By looking at the molecule explain why there is such a intermolecular strain using the knowledge of hybridization and bond angles.



Solutions

S1.9.1

The alkyne is a sp hybridized orbital. By looking at a sp orbital, we can see that the bond angle is 180°, but in cyclohexane the regular angles would be 109.5°. Therefore the molecule would be strained to force the 180° to be a 109°.

7.1.7: sp Hybrid Orbitals and the Structure of Acetylene is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Steven Farmer, Dietmar Kennepohl, Krista Cunningham, Tim Soderberg, William Reusch, & William Reusch.

- **1.9: sp Hybrid Orbitals and the Structure of Acetylene** by Dietmar Kennepohl, Krista Cunningham, Steven Farmer, Tim Soderberg, William Reusch is licensed CC BY-SA 4.0.

7.1.8: Hybridization of Nitrogen, Oxygen, Phosphorus and Sulfur

Objective

After completing this section, you should be able to apply the concept of hybridization of atoms such as N, O, P and S to explain the structures of simple species containing these atoms.

Key Terms

Make certain that you can define, and use in context, the key term below.

- lone pair electrons

Study Notes

Nitrogen is frequently found in organic compounds. As with carbon atoms, nitrogen atoms can be sp^3-, sp^2- or sp-hybridized.

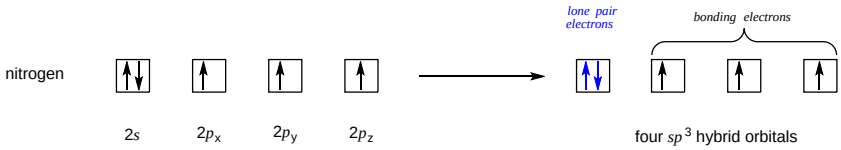
Note that, in this course, the term “lone pair” is used to describe an unshared pair of electrons.

The valence-bond concept of orbital hybridization can be extrapolated to other atoms including nitrogen, oxygen, phosphorus, and sulfur. In other compounds, covalent bonds that are formed can be described using hybrid orbitals.

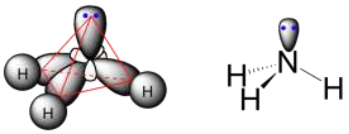
Nitrogen

Bonding in NH_3

The nitrogen in NH_3 has five valence electrons. After hybridization these five electrons are placed in the four equivalent sp^3 hybrid orbitals. The electron configuration of nitrogen now has one sp^3 hybrid orbital completely filled with two electrons and three sp^3 hybrid orbitals with one unpaired electron each. The two electrons in the filled sp^3 hybrid orbital are considered non-bonding because they are already paired. These electrons will be represented as a lone pair on the structure of NH_3. The three unpaired electrons in the hybrid orbitals are considered bonding and will overlap with the s orbitals in hydrogen to form N-H sigma bonds. Note! This bonding configuration was predicted by the Lewis structure of NH_3.

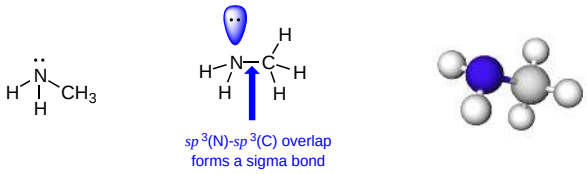


The four sp^3 hybrid orbitals of nitrogen orientate themselves to form a tetrahedral geometry. The three N-H sigma bonds of NH_3 are formed by sp^3(N)-1s(H) orbital overlap. The fourth sp^3 hybrid orbital contains the two electrons of the lone pair and is not directly involved in bonding.



Methyl amine

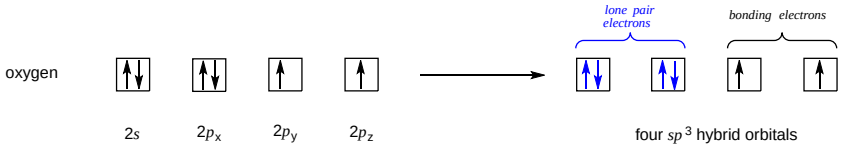
The nitrogen is sp^3 hybridized which means that it has four sp^3 hybrid orbitals. Two of the sp^3 hybridized orbitals overlap with s orbitals from hydrogens to form the two N-H sigma bonds. One of the sp^3 hybridized orbitals overlap with an sp^3 hybridized orbital from carbon to form the C-N sigma bond. The lone pair electrons on the nitrogen are contained in the last sp^3 hybridized orbital. Due to the sp^3 hybridization the nitrogen has a tetrahedral geometry. However, the H-N-H and H-N-C bonds angles are less than the typical 109.5º due to compression by the lone pair electrons.



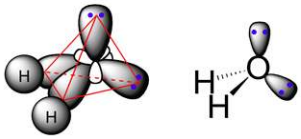
Oxygen

Bonding in H_2O

The oxygen in H_2O has six valence electrons. After hybridization these six electrons are placed in the four equivalent sp^3 hybrid orbitals. The electron configuration of oxygen now has two sp^3 hybrid orbitals completely filled with two electrons and two sp^3 hybrid orbitals with one unpaired electron each. The filled sp^3 hybrid orbitals are considered non-bonding because they are already paired. These electrons will be represented as a two sets of lone pair on the structure of H_2O . The two unpaired electrons in the hybrid orbitals are considered bonding and will overlap with the s orbitals in hydrogen to form O-H sigma bonds. Note! This bonding configuration was predicted by the Lewis structure of H_2O.

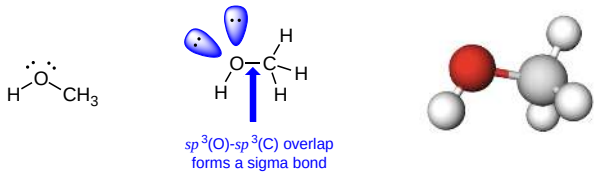


The four sp^3 hybrid orbitals of oxygen orientate themselves to form a tetrahedral geometry. The two O-H sigma bonds of H_2O are formed by sp^3(O)-1s(H) orbital overlap. The two remaining sp^3 hybrid orbitals each contain two electrons in the form of a lone pair.



Methanol

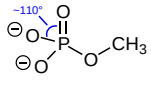
The oxygen is sp^3 hybridized which means that it has four sp^3 hybrid orbitals. One of the sp^3 hybridized orbitals overlap with s orbitals from a hydrogen to form the O-H sigma bonds. One of the sp^3 hybridized orbitals overlap with an sp^3 hybridized orbital from carbon to form the C-O sigma bond. Both the sets of lone pair electrons on the oxygen are contained in the remaining sp^3 hybridized orbital. Due to the sp^3 hybridization the oxygen has a tetrahedral geometry. However, the H-O-C bond angles are less than the typical 109.5° due to compression by the lone pair electrons.

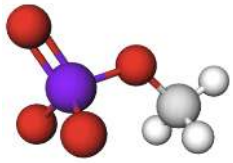


Phosphorus

Methyl phosphate

The bond pattern of phosphorus is analogous to nitrogen because they are both in period 15. However, phosphorus can have have expanded octets because it is in the n = 3 row. Typically, phosphorus forms five covalent bonds. In biological molecules, phosphorus is usually found in organophosphates. Organophosphates are made up of a phosphorus atom bonded to four oxygens, with one of the oxygens also bonded to a carbon. In methyl phosphate, the phosphorus is sp^3 hybridized and the O-P-O bond angle varies from 110° to 112°.



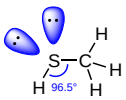


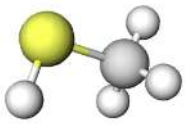
Sulfur

Methanethiol & Dimethyl Sulfide

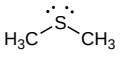
Sulfur has a bonding pattern similar to oxygen because they are both in period 16 of the periodic table. Because sulfur is positioned in the third row of the periodic table it has the ability to form an expanded octet and the ability to form more than the typical number of covalent bonds. In biological system, sulfur is typically found in molecules called thiols or sulfides. In a thiol, the sulfur atom is bonded to one hydrogen and one carbon and is analogous to an alcohol O-H bond. In a sulfide, the sulfur is bonded to two carbons. The simplest example of a thiol is methane thiol (CH_3SH) and the simplest example of a sulfide is dimethyl sulfide [$(CH_3)_3S$]. In both cases the sulfur is sp^3 hybridized, however the sulfur bond angles are much less than the typical tetrahedral 109.5^o being 96.6^o and 99.1^o respectively.

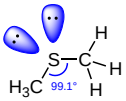


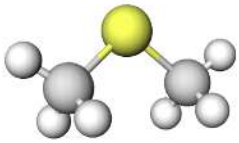




methanethiol





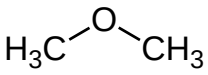


dimethyl sulfide

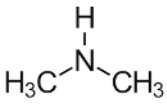
Exercises

1) Insert the missing lone pairs of electrons in the following molecules, and tell what hybridization you expect for each of the indicated atoms.

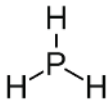
a) The oxygen is dimethyl ether:



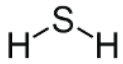
b) The nitrogen in dimethyl amine:



c) The phosphorus in phosphine:



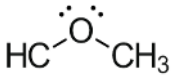
d) The sulfur in hydrogen sulfide:



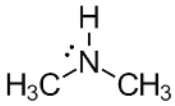
Solutions

1)

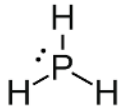
a) sp^3 hybridization



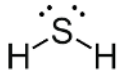
b) sp^3 hybridization



c) sp^3 hybridization



d) sp^3 hybridization



1.10: Hybridization of Nitrogen, Oxygen, Phosphorus and Sulfur

1.10 Exercises

Questions

Q1.10.1

Identify geometry and lone pairs on each heteroatom of the molecules given.



Solutions

S1.10.1

Diethyl ether would have two lone pairs of electrons and would have a bent geometry around the oxygen.

Dimethyl amine would have one lone pair and would show a pyramidal geometry around the nitrogen.

7.1.8: Hybridization of Nitrogen, Oxygen, Phosphorus and Sulfur is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Steven Farmer, Dietmar Kennepohl, Krista Cunningham, & Krista Cunningham.

- **1.10: Hybridization of Nitrogen, Oxygen, Phosphorus and Sulfur** by Dietmar Kennepohl, Krista Cunningham, Steven Farmer is licensed CC BY-SA 4.0.

7.1.9: Describing Chemical Bonds- Molecular Orbital Theory

Objectives

After completing this section, you should be able to

1. describe the formation of covalent bonds in terms of molecular orbitals.
2. account for differences in bond length and strength in terms of the efficiency with which atomic orbitals overlap.
3. draw simple molecular orbital diagrams (e.g., for the H_2 molecule) showing the formation of bonding and anti-bonding orbitals.

Key Terms

Make certain that you can define, and use in context, the key terms below.

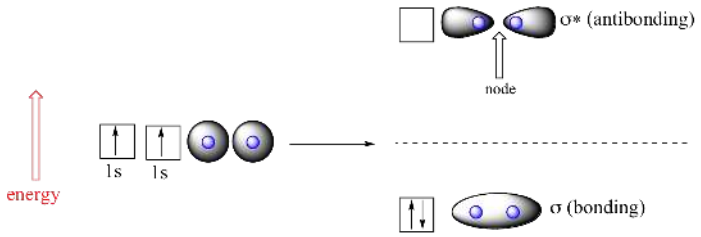
- anti-bonding molecular orbital
- bonding molecular orbital
- molecular orbital (MO) theory

As we have seen, valence bond theory does a remarkably good job of explaining the bonding geometry and properties of many organic compounds. There are some areas, however, where the valence bond theory falls short. It fails to adequately account, for example, for some interesting properties of compounds that contain alternating double and single bonds. In order to understand these properties, we need to think about chemical bonding in a new way, using the ideas of molecular orbital (MO) theory.

Another look at the H_2 molecule: bonding and anti-bonding sigma molecular orbitals

Let's consider again the simplest possible covalent bond: the one in molecular hydrogen (H_2). When we described the hydrogen molecule using valence bond theory, we said that the two 1*s* orbitals from each atom overlap, allowing the two electrons to be shared and thus forming a covalent bond. In molecular orbital theory, we make a further statement: we say that the two atomic 1*s* orbitals don't just overlap, they actually *combine to form two completely new orbitals*. These two new orbitals, instead of describing the likely location of an electron around a single nucleus, describe the location of an electron pair around two or more nuclei. The bonding in H_2, then, is due to the formation of a new **molecular orbital** (MO), in which a pair of electrons is delocalized around two hydrogen nuclei.

An important principle of quantum mechanical theory is that when orbitals combine, the number of orbitals before the combination takes place must equal the number of new orbitals that result – orbitals don't just disappear! We saw this previously when we discussed hybrid orbitals: one *s* and three *p* orbitals make four sp^3 hybrids. When two atomic 1*s* orbitals combine in the formation of H_2, the result is two molecular orbitals called **sigma (σ) orbitals**. According to MO theory, the first sigma orbital is lower in energy than either of the two isolated atomic 1*s* orbitals – thus this sigma orbital is referred to as a **bonding molecular orbital**. The second, **sigma-star (σ*) orbital** is higher in energy than the two atomic 1*s* orbitals, and is referred to as an **anti-bonding molecular orbital**. In MO theory, a star (*) sign always indicates an anti-bonding orbital.



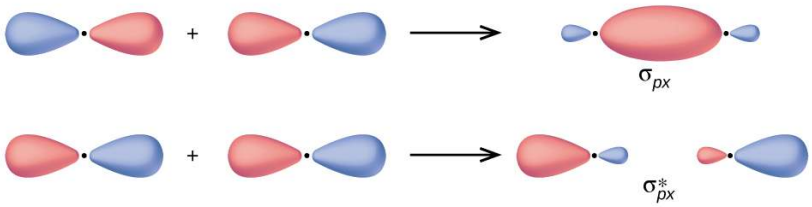
Following the *aufbau* ('building up') principle, we place the two electrons in the H_2 molecule in the lowest energy molecular orbital, which is the (bonding) sigma orbital.

The bonding sigma orbital, which holds both electrons in the ground state of the molecule, is egg-shaped, encompassing the two nuclei, and with the highest likelihood of electrons being in the area between the two nuclei. The high-energy, anti-bonding sigma-star orbital can be visualized as a pair of droplets, with areas of higher electron density near each nucleus and a 'node', (area of zero electron density) midway between the two nuclei.

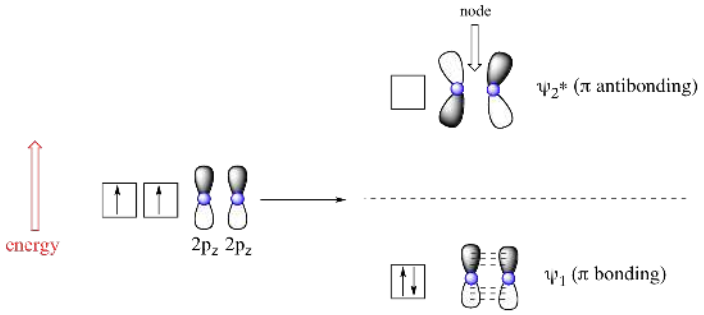
Remember that we are thinking here about electron behavior as *wave behavior*. When two separate waves combine, they can do so with what is called constructive interference, where the two amplitudes reinforce one another, or destructive interference, where the two amplitudes cancel one another out. Bonding MO's are the consequence of constructive interference between two atomic orbitals which results in an attractive interaction and an increase in electron density between the nuclei. Anti-bonding MO's are the consequence of destructive interference which results in a repulsive interaction and a 'canceling out' of electron density between the nuclei (in other words, a node).

MO theory and pi bonds

In p orbitals, the wave function gives rise to two lobes with opposite phases, analogous to how a two-dimensional wave has both parts above and below the average. We indicate the phases by shading the orbital lobes different colors. When orbital lobes of the same phase overlap, constructive wave interference increases the electron density. When regions of opposite phase overlap, the destructive wave interference decreases electron density and creates nodes. When p orbitals overlap end to end, they create σ and σ* orbitals. If two atoms are located along the x-axis in a Cartesian coordinate system, the two px orbitals overlap end to end and form σp_x (bonding) and $\sigma * p_x$ (antibonding) (read as "sigma-p-x" and "sigma-p-x star," respectively). Just as with s-orbital overlap, the asterisk indicates the orbital with a node between the nuclei, which is a higher-energy, antibonding orbital.



The advantage of MO theory becomes more apparent when we think about pi bonds, especially in those situations where two or more pi bonds are able to interact with one another. Let's first consider the pi bond in ethene from an MO theory standpoint (in this example we will be disregarding the various sigma bonds, and thinking *only* about the pi bond). According to MO theory, the two atomic $2p_z$ orbitals combine to form two **pi (π) molecular orbitals**, one a low-energy π bonding orbital and one a high-energy **π-star (π*) anti-bonding molecular orbital**. These are sometimes denoted, in MO diagrams like the one below, with the Greek letter psi (Ψ) instead of π.



In the bonding Ψ_1 orbital, the two shaded lobes of the $2p_z$ orbitals interact constructively with each other, as do the two unshaded lobes (remember, the shading choice represents mathematical (+) and (-) signs for the wavefunction). Therefore, there is increased electron density between the nuclei in the molecular orbital – this is why it is a bonding orbital.

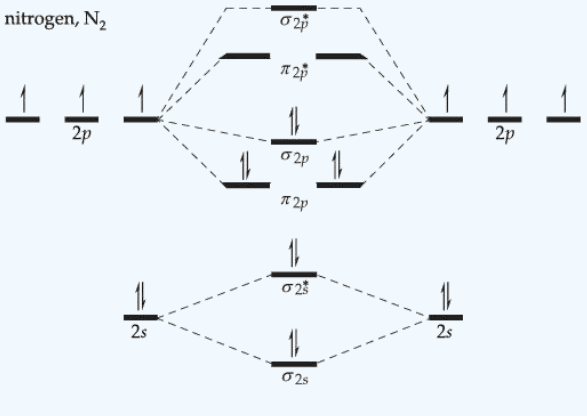
In the higher-energy anti-bonding Ψ_2* orbital, the shaded lobe of one $2p_z$ orbital interacts destructively with the unshaded lobe of the second $2p_z$ orbital, leading to a node between the two nuclei and overall repulsion. By the *aufbau* principle, the two electrons from the two atomic orbitals will be paired in the lower-energy Ψ_1 orbital when the molecule is in the ground state.

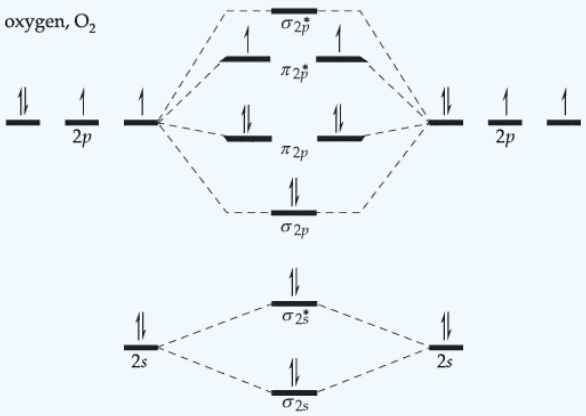
Example 7.1.9.1

Draw a simple molecular orbital diagram for each of the following molecules

a. nitrogen, N_2.
b. oxygen, O_2.

Solution





7.1.9: Describing Chemical Bonds- Molecular Orbital Theory is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Steven Farmer, Dietmar Kennepohl, Tim Soderberg, & Tim Soderberg.

- **1.11: Describing Chemical Bonds - Molecular Orbital Theory** by Dietmar Kennepohl, Steven Farmer, Tim Soderberg is licensed CC BY-SA 4.0.

7.2: Drawing Chemical Structures

Objectives

After completing this section, you should be able to

1. propose one or more acceptable Kekulé structures (structural formulas) for any given molecular formula
2. write the molecular formula of a compound, given its Kekulé structure.
3. draw the shorthand structure of a compound, given its Kekulé structure.
4. interpret shorthand structures and convert them to Kekulé structures.
5. write the molecular formula of a compound, given its shorthand structure.

Study Notes

When drawing the structure of a neutral organic compound, you will find it helpful to remember that

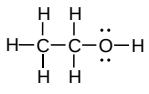
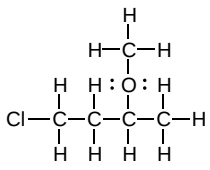
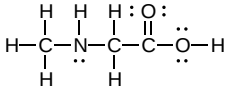
- each carbon atom has four bonds.
- each nitrogen atom has three bonds.
- each oxygen atom has two bonds.
- each hydrogen atom has one bond.

Through general chemistry, you may have already experienced looking at molecular structures using Lewis structures. Because organic chemistry can involve large molecules it would be beneficial if Lewis structures could be abbreviated. The three different ways to draw organic molecules include **Kekulé Formulas**, **Condensed Formulas**, and **Skeletal structures** (also called line-bond structures or line formulas). During this course, you will view molecules written in all three forms. It will be more helpful if you become comfortable going from one style of drawing to another, and look at drawings and understanding what they represent. Developing the ability to convert between different types of formulas requires practice, and in most cases the aid of molecular models. Many kinds of model kits are available to students and professional chemists, and the beginning student is encouraged to obtain one.

Simplification of structural formulas may be achieved without any loss of the information they convey. Kekule formulas is just organic chemistry's term for Lewis structures you have previously encountered. In **condensed structural formulas**, the bonds to each carbon are omitted, but each distinct structural unit (group) is written with subscript numbers designating multiple substituents, including the hydrogens. **Line formulas** omit the symbols for carbon and hydrogen entirely (unless the hydrogen is bonded to an atom other than carbon). Each straight line segment represents a bond, the ends and intersections of the lines are carbon atoms, and the correct number of hydrogens is calculated from the tetravalency of carbon. Non-bonding valence shell electrons are omitted in these formulas.

Kekulé (a.k.a. Lewis Structures)

A Kekulé Formula or structural formula displays the atoms of the molecule in the order they are bonded. It also depicts how the atoms are bonded to one another, for example single, double, and triple covalent bond. Covalent bonds are shown using lines. The number of dashes indicate whether the bond is a single, double, or triple covalent bond. All atom labels are shown and all lone pairs are shown.

		
A	**B**	**C**

Condensed Formula

A condensed formula is made up of the elemental symbols. Condensed structural formulas show the order of atoms like a structural formula but are written in a single line to save space and make it more convenient and faster to write out. The order of the atoms suggests the connectivity in the molecule. Condensed structural formulas are also helpful when showing that a group of atoms is connected to a single atom in a compound. When this happens, parenthesis are used around the group of atoms to show they are together. Also, if more than one of the same substituent is attached to a given atom, it is show with a subscript number. An example is CH_4, which represents four hydrogens attached to the same carbon. Condensed formulas can be read from either direction and H_3C is the same as CH_3, although the latter is more common.

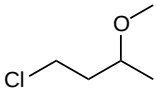
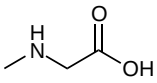
Look at the examples below and match them with their identical molecule under the Kekulé structures and the line formulas.

CH_3CH_2OH	$ClCH_2CH_2CH(OCH_3)CH_3$	CH_3NHCH_2COOH
A	**B**	**C**

Let's look closely at example B. As you go through a condensed formula, you want to focus on the carbons and other elements that aren't hydrogen. The hydrogen's are important, but are usually there to complete octets. Also, notice the $-OCH_3$ is in written in parentheses which tell you that it not part of the main chain of carbons. As you read through a a condensed formula, if you reach an atom that doesn't have a complete octet by the time you reach the next hydrogen, then it's possible that there are double or triple bonds. In example C, the carbon is double bonded to oxygen and single bonded to another oxygen. Notice how COOH means C(=O)-O-H instead of CH_3-C-O-O-H because carbon does not have a complete octet and oxygens.

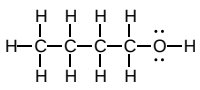
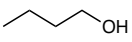
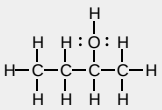
Line Formula

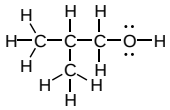
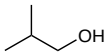
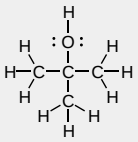
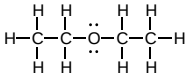
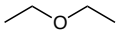
Because organic compounds can be complex at times, line-angle formulas are used to write carbon and hydrogen atoms more efficiently by replacing the letter "C" with lines. A carbon atom is present wherever a line intersects another line. Hydrogen atoms are omitted but are assumed to be present to complete each of carbon's four bonds. Hydrogens that are attached to elements other than carbon are shown. Atom labels for all other elements are shown. Lone pair electrons are usually omitted. They are assumed to be present to complete the octet of non-carbon atoms. Line formulas help show the structure and order of the atoms in a compound.

		
A	**B**	**C**

These molecules correspond to the exact same molecules depicted for Kekulé structures and condensed formulas. Notice how the carbons are no longer drawn in and are replaced by the ends and bends of a lines. In addition, the hydrogens have been omitted, but could be easily drawn in (see practice problems). Although we do not usually draw in the H's that are bonded to carbon, we do draw them in if they are connected to other atoms besides carbon (example is the OH group above in example A) . This is done because it is not always clear if the non-carbon atom is surrounded by lone pairs or hydrogens. Also in example A, notice how the OH is drawn with a bond to the second carbon, but it does not mean that there is a third carbon at the end of that bond/ line.

Table 7.2.1: Structural Formulas for $C_4H_{10}O$ isomers

Kekulé Formula	Condensed Formula	Line Formula
	$CH_3(CH_2)_3OH$	
	$CH_3CH_2CH(OH)CH_3$	

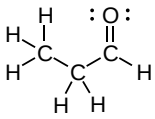
Kekulé Formula	Condensed Formula	Line Formula
	$(CH_3)_2CHCH_2OH$	
	$(CH_3)_3COH$	
	$CH_3CH_2OCH_2CH_3$	

Example: Converting between Structural Formulas

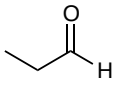
It is helpful to convert compounds into different structural formulas (Kekule, Line, and Condensed) depending on the type of question that is asked. Standardized exams frequently include a high percentage of condensed formulas because it is easier and cheaper to type letters and numbers than to import figures. Initially, it can be difficult writing a Line structure directly from a condensed formula. First, write the Kekule structure from the condensed formula and then draw the Line structure from the Kekule.

a) The condensed formula for propanal is CH_3CH_2CHO. Draw the Kekule structure.

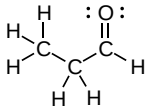
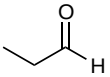
The Kekule structure for propanal is shown below. Remember that every carbon will have four bonds and oxygens octet is filled with lone pairs.



The bond-line structure for propanal is shown below. First, remove hydrogens. The hydrogen attached to the aldehyde group remains because it is part of a functional group. The remove the "C" labels from the structure and keep the lines in place. Lastly, remove any lone pairs.



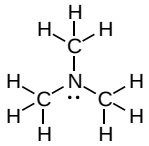
All three structures represent the same compound, propanal.

CH_3CH_2CHO =  = 

b) The following is the line structure of the molecule trimethyl amine.



To convert it to a Kekule structure first identify the carbons in the molecule. The will be at the corners and ends of line without an atom label. Trimethyl amine has three carbons. Next, add hydrogens to the carbons until four bonds are present. Each carbon in trimethyl amine is singly bonded to nitrogen. This means each carbon will need three additional C-H bonds to create its octet. Lastly, add lone pairs to other elements to fill their octets. The nitrogen in trimethyl amine is bonded to three carbons. This means it will require one of lone pair electrons to complete its octet.



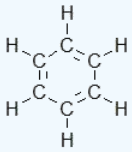
Exercise 7.2.1

How many carbons are in the following drawing? How many hydrogens?



Answer

Remember the octet rule and how many times carbons and hydrogens are able to bond to other atoms.

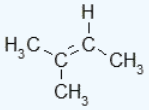


Exercise 7.2.2

How many carbons are in the following drawing? How many hydrogens?



Answer

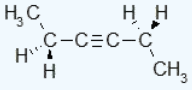


Exercise 7.2.3

How many carbons are in the following drawing? How many hydrogens?

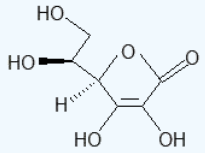


Answer



Exercise 7.2.4

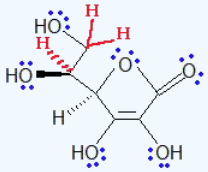
Look at the following molecule of vitamin A and draw in the hidden hydrogens and electron pairs.



Hint: Do all of the carbons have 4 bonds? Do all the oxygens have a full octet?

Answer

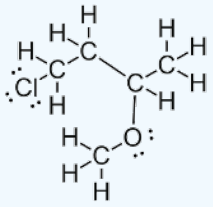
Electron pairs drawn in blue and hydrogens draw in red.



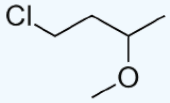
Exercise 7.2.5

Draw $ClCH_2CH_2CH(OCH_3)CH_3$ in Kekulé and line form.

Answer

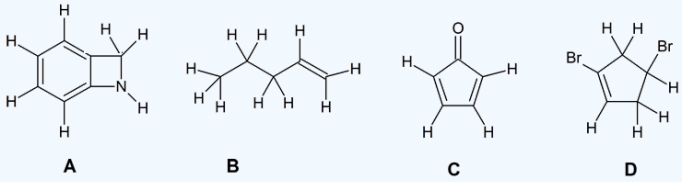


and



Exercise 7.2.6

Write down the molecular formula for each of the compounds shown here.



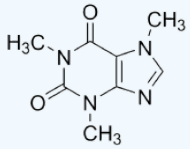
A B C D

Answer

a. C_7H_7N
b. C_5H_{10}
c. C_5H_4O
d. $C_5H_6Br_2$

Exercise 7.2.7

Below is the molecule for caffeine. Give the molecular formula for it.



Answer

$C_8H_{10}O_2N_4$

7.2: Drawing Chemical Structures is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Steven Farmer, Dietmar Kennepohl, Krista Cunningham, Tim Soderberg, William Reusch, & William Reusch.

- **1.12: Drawing Chemical Structures** by Dietmar Kennepohl, Krista Cunningham, Steven Farmer, Tim Soderberg, William Reusch is licensed CC BY-SA 4.0.

7.3: Functional Groups

Objectives

After completing this section, you should be able to

1. explain why the properties of a given organic compound are largely dependent on the functional group or groups present in the compound.
2. identify the functional groups present in each of the following compound types: alkenes, alkynes, arenes, (alkyl and aryl) halides, alcohols, ethers, aldehydes, ketones, esters, carboxylic acids, (carboxylic) acid chlorides, amides, amines, nitriles, nitro compounds, sulfides and sulfoxides.
3. identify the functional groups present in an organic compound, given its structure.
4. Given the structure of an organic compound containing a single functional group, identify which of the compound types listed under Objective 2, above, it belongs to.
5. draw the structure of a simple example of each of the compound types listed in Objective 2.

Key Terms

Make certain that you can define, and use in context, the key term below.

- functional group

Study Notes

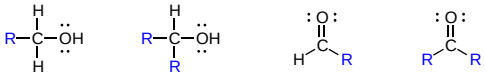
The concept of functional groups is a very important one. We expect that you will need to refer back to tables at the end of Section 3.1 quite frequently at first, as it is not really feasible to learn the names and structures of all the functional groups and compound types at one sitting. Gradually they will become familiar, and eventually you will recognize them automatically.

Functional groups are small groups of atoms that exhibit a characteristic reactivity. A particular functional group will almost always display its distinctive chemical behavior when it is present in a compound. Because of their importance in understanding organic chemistry, functional groups have specific names that often carry over in the naming of individual compounds incorporating the groups.

As we progress in our study of organic chemistry, it will become extremely important to be able to quickly recognize the most common functional groups, because they are the key structural elements that define how organic molecules react. For now, we will only worry about drawing and recognizing each functional group, as depicted by Lewis and line structures. Much of the remainder of your study of organic chemistry will be taken up with learning about how the different functional groups tend to behave in organic reactions.

Drawing abbreviated organic structures

Often when drawing organic structures, chemists find it convenient to use the letter 'R' to designate part of a molecule outside of the region of interest. If we just want to refer in general to a functional group without drawing a specific molecule, for example, we can use 'R groups' to focus attention on the group of interest:



a primary alcohol | a secondary alcohol | an aldehyde | a ketone

The 'R' group is a convenient way to abbreviate the structures of large biological molecules, especially when we are interested in something that is occurring specifically at one location on the molecule.

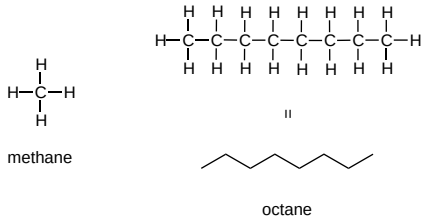
Common Functional Groups

In the following sections, many of the common functional groups found in organic chemistry will be described. Tables of these functional groups can be found at the bottom of the page.

Hydrocarbons

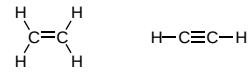
The simplest functional group in organic chemistry (which is often ignored when listing functional groups) is called an **alkane**, characterized by single bonds between two carbons and between carbon and hydrogen. Some examples of alkanes include methane, CH_4, is the natural gas you may burn in your furnace or on a stove. Octane, C_8H_{18}, is a component of gasoline.

Alkanes

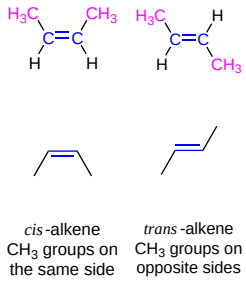


Alkenes (sometimes called **olefins**) have carbon-carbon double bonds, and **alkynes** have carbon-carbon triple bonds. Ethene, the simplest alkene example, is a gas that serves as a cellular signal in fruits to stimulate ripening. (If you want bananas to ripen quickly, put them in a paper bag along with an apple - the apple emits ethene gas, setting off the ripening process in the bananas). Ethyne, commonly called acetylene, is used as a fuel in welding blow torches.

Alkenes and alkynes



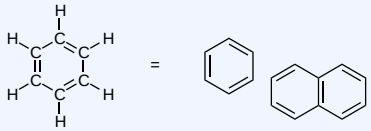
Alkenes have trigonal planar electron geometry (due to sp^2 hybrid orbitals at the alkene carbons) while alkynes have linear geometry (due to sp hybrid orbitals at the alkyne carbons). Furthermore, many alkenes can take two geometric forms: ***cis*** or ***trans*** *(or Z and E which will be explained in detail in Chapter 7)*. The *cis* and *trans* forms of a given alkene are different molecules with different physical properties there is a very high energy barrier to rotation about a double bond. In the example below, the difference between *cis* and *trans* alkenes is readily apparent.



Alkanes, alkenes, and alkynes are all classified as **hydrocarbons**, because they are composed solely of carbon and hydrogen atoms. Alkanes are said to be **saturated hydrocarbons**, because the carbons are bonded to the maximum possible number of hydrogens - in other words, they are *saturated* with hydrogen atoms. The double and triple-bonded carbons in alkenes and alkynes have fewer hydrogen atoms bonded to them - they are thus referred to as **unsaturated hydrocarbons**. As we will see in Chapter 7, hydrogen can be added to double and triple bonds, in a type of reaction called 'hydrogenation'.

The **aromatic** group is exemplified by benzene (which used to be a commonly used solvent on the organic lab, but which was shown to be carcinogenic), and naphthalene, a compound with a distinctive 'mothball' smell. Aromatic groups are planar (flat) ring structures, and are widespread in nature. We will learn more about the structure and reactions of aromatic groups in Chapter 15.

Aromatics

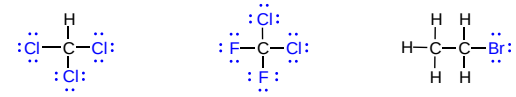


benzene naphthalene

Functional Groups with Carbon Single Bonds to other Atoms

Halides

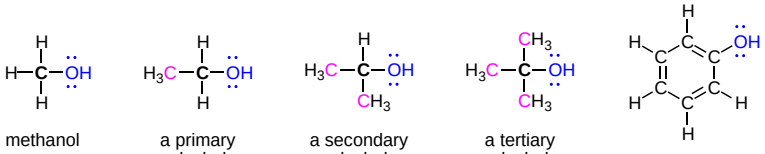
When the carbon of an alkane is bonded to one or more halogens, the group is referred to as a **alkyl halide** or **haloalkane**. The presence of a halogen atom (F, Cl, Br, or I), is often represented by X due to the similar chemistry of halogens. Chloroform is a useful solvent in the laboratory, and was one of the earlier anesthetic drugs used in surgery. Chlorodifluoromethane was used as a refrigerant and in aerosol sprays until the late twentieth century, but its use was discontinued after it was found to have harmful effects on the ozone layer. Bromoethane is a simple alkyl halide often used in organic synthesis. Alkyl halides groups are quite rare in biomolecules.



trichloromethane (chloroform) dichlorodifluoromethane (Freon-12) bromoethane

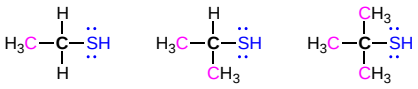
Alcohols and Thiols

In the **alcohol** functional group, a carbon is single-bonded to an OH group (the OH group, by itself, is referred to as a **hydroxyl**). Except for methanol, all alcohols can be classified as primary, secondary, or tertiary. In a **primary alcohol**, the carbon bonded to the OH group is also bonded to only one other carbon. In a **secondary alcohol** and **tertiary alcohol,** the carbon is bonded to two or three other carbons, respectively. When the hydroxyl group is *directly* attached to an aromatic ring, the resulting group is called a **phenol**.



methanol a primary alcohol a secondary alcohol a tertiary alcohol a phenol

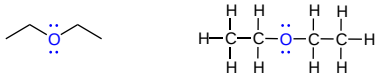
The sulfur analog of an alcohol is called a **thiol** (the prefix *thio*, derived from the Greek, refers to sulfur).



a primary thiol a secondary thiol a tertiary thiol

Ethers and sulfides

In an **ether** functional group, a central oxygen is bonded to two carbons. Below are the line and Lewis structures of diethyl ether, a common laboratory solvent and also one of the first medical anaesthesia agents.

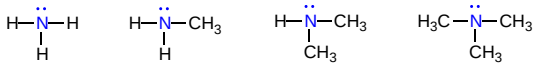


In **sulfides**, the oxygen atom of an ether has been replaced by a sulfur atom.



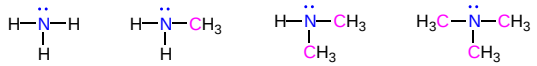
Amines

Amines are characterized by nitrogen atoms with single bonds to hydrogen and carbon. Just as there are primary, secondary, and tertiary alcohols, there are primary, secondary, and tertiary amines. Ammonia is a special case with no carbon atoms.

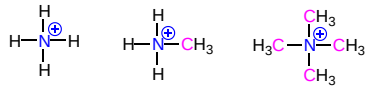


ammonia | a primary amine | a secondary amine | a tertiary amine

One of the most important properties of amines is that they are basic, and are readily protonated to form **ammonium** cations. In the case where a nitrogen has four bonds to carbon (which is somewhat unusual in biomolecules), it is called a quaternary ammonium ion.



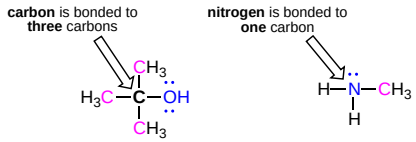
ammonia | a primary amine | a secondary amine | a tertiary amine



ammonium ion | a primary ammonium ion | a quaternary ammonium ion

Caution

Do not be confused by how the terms 'primary', 'secondary', and 'tertiary' are applied to alcohols and amines - the definitions are different. In alcohols, what matters is how many other carbons the alcohol *carbon* is bonded to, while in amines, what matters is how many carbons the *nitrogen* is bonded to.

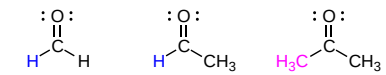


a tertiary alcohol | a primary amine

Carbonyl Containing Functional Groups

Aldehydes and Ketones

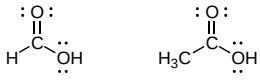
There are a number of functional groups that contain a carbon-oxygen double bond, which is commonly referred to as a **carbonyl**. **Ketones** and **aldehydes** are two closely related carbonyl-based functional groups that react in very similar ways. In a ketone, the carbon atom of a carbonyl is bonded to two other carbons. In an aldehyde, the carbonyl carbon is bonded on one side to a hydrogen, and on the other side to a carbon. The exception to this definition is formaldehyde, in which the carbonyl carbon has bonds to two hydrogens.



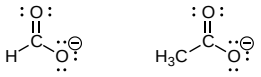
formaldehyde | an aldehyde | a ketone

Carboxylic acids and acid derivatives

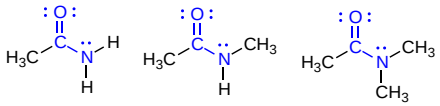
If a carbonyl carbon is bonded on one side to a carbon (or hydrogen) and on the other side to a **heteroatom** (in organic chemistry, this term generally refers to oxygen, nitrogen, sulfur, or one of the halogens), the functional group is considered to be one of the '**carboxylic acid derivatives'**, a designation that describes a grouping of several functional groups. The eponymous member of this grouping is the **carboxylic acid** functional group, in which the carbonyl is bonded to a hydroxyl (OH) group.



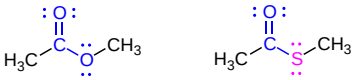
As the name implies, carboxylic acids are acidic, meaning that they are readily deprotonated to form the conjugate base form, called a **carboxylate** (much more about carboxylic acids in Chapter 20).



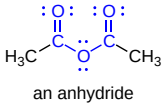
In **amides**, the carbonyl carbon is bonded to a nitrogen. The nitrogen in an amide can be bonded either to hydrogens, to carbons, or to both. Another way of thinking of an amide is that it is a carbonyl bonded to an amine.



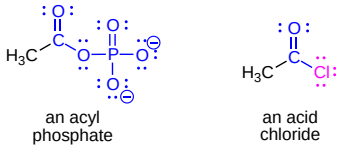
In **esters**, the carbonyl carbon is bonded to an oxygen which is itself bonded to another carbon. Another way of thinking of an ester is that it is a carbonyl bonded to an alcohol. **Thioesters** are similar to esters, except a sulfur is in place of the oxygen.



In an **acid anhydride**, there are two carbonyl carbons with an oxygen in between. An acid anhydride is formed from combination of two carboxylic acids with the loss of water (anhydride).

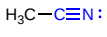


In an **acyl phosphate**, the carbonyl carbon is bonded to the oxygen of a phosphate, and in an **acid chloride**, the carbonyl carbon is bonded to a chlorine.



Nitriles and Imines

In a **nitrile** group, a carbon is triple-bonded to a nitrogen. Nitriles are also often referred to as **cyano** groups.

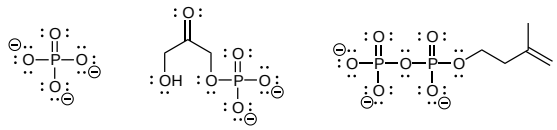


Molecules with carbon-nitrogen double bonds are called **imines**, or **Schiff bases**.

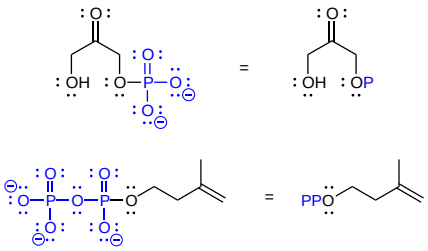


Phosphates

Phosphorus is a very important element in biological organic chemistry, and is found as the central atom in the **phosphate** group. Many biological organic molecules contain phosphate, diphosphate, and triphosphate groups, which are linked to a carbon atom by the **phosphate ester** functionality.

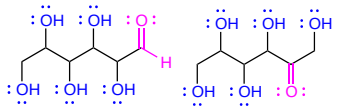


Because phosphates are so abundant in biological organic chemistry, it is convenient to depict them with the abbreviation 'P'. Notice that this 'P' abbreviation includes the oxygen atoms and negative charges associated with the phosphate groups.

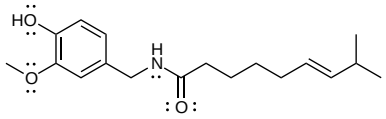


Molecules with Multiple Functional Groups

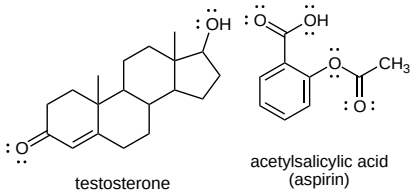
A single compound may contain several different functional groups. The six-carbon sugar molecules glucose and fructose, for example, contain aldehyde and ketone groups, respectively, and both contain five alcohol groups (a compound with several alcohol groups is often referred to as a '**polyol**').



Capsaicin, the compound responsible for the heat in hot peppers, contains phenol, ether, amide, and alkene functional groups.



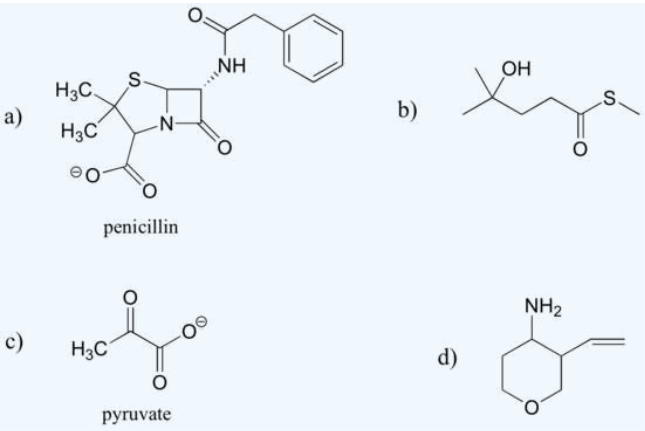
The male sex hormone testosterone contains ketone, alkene, and secondary alcohol groups, while acetylsalicylic acid (aspirin) contains aromatic, carboxylic acid, and ester groups.



While not in any way a complete list, this section has covered most of the important functional groups that we will encounter in biological and laboratory organic chemistry. The table found below provides a summary of all of the groups listed in this section, plus a few more that will be introduced later in the text.

? Exercise 7.3.1

Identify the functional groups in the following organic compounds. State whether alcohols and amines are primary, secondary, or tertiary.



Answer

a) carboxylate, sulfide, aromatic, two amide groups (one of which is cyclic)

b) tertiary alcohol, thioester

c) carboxylate, ketone

d) ether, primary amine, alkene

2: Draw one example each (there are many possible correct answers) of compounds fitting the descriptions below, using line structures. Be sure to designate the location of all non-zero formal charges. All atoms should have complete octets (phosphorus may exceed the octet rule).

a) a compound with molecular formula $C_6H_{11}NO$ that includes alkene, secondary amine, and primary alcohol functional groups

b) an ion with molecular formula $C_3H_5O_6P^{2-}$ that includes aldehyde, secondary alcohol, and phosphate functional groups.

c) A compound with molecular formula C_6H_9NO that has an amide functional group, and does *not* have an alkene group.

Functional Group Tables

Exclusively Carbon Functional Groups

Group Formula	Class Name	Specific Example	IUPAC Name	Common Name
	alkene	$H_2C{=}CH_2$	ethene	ethylene
	alkyne	$HC{\equiv}CH$	ethyne	acetylene
	arene	C_6H_6	benzene	benzene

Functional Groups with Single Bonds to Heteroatoms

Group Formula	Class Name	Specific Example	IUPAC Name	Common Name
	halide	H_3C-I	iodomethane	methyl iodide
	alcohol	CH_3CH_2OH	ethanol	ethyl alcohol
	ether	$CH_3CH_2OCH_2CH_3$	diethyl ether	ether
	amine	H_3C-NH_2	aminomethane	methylamine

Group Formula	Class Name	Specific Example	IUPAC Name	Common Name
	nitro compound	$H_3C\text{-}NO_2$	nitromethane	
	thiol	$H_3C\text{-}SH$	methanethiol	methyl mercaptan
	sulfide	$H_3C\text{-}S\text{-}CH_3$	dimethyl sulfide	

Functional Groups with Multiple Bonds to Heteroatoms

Group Formula	Class Name	Specific Example	IUPAC Name	Common Name
	nitrile	$H_3C\text{-}CN$	ethanenitrile	acetonitrile
	aldehyde	H_3CCHO	ethanal	acetaldehyde
	ketone	H_3CCOCH_3	propanone	acetone
	carboxylic acid	H_3CCO_2H	ethanoic Acid	acetic acid
	ester	$H_3CCO_2CH_2CH_3$	ethyl ethanoate	ethyl acetate
	acid halide	H_3CCOCl	ethanoyl chloride	acetyl chloride
	amide	$H_3CCON(CH_3)_2$	N,N-dimethylethanamide	N,N-dimethylacetamide
	acid Anhydride	$(H_3CCO)_2O$	ethanoic anhydride	acetic anhydride

Exercises

7.3: Functional Groups is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Steven Farmer, Dietmar Kennepohl, Layne Morsch, Krista Cunningham, Tim Soderberg, & Tim Soderberg.

- **3.1: Functional Groups** by Dietmar Kennepohl, Krista Cunningham, Layne Morsch, Steven Farmer, Tim Soderberg is licensed CC BY-SA 4.0.

7.4: Alkanes and Alkane Isomers

Objectives

After completing this section, you should be able to

1. draw the Kekulé structure, condensed structure and shorthand structure of each of the first ten straight-chain alkanes.
2. name each of the first ten straight-chain alkanes, given its molecular formula, Kekulé structure, condensed structure or shorthand structure.
3. explain the difference in structure between a straight- and a branched-chain alkane, and illustrate the difference using a suitable example.
4. explain why the number of possible isomers for a given molecular formula increases as the number of carbon atoms increases.
5. draw all the possible isomers that correspond to a given molecular formula of the type $C_n H_{2n+2}$, where *n* is ≤ 7.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- branched-chain alkane
- constitutional or structural isomer
- homologous series
- isomer
- saturated hydrocarbon
- straight-chain alkane (or normal alkane)

Study Notes

A series of compounds in which successive members differ from one another by a CH_2 unit is called a homologous series. Thus, the series CH_4, C_2H_6, C_3H_8 . . . C_nH_{2n+2}, is an example of a homologous series.

It is important that you commit to memory the names of the first 10 straight-chain alkanes (i.e., from CH_4 to $C_{10}H_{22}$). You will use these names repeatedly when you begin to learn how to derive the systematic names of a large variety of organic compounds. You need not remember the number of isomers possible for alkanes containing more than seven carbon atoms. Such information is available in reference books when it is needed. When drawing isomers, be careful not to deceive yourself into thinking that you can draw more isomers than you are supposed to be able to. Remember that it is possible to draw each isomer in several different ways and you may inadvertently count the same isomer more than once.

Alkanes are organic compounds that consist entirely of single-bonded carbon and hydrogen atoms and lack any other functional groups. Alkanes are often called saturated hydrocarbons because they have the maximum possible number of hydrogens per carbon. In Section 1.7, thealkane molecule, ethane, was shown to contain a C-C sigma bond. By adding more C-C sigma bond larger and more complexed alkanes can be formed. 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. 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.

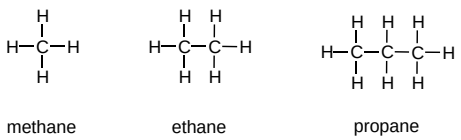


Figure 25.3.1 : The Three Simplest Alkanes

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. Consider the series in Figure 25.3.3. 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.

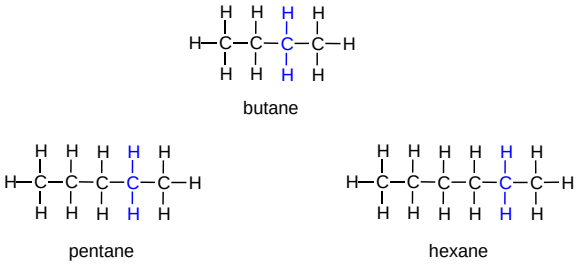


Figure 25.3.2: Members of a Homologous Series. Each succeeding formula incorporates one carbon atom and two hydrogen atoms more than the previous formula.

The homologous series 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 $C_8H_{(2\,\times\,8)\,+\,2} = C_8H_{18}$.

Molecular Formulas

Alkanes are the simplest family of hydrocarbons - compounds containing carbon and hydrogen only. Alkanes only contain carbon-hydrogen bonds and carbon-carbon single bonds. The first six alkanes are as follows:

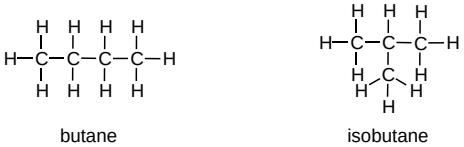
Table 7.4.1: Molecular formulas for small alkanes

methane	CH_4
ethane	C_2H_6
propane	C_3H_8
butane	C_4H_{10}
pentane	C_5H_{12}
hexane	C_6H_{14}

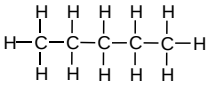
You can work out the formula of any of the alkanes using the general formula C_nH_{2n+2}

Isomerism

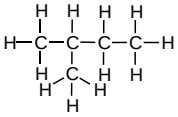
All of the alkanes containing 4 or more carbon atoms show structural isomerism, meaning that there are two or more different structural formulas that you can draw for each molecular formula. Isomers (from the Greek *isos* + *meros*, meaning "made of the same parts") are molecules that have the same molecular formula, but have a different arrangement of the atoms in space. Alkanes with 1-3 carbons, 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. However, C_4H_{10}, has more than possible structure. The four carbons can be drawn in a row to form butane or the can branch to form isobutane. The two compounds have different properties—for example, butane boils at −0.5°C, while isobutane boils at −11.7°C.



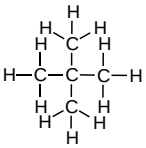
Likewise the molecular formula: C_5H_{12} has three possible isomer. The compound at the far left is pentane because it has all five carbon atoms in a continuous chain. The compound in the middle is isopentane; like isobutane, it has a one CH_3 branch off the second carbon atom of the continuous chain. 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.



pentane



isopentane



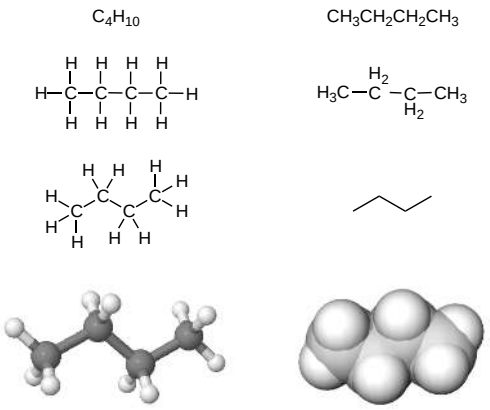
neopentane

Of the structures show above, butane and pentane are called **normal alkanes** or **straight-chain alkanes**, indicating that all contain a single continuous chain of carbon atoms and can be represented by a projection formula whose carbon atoms are in a straight line. The other structures, isobutane, isopentane, and neopentane are called called branched-chain alkanes. As the number of carbons in an akane increases the number of possible isomers also increases as shown in the table below.

Table 7.4.2: Number of isomers for hydrocarbons

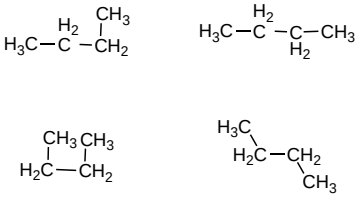
Molecular Formula	Number of Structural Isomers
CH_4	1
C_2H_6	1
C_3H_8	1
C_4H_{10}	2
C_5H_{12}	3
C_6H_{14}	5
C_7H_{16}	9
C_8H_{18}	18
C_9H_{20}	35
$C_{10}H_{22}$	75
$C_{14}H_{30}$	1858
$C_{18}H_{38}$	60,523
$C_{30}H_{62}$	4,111,846,763

Akanes can be represented in many different ways. The figure below shows some of the different ways straight-chain butane can be represented. Most often chemists refer to butane by the condensed structure $CH_3CH_2CH_2CH_3$ or *n*-C_4H_{10} where n denotes a normal straight alkane.



Note that many of these structures only imply bonding connections and do not indicate any particular geometry. The bottom two structures, referred to as "ball and stick" and "space filling" do show 3D geometry for butane. Because the four-carbon chain in butane may be bent in various ways 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 nomenclature of straight alkanes is based on the number of carbon atoms they contain. The number of carbons are indicated by a prefix and the suffix -ane is added to indicate the molecules is an alkane. The prefix for three carbons is prop so adding -ane, the IUPAC name for C_3H_8 is propane. Likewise, the prefix for six is hex so the name for the straight chain isomer of C_6H_{14} is called hexane. The first ten prefixes should be memorized, because these alkane names from the basis for naming many other organic compounds.

9.2.1

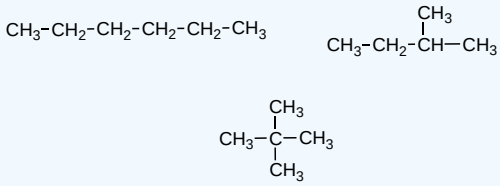
" role="presentation" style="position:relative;" tabindex="0">

Table 7.4.3: The First 10 Straight-Chain Alkanes

Molecular Formula	Prefix	Condensed Structural Formula	Name
CH_4	Meth	CH_4	methane
C_2H_6	Eth	CH_3CH_3	ethane
C_3H_8	Prop	$CH_3CH_2CH_3$	propane
C_4H_{10}	But	$CH_3CH_2CH_2CH_3$	butane
C_5H_{12}	Pent	$CH_3CH_2CH_2CH_2CH_3$	pentane
C_6H_{14}	Hex	$CH_3(CH_2)_4CH_3$	hexane
C_7H_{16}	Hept	$CH_3(CH_2)_5CH_3$	heptane
C_8H_{18}	Oct	$CH_3(CH_2)_6CH_3$	octane
C_9H_{20}	Non	$CH_3(CH_2)_7CH_3$	nonane
$C_{10}H_{22}$	Dec	$CH_3(CH_2)_8CH_3$	decane

Example 7.4.1: Chain Isomers in Pentane

Pentane, C_5H_{12}, has three chain isomers. If you think you can find any others, they are simply twisted versions of the ones below. If in doubt make some models.

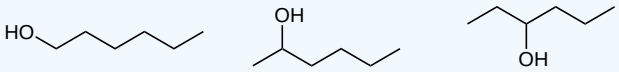


Exercises

Exercise 7.4.1

Draw all of the isomers for $C_6H_{14}O$ that contain a 6 carbon chain and an alcohol (-OH) functional group.

Answer

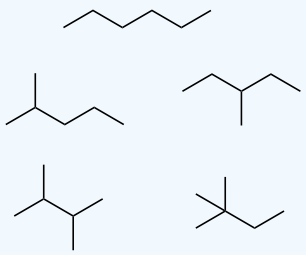


https://chem.libretexts.org/@go/page/418542

Exercise 7.4.2

Draw all possible isomers for C_6H_{14} (There are five total).

Answer



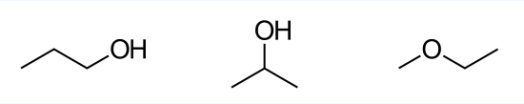
The top structure is when it is a 6 carbon chain. The middle row contains the 5 carbon chained isomers with branching at the 2nd and 3rd carbon. The bottom row contains the two 4 carbon chain isomers that can be drawn.

Exercise 7.4.3

Draw all possible isomers for C_3H_8O.

Answer

The first structure is when an alcohol comes off the first carbon. The second structure is when the alcohol is coming off the central carbon. The third structure is the only possible ether form of C_3H_8O.



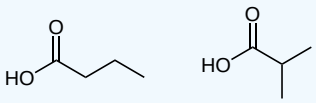
https://chem.libretexts.org/@go/page/418542

Exercise 7.4.4

Draw all possible isomers for $C_4H_8O_2$ that contain a carboxylic acid.

Answer

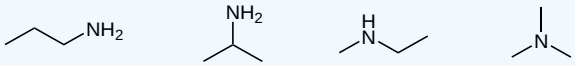
There are only 2 possibilities.



Exercise 7.4.5

Draw all possible isomers for C_3H_9N and indicate whether each amine is primary, secondary, or tertiary.

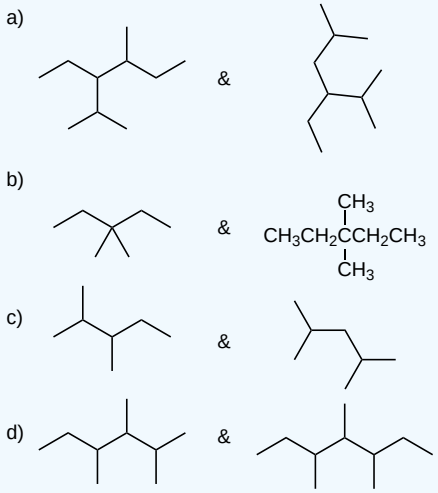
Answer



The first and second structures are primary amines. The third structure is a secondary amine. The last structure is a tertiary amine.

Exercise 7.4.6

Indicate whether each of the following sets are constitutional isomers, the same compound, or different compounds.



Answer

a) Both structures have formulas of $C_{10}H_{22}$ and have different connectivity which makes these **constitutional isomers**.

b) Both structures have formulas of C_7H_{16} and have the same connectivity which makes these the **same compound**.

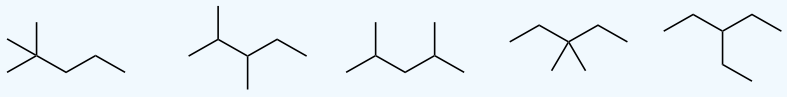
c) Both structure have formulas of C_7H_{16} and have different connectivity which makes these **constitutional isomers**.

d) The structure on the left has a formula of C_9H_{20} and the structure on the right has a formula of $C_{10}H_{22}$ so these are **different compounds**.

? Exercise 7.4.7

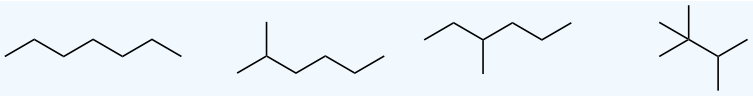
Draw the 5 constitutional isomers of C_7H_{16} (of the 9 total isomers possible) that have 5 carbons as the longest carbon chain length.

Answer



The 5 constitutional isomers with a 5 carbon chain length are shown above. Since there needs to be 7 carbons total, the 2 extra carbons are added as substituents. From left to right, the methyl group substitution pattern is 2,2, 2,3, 2,4, and 3,3, and the last one (on right) has a 3-ethyl substituent.

The other 4 possible constitutional isomers (with different length carbon chains) are shown below.



7.4: Alkanes and Alkane Isomers is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Steven Farmer, Dietmar Kennepohl, Zachary Sharrett, Layne Morsch, Krista Cunningham, Tim Soderberg, & Tim Soderberg.

- **3.2: Alkanes and Alkane Isomers** by Dietmar Kennepohl, Krista Cunningham, Layne Morsch, Steven Farmer, Tim Soderberg, Zachary Sharrett is licensed CC BY-SA 4.0.

SECTION OVERVIEW

7.5: Naming of Alkanes and Cycloalkanes

Topic hierarchy

7.5.1: Naming Alkanes

7.5.2: Naming Cycloalkanes

7.5: Naming of Alkanes and Cycloalkanes is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

7.5.1: Naming Alkanes

Objectives

After completing this section, you should be able to

1. provide the correct IUPAC name for any given alkane structure (Kekulé, condensed or shorthand).
2. draw the Kekulé, condensed or shorthand structure of an alkane, given its IUPAC name.

Key Terms

Make certain that you can define, and use in context, the key term below.

- IUPAC system

Study Notes

The IUPAC system of nomenclature aims to ensure

1. that every organic compound has a unique, unambiguous name.
2. that the IUPAC name of any compound conveys the structure of that compound to a person familiar with the system.

One way of checking whether the name you have given to an alkane is reasonable is to count the number of carbon atoms implied by the chosen name. For example, if you named a compound 3-ethyl-4-methylheptane, you have indicated that the compound contains a total of 10 carbon atoms—seven carbon atoms in the main chain, two carbon atoms in an ethyl group, and one carbon atom in a methyl group. If you were to check the given structure and find 11 carbon atoms, you would know that you had made a mistake. Perhaps the name you should have written was 3-ethyl-4,4-dimethylheptane!

When naming alkanes, a common error of beginning students is a failure to pick out the longest carbon chain. For example, the correct name for the compound shown below is 3-methylheptane, not 2-ethylhexane.

Remember that every substituent must have a number, and do not forget the prefixes: di, tri, tetra, etc.

You must use commas to separate numbers, and hyphens to separate numbers and substituents. Notice that 3-methylhexane is one word.

Hydrocarbons having no double or triple bond functional groups are classified as **alkanes** or **cycloalkanes**, depending on whether the carbon atoms of the molecule are arranged only in chains or also in rings. Although these hydrocarbons have no functional groups, they constitute the framework on which functional groups are located in other classes of compounds, and provide an ideal starting point for studying and naming organic compounds. The alkanes and cycloalkanes are also members of a larger class of compounds referred to as **aliphatic**. Simply put, aliphatic compounds are compounds that do not incorporate any aromatic rings in their molecular structure.

The following table lists the IUPAC names assigned to simple continuous-chain alkanes from C-1 to C-10. A common **"ane"** suffix identifies these compounds as alkanes. Longer chain alkanes are well known, and their names may be found in many reference and text books. The names **methane** through **decane** should be memorized, since they constitute the root of many IUPAC names. Fortunately, common numerical prefixes are used in naming chains of five or more carbon atoms.

Table 7.5.1.1 : Simple Unbranched Alkanes

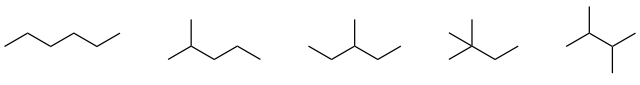
Name	Molecular Formula	Structural Formula	Isomers	Name	Molecular Formula	Structural Formula	Isomers

Name	Molecular Formula	Structural Formula	Isomers		Name	Molecular Formula	Structural Formula	Isomers
meth**ane**	CH_4	CH_4	1		hex**ane**	C_6H_{14}	$CH_3(CH_2)_4CH_3$	5
eth**ane**	C_2H_6	CH_3CH_3	1		hept**ane**	C_7H_{16}	$CH_3(CH_2)_5CH_3$	9
prop**ane**	C_3H_8	$CH_3CH_2CH_3$	1		oct**ane**	C_8H_{18}	$CH_3(CH_2)_6CH_3$	18
but**ane**	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2		non**ane**	C_9H_{20}	$CH_3(CH_2)_7CH_3$	35
pent**ane**	C_5H_{12}	$CH_3(CH_2)_3CH_3$	3		dec**ane**	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	75

Some important behavior trends and terminologies

1. The formulas and structures of these alkanes increase uniformly by a CH_2 increment.
2. A uniform variation of this kind in a series of compounds is called **homologous**.
3. These formulas all fit the $\mathbf{C_nH_{2n+2}}$ rule. This is also the highest possible H/C ratio for a stable hydrocarbon.
4. Since the H/C ratio in these compounds is at a maximum, we call them **saturated** (with hydrogen).

Beginning with butane (C_4H_{10}), and becoming more numerous with larger alkanes, we note the existence of alkane isomers. For example, there are five C_6H_{14} isomers, shown below as abbreviated line formulas (**A** through **E**):



Although these distinct compounds all have the same molecular formula, only one (**A**) can be called hexane. How then are we to name the others?

The **IUPAC** system requires first that we have names for simple unbranched chains, as noted above, and second that we have names for simple alkyl groups that may be attached to the chains. Examples of some common **alkyl groups** are given in the following table. Note that the "ane" suffix is replaced by "**yl**" in naming groups. The symbol **R** is used to designate a generic (unspecified) alkyl group.

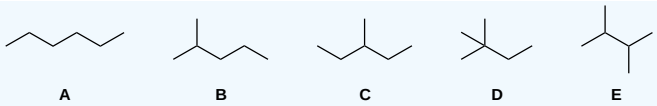
Table 7.5.1.2 : Alkyl Groups Names

Group	$CH_3–$	$C_2H_5–$	$CH_3CH_2CH_2–$	$(CH_3)_2CH–$	$CH_3CH_2CH_2CH_2–$	$(CH_3)_2CHCH_2–$	$CH_3CH_2CH(CH_3)–$	$(CH_3)_3C–$	R–
Name	Methyl	Ethyl	Propyl	Isopropyl	Butyl	Isobutyl	sec-Butyl	tert-Butyl	Alkyl

IUPAC Rules for Alkane Nomenclature

1. Find and name the longest continuous carbon chain.
2. Identify and name groups attached to this chain.
3. Number the chain consecutively, starting at the end nearest a substituent group.
4. Designate the location of each substituent group by an appropriate number and name.
5. Assemble the name, listing groups in alphabetical order.
6. The prefixes di, tri, tetra etc., used to designate several groups of the same kind, are not considered when alphabetizing

Example 7.5.1.1 : Alkanes



The IUPAC names of the isomers of hexane are: **A** hexane **B** 2-methylpentane **C** 3-methylpentane **D** 2,2-dimethylbutane **E** 2,3-dimethylbutane

Halogen Groups

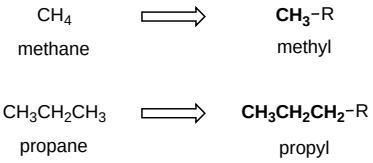
Halogen substituents are easily accommodated, using the names: fluoro (F-), chloro (Cl-), bromo (Br-) and iodo (I-).

Example 7.5.1.2 : Halogen Substitution

For example, $(CH_3)_2CHCH_2CH_2Br$ would be named 1-bromo-3-methylbutane. If the halogen is bonded to a simple alkyl group an alternative "alkyl halide" name may be used. Thus, C_2H_5Cl may be named chloroethane (no locator number is needed for a two carbon chain) or ethyl chloride.

Alkyl Groups

Alkanes can be described by the general formula C_nH_{2n+2}. An alkyl group is formed by removing one hydrogen from the alkane chain and is described by the formula C_nH_{2n+1}. The removal of this hydrogen results in a stem change from **-ane** to **-yl**. Take a look at the following examples.



The same concept can be applied to any of the straight chain alkane names provided in the table below.

Name	Molecular Formula	Condensed Structural Formula
Methane	CH_4	CH_4
Ethane	C_2H_6	CH_3CH_3
Propane	C_3H_8	$CH_3CH_2CH_3$
Butane	C_4H_{10}	$CH_3(CH_2)_2CH_3$
Pentane	C_5H_{12}	$CH_3(CH_2)_3CH_3$
Hexane	C_6H_{14}	$CH_3(CH_2)_4CH_3$
Heptane	C_7H_{16}	$CH_3(CH_2)_5CH_3$
Octane	C_8H_{18}	$CH_3(CH_2)_6CH_3$
Nonane	C_9H_{20}	$CH_3(CH_2)_7CH_3$
Decane	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$
Undecane	$C_{11}H_{24}$	$CH_3(CH_2)_9CH_3$
Dodecane	$C_{12}H_{26}$	$CH_3(CH_2)_{10}CH_3$
Tridecane	$C_{13}H_{28}$	$CH_3(CH_2)_{11}CH_3$
Tetradecane	$C_{14}H_{30}$	$CH_3(CH_2)_{12}CH_3$
Pentadecane	$C_{15}H_{32}$	$CH_3(CH_2)_{13}CH_3$
Hexadecane	$C_{16}H_{34}$	$CH_3(CH_2)_{14}CH_3$

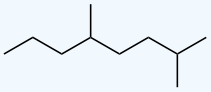
Name	Molecular Formula	Condensed Structural Formula
Heptadecane	$C_{17}H_{36}$	$CH_3(CH_2)_{15}CH_3$
Octadecane	$C_{18}H_{38}$	$CH_3(CH_2)_{16}CH_3$
Nonadecane	$C_{19}H_{40}$	$CH_3(CH_2)_{17}CH_3$
Eicosane	$C_{20}H_{42}$	$CH_3(CH_2)_{18}CH_3$

Three Rules for Naming Alkanes

1. Choose the longest, most substituted carbon chain containing a functional group.
2. A carbon bonded to a functional group must have the lowest possible carbon number. If there are no functional groups, then any substituent present must have the lowest possible number.
3. Take the alphabetical order into consideration; that is, after applying the first two rules given above, make sure that your substituents and/or functional groups are written in alphabetical order.

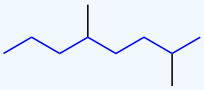
Example 7.5.1.3

What is the name of the follow molecule?

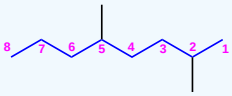


Solution

Rule #1: Choose the longest, most substituted carbon chain containing a functional group. This example does not contain any functional groups, so we only need to be concerned with choosing the longest, most substituted carbon chain. The longest carbon chain has been highlighted in blue and consists of eight carbons.



Rule #2: Carbons bonded to a functional group must have the lowest possible carbon number. If there are no functional groups, then any substitute present must have the lowest possible number. Because this example does not contain any functional groups, we only need to be concerned with the two substitutes present, that is, the two methyl groups. If we begin numbering the chain from the left, the methyls would be assigned the numbers 4 and 7, respectively. If we begin numbering the chain from the right, the methyls would be assigned the numbers 2 and 5. Therefore, to satisfy the second rule, numbering begins on the right side of the carbon chain as shown below. This gives the methyl groups the lowest possible numbering.

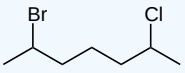


Rule 3: In this example, there is no need to utilize the third rule. Because the two substitutes are identical, neither takes alphabetical precedence with respect to numbering the carbons. This concept will become clearer in the following examples.

The name of this molecule is **2,5-dimethyloctane**

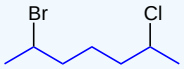
Example 7.5.1.4

What is the name of the follow molecule?



Solution

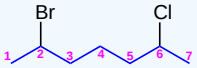
Rule #1: Choose the longest, most substituted carbon chain containing a functional group. This example contains two functional groups, bromine and chlorine. The longest carbon chain has been highlighted in blue and consists of seven carbons.



Rule #2: Carbons bonded to a functional group must have the lowest possible carbon number. If there are no functional groups, then any substituent present must have the lowest possible number. In this example, numbering the chain from either the left or the right would satisfy this rule. If we number the chain from the left, bromine and chlorine would be assigned the second and sixth carbon positions, respectively. If we number the chain from the right, chlorine would be assigned the second position and bromine would be assigned the sixth position. In other words, whether we choose to number from the left or right, the functional groups occupy the second and sixth positions in the chain. To select the correct numbering scheme, we need to utilize the third rule.



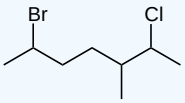
Rule #3: After applying the first two rules, take the alphabetical order into consideration. Alphabetically, bromine comes before chlorine. Therefore, bromine is assigned the second carbon position, and chlorine is assigned the sixth carbon position.



The name of this molecule is: **2-bromo-6-chloroheptane**

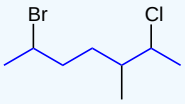
Example 7.5.1.5

What is the name of the follow molecule?

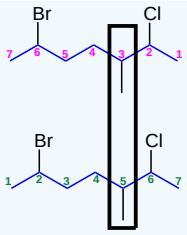


Solution

Rule #1: Choose the longest, most substituted carbon chain containing a functional group. This example contains two functional groups, bromine and chlorine, and one substitute, the methyl group. The longest carbon chain has been highlighted in blue and consists of seven carbons.



Rule #2: Carbons bonded to a functional group must have the lowest possible carbon number. After taking functional groups into consideration, any substitutes present must have the lowest possible carbon number. This particular example illustrates the **point of difference principle**. If we number the chain from the left, bromine, the methyl group and chlorine would occupy the second, fifth and sixth positions, respectively. This concept is illustrated in the second drawing below. If we number the chain from the right, chlorine, the methyl group and bromine would occupy the second, third and sixth positions, respectively, which is illustrated in the first drawing below. The position of the methyl, therefore, becomes a **point of difference**. In the first drawing, the methyl occupies the third position. In the second drawing, the methyl occupies the fifth position. To satisfy the second rule, we want to choose the numbering scheme that provides the lowest possible numbering of this substitute. Therefore, the first of the two carbon chains shown below is correct.



Therefore, the first numbering scheme is the appropriate one to use.



Once you have determined the correct numbering of the carbons, it is often useful to make a list, including the functional groups, substitutes, and the name of the parent chain.

Rule #3: After applying the first two rules, take the alphabetical order into consideration. Alphabetically, bromine comes before chlorine. Therefore, bromine is assigned the second carbon position, and chlorine is assigned the sixth carbon position.

Parent chain: heptane Substitutents: 2-chloro 3-methyl 6-bromo

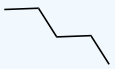
The name of this molecule is: **6-bromo-2-chloro-3-methylheptane**

Exercises

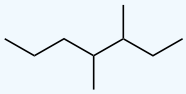
Exercise 7.5.1.1

Give the proper IUPAC names of the following compounds.

a)



b)



c)

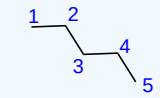


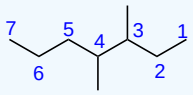
Answer

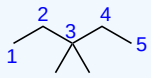
a) Since this structure is an unbranched alkane (all single bonds) with a 5 carbon chain length, its name would be **pentane**.

b) This alkane has a 7 carbon longest continuous chain length that we number from right to left to get the first methyl substituent we encounter to have the lowest possible number (3 versus being 4 if numbering from left to right). This causes it to have 2 methyl substituents at positions 3 & 4 so we would name it indicating those numbers and the prefix dimethyl which gives a proper IUPAC name of **3,4-dimethylheptane**.

c) This alkane has a 5 carbon longest continuous chain length (which could be numbered from left to right or right to left due to the symmetry at C-3). It has two methyl substituents off of C-3 so the proper IUPAC name is **3,3-dimethylpentane.**

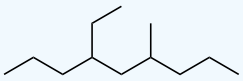
a) 

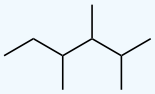
b) 

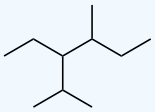
c) 

Exercise 7.5.1.2

Give the proper IUPAC names of the following compounds.

a) 

b) 

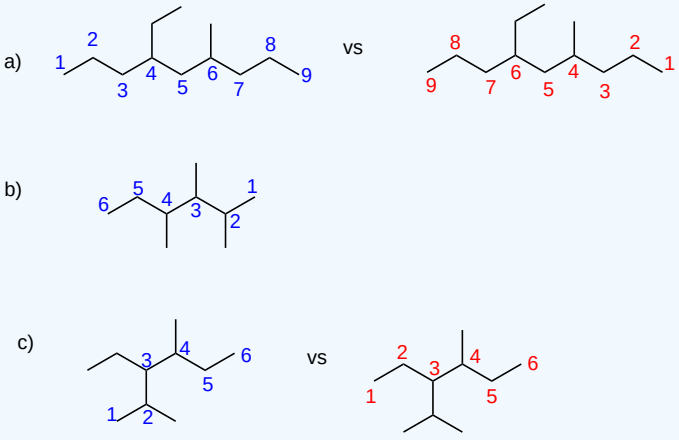
c) 

Answer

a) This alkane has a 9 carbon longest continuous chain length that we number from left to right (structure on left numbered in blue) to make the ethyl substituent be number 4. For the structure on the right (numbered in red) going from right to left, the methyl substituent is number 4. Since ethyl is higher in the alphabetical order, you want to make it have the lower number so the structure on the left (blue numbering) takes priority and the name is **4-ethyl-6-methylnonane**.

b) This alkane has a 6 carbon longest continuous chain length that we number from right to left to make the first methyl be C-2 (versus the opposite direction which would make the first methyl C-3). Since there are 3 methyl substituents at positions 2,3, & 4, this compound would have the name **2,3,4-trimethylhexane**.

c) This 6 carbon alkane can be numbered along different chains (see below) as well as in the opposite directions. This shows the two different chains that can be drawn (making the first substituent in that chain the lowest number). The structure on the left (numbered in blue) is the correct choice since it causes more substituents to be on the longest continuous chain (3 vs 2 in the structure on the right). This would make the IUPAC name of the structure **3-ethyl-2,4-dimethylhexane**. (Notice how ethyl takes priority over methyl and the di- is not considered for alphabetizing.)



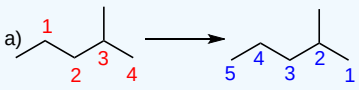
Exercise 7.5.1.3

All of the following names represent a compound that has been named improperly. Draw out the structure from the name and give the proper IUPAC name for the compounds.

a. 1,3-dimethylbutane
b. 4-ethylpentane
c. 2-ethyl-3-methylpentane

Answer

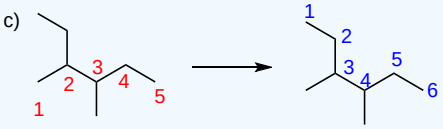
a) The structure that can be drawn for the improper name is shown below on the left. When you renumber it properly (structure on the right), the correct name should be **2-methylpentane**.



b) The structure that can be drawn for the improper name is shown below on the left. When you renumber it properly (structure on the right), notice that the longest chain is 6 C's and we start the numbering on the end to the right to make the methyl substituent come off at C-3 (instead of beong at C-4 if we numbered it the opposite direction) the correct name should be **3-methyl hexane**.



c) The structure that can be drawn for the improper name is shown below on the left. When you renumber it properly (structure on the right), notice that the longest chain is 6 C's and since this molecule is symmetrical (between carbon 3 & 4), you can start the numbers from either end. In this case, we have methyl substituents coming off of carbons 3 & 4 so the proper name is **3,4-dimethyl hexane**.



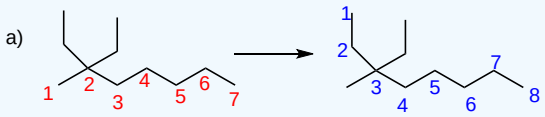
Exercise 7.5.1.4

All of the following names represent a compound that has been named improperly. Draw out the structure from the name and give the proper IUPAC name for the compounds.

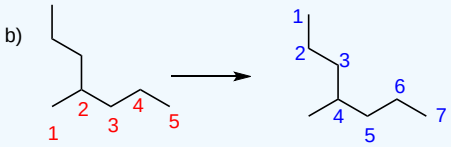
a. 2,2-diethylheptane
b. 2-propylpentane
c. 4,4-diethylbutane

Answer

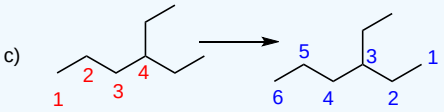
a) The structure that can be drawn for the improper name is shown below on the left. When you renumber it properly (structure on the right), notice that the longest chain is now 8 C's and you have an ethyl substituent at C-3 and a methyl substituent also at C-3 so the proper name is **3- ethyl-3-methyloctane**.



b) The structure that can be drawn for the improper name is shown below on the left. When you renumber it properly (structure on the right), notice that the longest chain is now 7 C's and since this molecule is symmetrical (at carbon 4), you can start the numbers from either end. There is a methyl substituent at C-4 so the proper name is **4-methylheptane**.



c) The structure that can be drawn for the improper name is shown below on the left. When you renumber it properly (structure on the right) going from right to left (to make the ethyl substituent have the lowest number possible), the correct name is **3-ethylhexane**



7.5.1: Naming Alkanes is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Steven Farmer, Dietmar Kennepohl, Zachary Sharrett, Krista Cunningham, Tim Soderberg, & Tim Soderberg.

- **3.4: Naming Alkanes** by Dietmar Kennepohl, Krista Cunningham, Steven Farmer, Tim Soderberg, Zachary Sharrett is licensed CC BY-SA 4.0.

7.5.2: Naming Cycloalkanes

Objectives

After completing this section, you should be able to

1. name a substituted or unsubstituted cycloalkane, given its Kekulé structure, shorthand structure or condensed structure.
2. draw the Kekulé, shorthand or condensed structure for a substituted or unsubstituted cycloalkane, given its IUPAC name.

Key Terms

Make certain that you can define, and use in context, the key terms below.

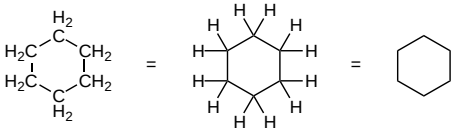
- cycloalkane

Study Notes

Provided that you have mastered the IUPAC system for naming alkanes, you should find that the nomenclature of cycloalkanes does not present any particular difficulties.

Many organic compounds found in nature contain rings of carbon atoms. These compounds are known as **cycloalkanes**. Cycloalkanes only contain carbon-hydrogen bonds and carbon-carbon single bonds. The simplest examples of this class consist of a single, un-substituted carbon ring, and these form a homologous series similar to the unbranched alkanes.

Like alkanes, cycloalkane molecules are often drawn as skeletal structures in which each intersection between two lines is assumed to have a carbon atom with its corresponding number of hydrogens. Cyclohexane, one of the most common cycloalkanes is shown below as an example.



Cyclic hydrocarbons have the prefix "cyclo-". The IUPAC names, molecular formulas, and skeleton structures of the cycloalkanes with 3 to 10 carbons are given in Table 4.1.1. Note that the general formula for a cycloalkane composed of **n** carbons is $\mathbf{C_nH_{2n}}$, and not $\mathbf{C_nH_{2n+2}}$ as for alkanes. Although a cycloalkane has two fewer hydrogens than the equivalent alkane, each carbon is bonded to four other atoms so are still considered to be **saturated** with hydrogen.

Table 7.5.2.1: Examples of Simple Cycloalkanes

Cycloalkane	Molecular Formula	Skeleton Structure
Cyclopropane	C_3H_6	
Cyclobutane	C_4H_8	
Cyclopentane	C_5H_{10}	
Cyclohexane	C_6H_{12}	
Cycloheptane	C_7H_{14}	
Cyclooctane	C_8H_{16}	
Cyclononane	C_9H_{18}	

Cycloalkane	Molecular Formula	Skeleton Structure
Cyclodecane	$C_{10}H_{20}$	

IUPAC Rules for Nomenclature

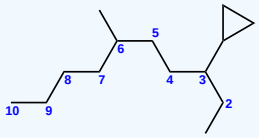
The naming of substituted cycloalkanes follows the same basic steps used in naming alkanes.

1. Determine the parent chain.
2. Number the substituents of the ring beginning at one substituent so that the nearest substituent is numbered the lowest possible. If there are multiple choices that are still the same, go to the next substituent and give it the lowest number possible.
3. Name the substituents and place them in alphabetical order.

More specific rules for naming substituted cycloalkanes with examples are given below.

1. Determine the cycloalkane to use as the parent. If there is an alkyl straight chain that has a greater number of carbons than the cycloalkane, then the alkyl chain must be used as the primary parent chain. Cycloalkanes substituents have an ending "-yl". If there are two cycloalkanes in the molecule, use the cycloalkane with the higher number of carbons as the parent.

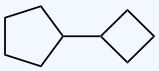
Example 7.5.2.1



The longest straight chain contains 10 carbons, compared with cyclopropane, which only contains 3 carbons. The parent chain in this molecule is decane and cyclopropane is a substituent. The name of this molecule is 3-cyclopropyl-6-methyldecane.

Example 7.5.2.2

Name the cycloalkane structure.

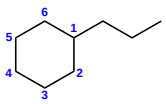


Solution

There are two different cycloalkanes in this molecule. Because it contains more carbons, the cyclopentane ring will be named as the parent chain. The smaller ring, cyclobutane, is named as a substituent on the parent chain. The name of this molecule is cyclobutylcyclopentane.

2) When there is only one substituent on the ring, the ring carbon attached to the substituent is automatically carbon #1. Indicating the number of the carbon with the substituent in the name is optional.

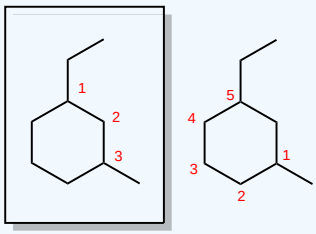
Example 7.5.2.3

	
1-chlorocyclobutane or cholorocyclobutane	1-propylcyclohexane or propylcyclohexane

3) If there are multiple substituents on the ring, number the carbons of the cycloalkane so that the carbons with substituents have the lowest possible number. A carbon with multiple substituents should have a lower number than a carbon with only one substituent or functional group. One way to make sure that the lowest number possible is assigned is to number the carbons so that when the numbers corresponding to the substituents are added, their sum is the lowest possible.

4) When naming the cycloalkane, the substituents must be placed in alphabetical order. Remember the prefixes di-, tri-, etc. , are not used for alphabetization.

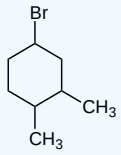
Example 7.5.2.4



In this example, the ethyl or the methyl subsistent could be attached to carbon one. The ethyl group attachment is assigned carbon 1 because ethyl comes before methyl alphabetically. After assigning carbon 1 the cyclohexane ring can be numbered going clockwise or counterclockwise. When looking at the numbers produced going clockwise produces lower first substituent numbers (1,3) than when numbered counterclockwise (1,5). So the correct name is 1-ethyl-3-methylcyclohexane.

Example 7.5.2.5

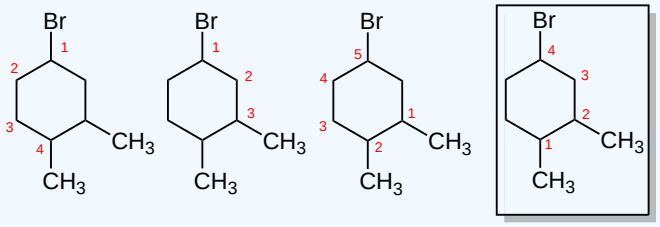
Name the following structure using IUPAC rules.



Solution

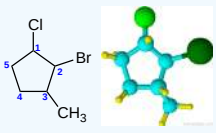
Remember when dealing with cycloalkanes with more than two substituents, finding the lowest possible 2nd substituent numbering takes precedence. Consider a numbering system with each substituent attachment point as being carbon one. Compare them and whichever produces the lowest first point of difference will be correct.

The first structure would have 1,4 for the relationship between the first two groups. The next structure would have 1,3. The final 2 structures both have 1,2 so those are preferable to the first two. Now we have to determine which is better between the final 2 structures. The 3rd substituent on structure 3 would be at the 5 position leading to 1,2,5 while in the final structure the 3rd methyl group is on carbon 4 leading to 1,2,4. This follows the rules of giving the lowest numbers at the first point of difference.



The correct name for the molecule is 4-Bromo-1,2-dimethylcyclohexane.

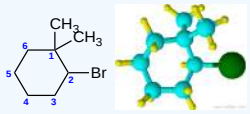
Example 7.5.2.6



2-bromo-1-chloro-3-methylcyclopentane

Notice that "b" of bromo alphabetically precedes the "m" of methyl. Also, notice that the chlorine attachment point is assigned carbon 1 because it comes first alphabetically and the overall sum of numbers would be the same if the methyl attachment carbon was assigned as 1 and the chlorine attachment as 3.

Example 7.5.2.7



(2-bromo-1,1-dimethylcyclohexane)

Although "di" alphabetically precedes "f", "di" is not used in determining the alphabetical order.

Example 7.5.2.8



2-fluoro-1,1,-dimethylcyclohexane **NOT** 1,1-dimethyl-2-fluorocyclohexane

also

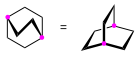
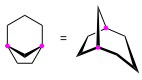
2-fluoro-1,1,-dimethylcyclohexane **NOT** 1-fluoro-2,2-dimethylcyclohexane (as that would give a larger number to the first point of difference)

Although "di" alphabetically precedes "f", "di" is not used in determining the alphabetical order of the substituents. Notice that the attachment point of the two methyl groups is assigned carbon 1 despite the fact that fluorine comes first alphabetically. This is because this assignment allows for a lower overall numbering of substituents, so assigning alphabetical priority is not necessary.

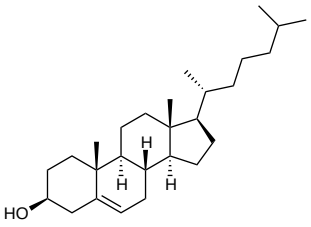
Polycyclic Compounds

Hydrocarbons having more than one ring are common, and are referred to as **bicyclic** (two rings), **tricyclic** (three rings) and in general, **polycyclic compounds**. The molecular formulas of such compounds have H/C ratios that decrease with the number of rings. In general, for a hydrocarbon composed of n carbon atoms associated with m rings the formula is: $\mathrm{CnH_{2\,n+2\,-2\,m}}$. The structural relationship of rings in a polycyclic compound can vary. They may be separate and independent, or they may share one or two common atoms. Some examples of these possible arrangements are shown in the following table.

Table 7.5.2.2: Examples of Isomeric $\mathrm{C_8H_{14}}$ Bicycloalkanes

Isolated Rings	Spiro Rings	Fused Rings	Bridged Rings
No common atoms	One common atom	One common bond	Two common atoms
			
			

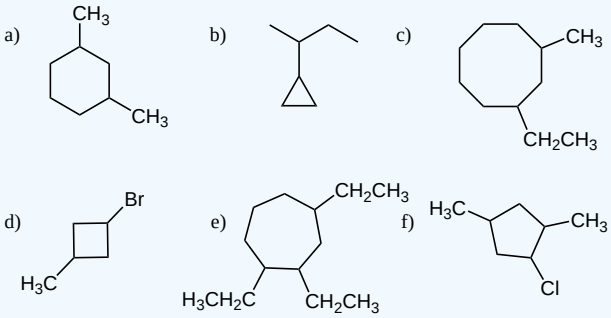
Polycyclic compounds, like cholesterol shown below, are biologically important and typically have common names accepted by IUPAC. However, the common names do not generally follow the basic IUPAC nomenclature rules, and will not be covered here.



Cholesterol (polycyclic)

Exercise 7.5.2.1

Give the IUPAC names for the following cycloalkane structures.



Answer

a) 1,3-Dimethylcyclohexane

b) 2-Cyclopropylbutane

c) 1-Ethyl-3-methylcyclooctane

d) 1-Bromo-3-methylcyclobutane

e) 1,2,4-Triethylcycloheptane

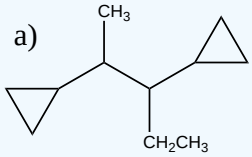
f) 1-Chloro-2,4-dimethylcyclopentane

Exercise 7.5.2.2

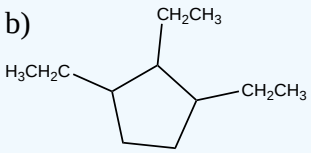
Draw the structures for the IUPAC names below.

a. 2,3-dicyclopropylpentane
b. 1,2,3-triethylcyclopentane
c. 3-cyclobutyl-2-methylhexane
d. 2-bromo-1-chloro-4-methylcyclohexane
e. 1-bromo-5-propylcyclodecane

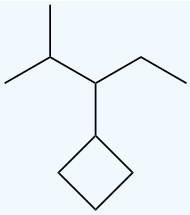
Answer

a) 

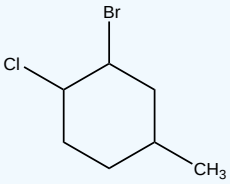
2,3-dicyclopropylpentane

b) 

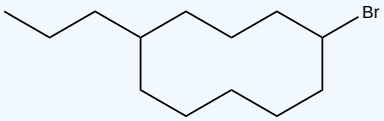
1,2,3-triethylcyclopentane

c) 

3-cyclobutyl-2-methylhexane

d) 

2-bromo-1-chloro-4-methylcyclohexane

e) 

1-bromo-5-propylcyclodecane

7.5.2: Naming Cycloalkanes is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Jim Clark, Steven Farmer, Dietmar Kennepohl, Zachary Sharrett, Layne Morsch, Krista Cunningham, Tim Soderberg, Pwint Zin, Kelly Matthews, & Kelly Matthews.

- **4.1: Naming Cycloalkanes** by Dietmar Kennepohl, Jim Clark, Kelly Matthews, Krista Cunningham, Layne Morsch, Pwint Zin, Steven Farmer, Tim Soderberg, Zachary Sharrett is licensed CC BY-SA 4.0.

7.6: Study Guide

7: Organic Chemistry I - Bonding and Structure

Key Topics for TRU students taking CHEM1500

- structure of hydrocarbons
- functional groups
- structural isomers
- nomenclature
- physical properties
- intermolecular forces in organic molecules
- acidity and basicity
- pKa and substituent effect on pKa
- Lewis acids and bases
- conjugation
- partial p-orbital overlap
- resonance stabilization of ions

Key Learning Outcomes (Examples)

- identify functional groups from the molecular structures of organic molecules including some common pharmaceuticals and bio-chemical substances
- name simple organic compounds from their molecular structures and draw molecular structures from names of simple organic compounds
- draw and name isomers for simple organic compounds
- identify the acid or base properties of organic compounds

7.6: Study Guide is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

8: Organic Chemistry II - Stereochemistry

8.1: Types of Isomers
8.2: Chiral Molecules
8.3: Optical Activity
8.4: Absolute Configuration- R-S Sequence Rules
8.5: Stereochemistry of the Alkenes
8.5.1: Cis-Trans Isomerism in Alkenes
8.5.2: Sequence Rules - The E,Z Designation
8.6: Study Guide

8: Organic Chemistry II - Stereochemistry is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

8.1: Types of Isomers

Objective

After completing this section, you should be able to explain the differences among constitutional (structural) isomers and stereoisomers (geometric isomers).

Key Terms

Make certain that you can define, and use in context, the key terms below.

- constitutional
- (structural) isomers
- stereoisomers

The following flow chart can be used to identify the relationship of two compounds with respect to isomerization:

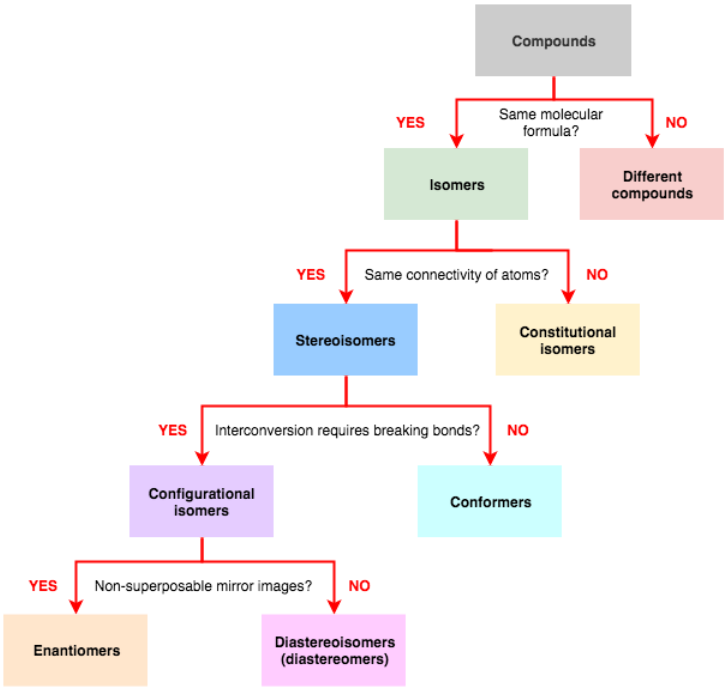
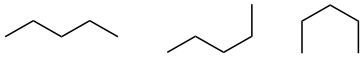


Figure 8.1.1: Different types of isomers. When using the flow chart, it is really important to remember that each decision on the flow chart is related to comparing two molecules, ie. it doesn't make sense to ask "what is compound A", but it does make sense to ask "how are compounds A and B related"? A molecule may be the enantiomer of another molecule, but a diastereomer of another. (CC-BY-SA 4.0; Mark Coster via StackExchange)

Conformational Isomers

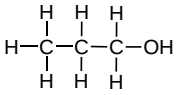
The C–C single bonds in ethane, propane, and other alkanes are formed by the overlap of an sp^3 hybrid orbital on one carbon atom with an sp^3 hybrid orbital on another carbon atom, forming a σ bond. Each sp^3 hybrid orbital is cylindrically symmetrical (all cross-sections are circles), resulting in a carbon–carbon single bond that is also cylindrically symmetrical about the C–C axis. Because rotation about the carbon–carbon single bond can occur without changing the overlap of the sp^3 hybrid orbitals, there is no significant electronic energy barrier to rotation. Consequently, many different arrangements of the atoms are possible, each corresponding to different degrees of rotation. Differences in three-dimensional structure resulting from rotation about a σ bond are called differences in conformation, and each different arrangement is called a conformational isomer (or conformer).



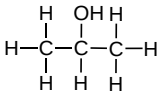
Conformational Isomers of Pentane

Structural Isomers

Unlike conformational isomers, which do not differ in connectivity, structural isomers differ in connectivity, as illustrated here for 1-propanol and 2-propanol. Although these two alcohols have the same molecular formula (C_3H_8O), the position of the –OH group differs, which leads to differences in their physical and chemical properties.

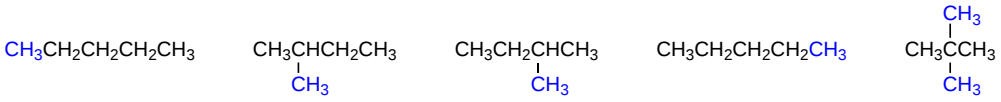


1-propanol (*n*-propanol)



2-propanol (isopropanol)

In the conversion of one structural isomer to another, at least one bond must be broken and reformed at a different position in the molecule. Consider, for example, the following five structures represented by the formula C_5H_{12}:



(a) (b) (c) (d) (e)

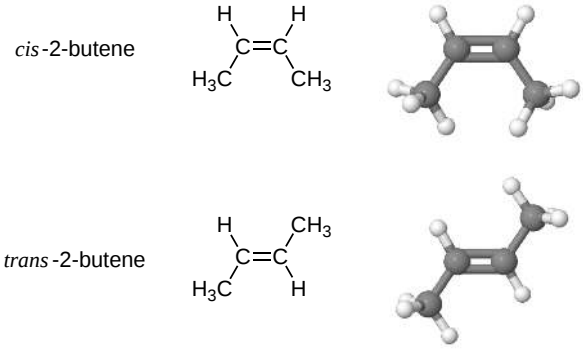
Of these structures, (a) and (d) represent the same compound, as do (b) and (c). No bonds have been broken and reformed; the molecules are simply rotated about a 180° vertical axis. Only three—n-pentane (a) and (d), 2-methylbutane (b) and (c), and 2,2-dimethylpropane (e)—are structural isomers. Because no bonds are broken in going from (a) to (d) or from (b) to (c), these alternative representations are not structural isomers. The three structural isomers—either (a) or (d), either (b) or (c), and (e)—have distinct physical and chemical properties.

Stereoisomers

Stereoisomers have the same connectivity in their atoms but a different arrangement in three-dimensional space. There are different classifications of stereoisomers depending on how the arrangements differ from one another. Notice that in the structural isomers, there was some difference in the connection of atoms. For example, 1-butene has a double bond followed by two single bonds while 2-butene has a single bond, then a double bond, then a single bond. A stereoisomer will have the same connectivity among all atoms in the molecule.

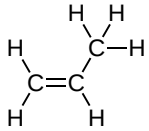
Geometric Isomers

With a molecule such as 2-butene, a different type of isomerism called geometric isomerism can be observed. **Geometric isomers** are isomers in which the order of atom bonding is the same but the arrangement of atoms in space is different. The double bond in an alkene is not free to rotate because of the nature of the bond. Therefore, there are two different ways to construct the 2-butene molecule (see figure below). The image below shows the two geometric isomers, called *cis*-2-butene and *trans*-2-butene.



Geometric Isomers of 2-Butene

The *cis* isomer has the two single hydrogen atoms on the same side of the molecule, while the *trans* isomer has them on opposite sides of the molecule. In both molecules, the bonding order of the atoms is the same. In order for geometric isomers to exist, there must be a rigid structure in the molecule to prevent free rotation around a bond. This occurs with a double bond or a ring. In addition, the two carbon atoms must each have two different groups attached in order for there to be geometric isomers. Propene (see figure below) has no geometric isomers because one of the carbon atoms (the one on the far left) involved in the double bond has two single hydrogens bonded to it.

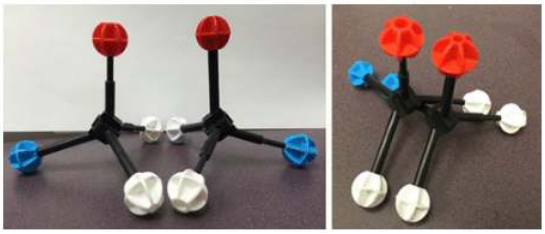


Physical and chemical properties of geometric isomers are generally different. As with alkenes, alkynes display structural isomerism beginning with 1-butyne and 2-butyne. However, there are no geometric isomers with alkynes because there is only one other group bonded to the carbon atoms that are involved in the triple bond.

Optical Isomers

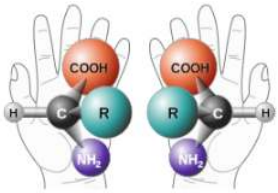
Stereoisomers that are not geometric isomers are known as optical isomers. Optical isomers differ in the placement of substituted groups around one or more atoms of the molecule. They were given their name because of their interactions with plane-polarized light. Optical isomers are labeled enantiomers or diastereomers.

Enantiomers are non-superimposable mirror images. A common example of a pair of enantiomers is your hands. Your hands are mirror images of one another but no matter how you turn, twist, or rotate your hands, they are not superimposable.



Two models that are mirror images and superimposable.

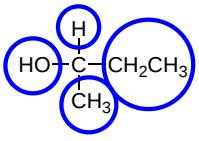
Since they are superimposable, they are the same molecule and are not isomers.



Your hands and some molecules are mirror images but are not superimposable.

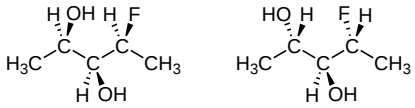
These pairs of molecules are called enantiomers.

Objects that have non-superimposable mirror images are called **chiral**. When examining a molecule, carbon atoms with four unique groups attached are considered chiral. Look at the figure below to see an example of a chiral molecule. Note that we have to look beyond the first atom attached to the central carbon atom. The four circles indicate the four unique groups attached to the central carbon atom, which is chiral.



A chiral carbon has four unique groups attached to it

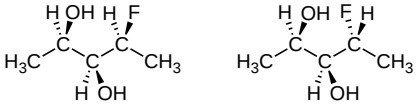
Another type of optical isomer are **diastereomers**, which are non-mirror image optical isomers. Diastereomers have a different arrangement around one or more atoms while some of the atoms have the same arrangement. As shown in the figure below, note that the orientation of groups on the first and third carbons are different but the second one remains the same so they are not the same molecule. The solid wedge indicates a group coming out of the page/screen towards you and the dashed line indicates that a group is going away from you "behind" the page/screen.



Diastereomers differ at one or more atom. These molecules are not mirror images and they are not superimposable.

They are optical isomers because they have the same connectivity between atoms but a different arrangement of substituent groups.

Epimers are a sub-group of diastereomers that differ at only one location. All epimers are diastereomers but not all diastereomers are epimers.



Epimers have a different arrangement around one atom, while arrangements around the other atoms are the same

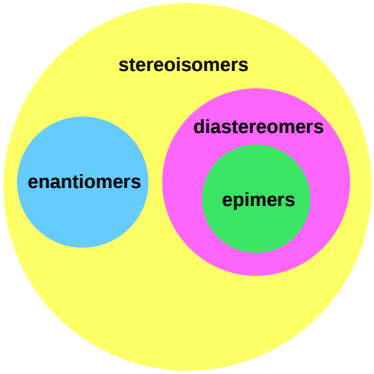
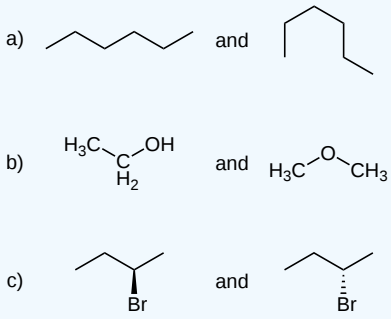


Diagram showing the division of stereoisomers (also known as optical isomers)

Exercise 8.1.1

What kind of isomers are the following pairs?



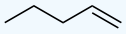
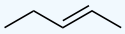
Answer

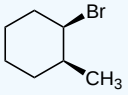
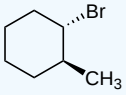
a. Since both structures have the same formula (C_6H_{12}) and they have the same connectivity, but are in a different arrangement of the atoms in space, they are conformational isomers.
b. Since both structures have the same formula (C_2H_6O) but different connectivity, they are structural isomers.

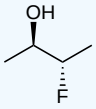
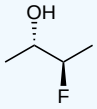
c. Since both structures have the same formula (C_3H_9Br) and the same connectivity but the structure on the left has *R* stereochemistry and the structure on the right has *S* stereochemistry, they are stereoisomers called enantiomers.

Exercise 8.1.2

What kind of isomers are the following pairs?

a)  and 

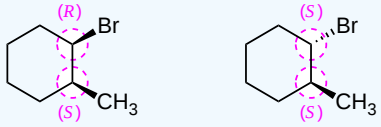
b)  and 

c)  and 

Answer

a) Since both structures have the same formula (C_2H_6O) but different connectivity of where the double bond is, they are structural isomers.

b) Both structures have the same formula and the same connectivity but the structure on the left has (*R*,*S*) stereochemistry and the structure on the right has (S,S) stereochemistry, they are stereoisomers that are diastereomers.

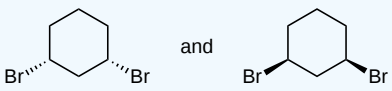


c) Both structures and have the same connectivity but their stereochemistry differs so they are stereoisomers. Since the one on the left is (R,S) and the one on the right is (S,R), they are non-super imposable mirror images of each other and enantiomers.



Exercise 8.1.3

What is the relationship between the following pairs?

a) 

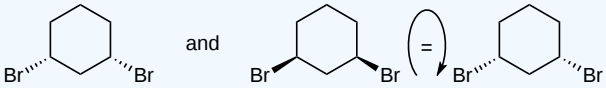
b) 

c) (*R*) – 2 chlorohexane & 1-chlorohexane

d) (2*R*, 3*R*) dichlorohexane & (2*S*, 3*R*) dichlorohexane

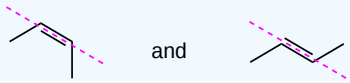
Answer

a) Both structures have the same connectivity and same chemical formula and when you rotate the structure on the right you can see that these are the same compound both with (R,S) stereochemistry.



b)) Since both structures have the same formula (C_4H_8) and the same connectivity they are stereoisomers since they differ in what is known as cis/trans isomerism (covered more in Ch 7).Due to the pi bond between carbons 2 & 3, there is not free

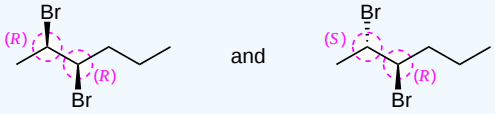
rotation between the C2-C3 bond so the structure on the left has the carbon chains on the same side of the double bond (cis) and the structure on the right has the carbon chains on opposite sides of the double bond (trans).



c) Looking at the structures below, you can see that they have the same formula ($C_6H_{13}Cl$) and different connectivity, so they are structural isomers.



d) Looking at the structures below, you can see that they have the same formula ($C_6H_{12}Br_2$) and the same connectivity, but the structure on the left is (*R*,*R*) and the structure on the right is (*S*,*R*) so since they differ by only one stereocenter, they are stereoisomers that are diastereomers (& epimers in this case).



8.1: Types of Isomers is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Steven Farmer, Dietmar Kennepohl, Zachary Sharrett, William Reusch, & William Reusch.

- **5.9: A Review of Isomerism** by Dietmar Kennepohl, Steven Farmer, William Reusch, Zachary Sharrett is licensed CC BY-SA 4.0.

8.2: Chiral Molecules

Objectives

After completing this section, you should be able to

1. use molecular models to show that only a tetrahedral carbon atom satisfactorily accounts for the lack of isomerism in molecules of the type CH_2XY, and for the existence of optical isomerism in molecules of the type CHXYZ.
2. determine whether two differently oriented wedge-and-broken-line structures are identical or represent a pair of enantiomers.

Key Terms

Make certain that you can define, and use in context, the key term below.

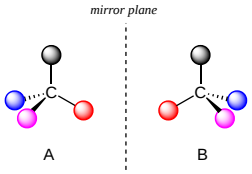
- enantiomer

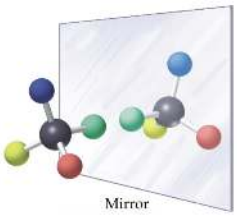
Study Notes

Stereoisomers are isomers that differ in spatial arrangement of atoms, rather than order of atomic connectivity. One of the most interesting types of isomer is the mirror-image stereoisomer, a non-superimposable set of two molecules that are mirror images of one another. The existence of these molecules are determined by a a concept known as **chirality**. The word “chiral” was derived from the Greek word for hand, because our hands are a good example of chirality since they are non-superimposable mirror images of each other.

Chiral Molecules

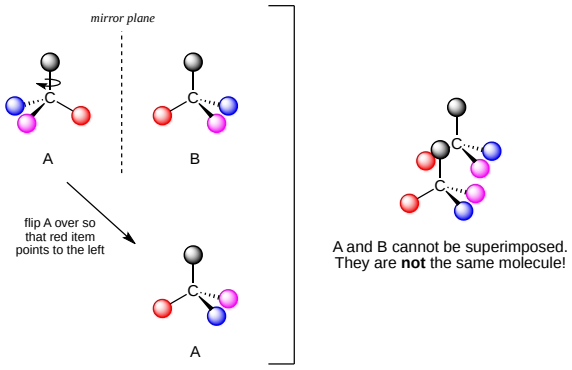
The term **chiral**, from the Greek work for 'hand', refers to anything which cannot be superimposed on its own mirror image. Certain organic molecules are chiral meaning that they are not superimposable on their mirror image. Chiral molecules contain one or more **chiral centers**, which are almost always tetrahedral (sp^3-hybridized) carbons with four different substituents. Consider the molecule A below: a tetrahedral carbon, with four different substituents denoted by balls of four different colors.





The mirror image of A, which we will call B, is drawn on the right side of the figure, and an imaginary mirror is in the middle. Notice that every point on A lines up through the mirror with the same point on B: in other words, if A looked in the mirror, it would see B looking back.

Now, if we flip compound A over and try to superimpose it point for point on compound B, we find that we cannot do it: if we superimpose any two colored balls, then the other two are misaligned.



A is not superimposable on its mirror image (B), thus by definition A is a chiral molecule. It follows that B also is not superimposable on *its* mirror image (A), and thus it is also a chiral molecule.

A and B are called **stereoisomers or optical isomers**: molecules with the same molecular formula and the same bonding arrangement, but *a different arrangement of atoms in space*. **Enantiomers** are pairs of stereoisomers which are mirror images of each other: thus, A and B are enantiomers. It should be self-evident that a chiral molecule will always have one (and *only* one) enantiomer: enantiomers come in pairs. Enantiomers have identical physical properties (melting point, boiling point, density, and so on). However, enantiomers do differ in how they interact with polarized light (we will learn more about this soon) and they may also interact in very different ways with other chiral molecules - proteins, for example. We will begin to explore this last idea in later in this chapter, and see many examples throughout the remainder of our study of biological organic chemistry.

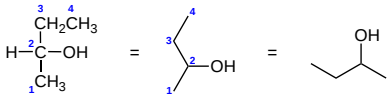
The Many Synonyms of the Chiral Carbon

Be aware - all of the following terms can be used to describe a chiral carbon.

chiral carbon = asymmetric carbon = optically active carbon = stereo carbon = stereo center = chiral center

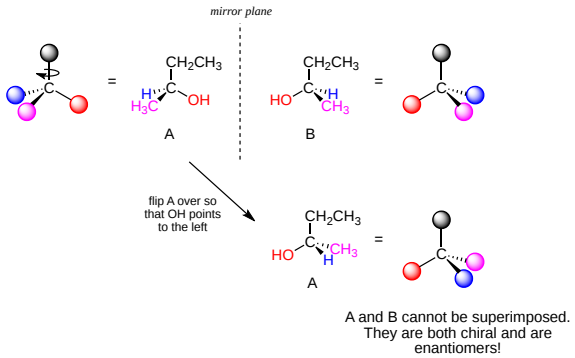
Let's apply our chirality discussion to real molecules.

Consider 2-butanol, drawn in two dimensions below.



2-butanol
(drawn in 2D)

Carbon #2 is a chiral center: it is sp^3-hybridized and tetrahedral (even though it is not drawn that way above), and the four substituents attached to is are different: a hydrogen (H) , a methyl ($-CH_3$) group, an ethyl ($-CH_2CH_3$) group, and a hydroxyl (OH) group. If the bonding at C_2 of 2-butanol is drawn in three dimensions and this structure called A. Then the mirror image of A can be drawn to form structure B.



When we try to superimpose A onto B, we find that we cannot do it. Because structure A and B are not superimposable on their mirror image they are both chiral molecules. Because A and B are different due only to the arrangement of atoms in space they are stereoisomers. Because A and B are mirror images of each other they are also enantiomers. When looking at simplified line structures is clear that there are two distinct ways of drawing 2-butanol which only differ in their spatial arrangement around a chiral carbon.

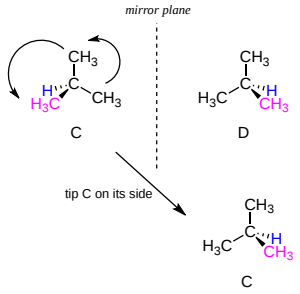
The 3D Structures of the Two Enantiomers of 2-Butanol



two enantiomers of 2-butanol

For comparison, 2-propanol, is an achiral molecule because is lacks a chiral carbon. Carbon #2 is bonded to two identical substituents (methyl groups), and so it is not a chiral carbon. Being achiral means that 2-propanol should be superimposable on its mirror image which is shown in the figure below. A more detailed explaination on why 2-propanol is achiral will be given in the next section.

2-propanol is achiral:



C and D can be superimposed.
They are the same molecule!

Stereoisomers

Stereoisomers have been defined as molecules with the same connectivity but different arrangements of the atoms in space. It is important to note that there are two types of stereoisomers: geometric and optical.

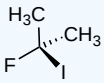
Optical isomers are molecules whose structures are mirror images but cannot be superimposed on one another in any orientation. Optical isomers have identical physical properties, although their chemical properties may differ in asymmetric environments. Molecules that are nonsuperimposable mirror images of each other are said to be chiral. Optical activity will be discussed in more detail in **Section 8.3**.

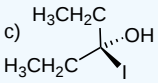
Geometric isomers differ in the relative position(s) of substituents in a rigid molecule. Simple rotation about a C–C σ bond in an alkene, for example, cannot occur because of the presence of the π bond. The substituents are therefore rigidly locked into a particular spatial arrangement. Thus a carbon–carbon multiple bond, or in some cases a ring, prevents one geometric isomer from being readily converted to the other. The members of an isomeric pair are identified as either cis or trans, and interconversion between the two forms requires breaking and reforming one or more bonds. Because their structural difference causes them to have different physical and chemical properties, cis and trans isomers are actually two distinct chemical compounds.mers have the same connectivity, but different arrangements of atoms in space. Geometric isomers will be discussed in more detain in **Sections 8.5**.

Exercise 8.2.1

Identify the following molecules as chiral or achiral.

a) 

b) 

c) 

d) 

e) 

f) 

Answer

a) chiral (4 different groups off C)

b) achiral (2 identical -CH_3 substituents off central C)

c) achiral (2 identical -CH_2CH_3 substituents off central C)

d) achiral (2 identical CH_3 substituents off carbon 2)

e) chiral (4 different groups off carbon 2)

f) achiral (2 identical CH_3 substituents off central C)

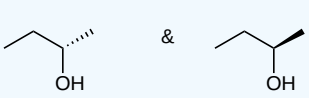
Exercise 8.2.2

Determine if the following sets of compounds in each group are enantiomers or the same compound.

a) 

b) 

c) 

d) 

Answer

a) enantiomers – non superimposable mirror images

b) same compound – when you rotate the molecule on the right it is identical to the one on the left

c) enantiomers – non superimposable mirror images

d) enantiomers – non superimposable mirror images

Objectives

After completing this section, you should be able to

1. determine whether or not a compound is chiral, given its Kelulé, condensed or shorthand structure, with or without the aid of molecular models.
2. label the chiral centres (carbon atoms) in a given Kelulé, condensed or shorthand structure.

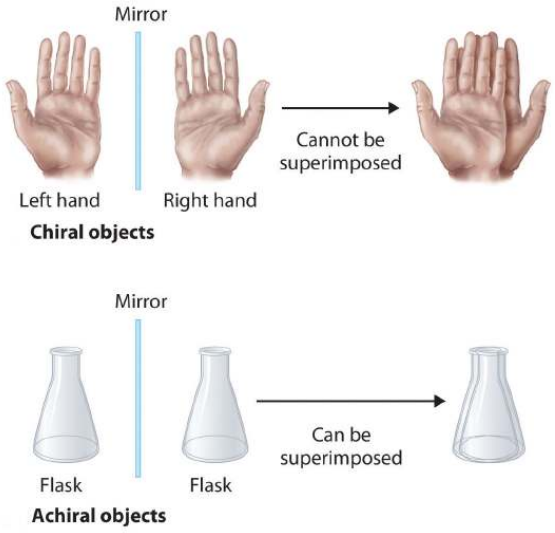
Key Terms

Make certain that you can define, and use in context, the key terms below.

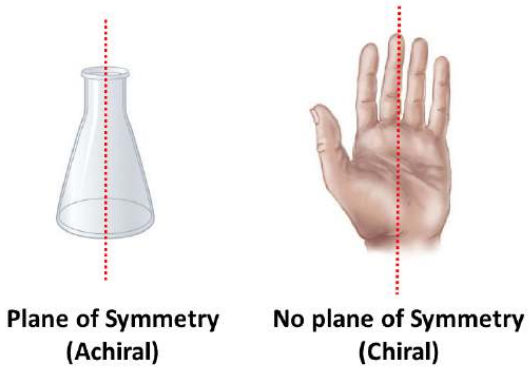
- achiral
- chiral
- chiral (stereogenic) centre
- plane of symmetry

Symmetry and Chirality

Molecules that are nonsuperimposable mirror images of each other are said to be chiral (pronounced “ky-ral,” from the Greek cheir, meaning “hand”). Examples of some familiar chiral objects are your hands. Your left and right hands are nonsuperimposable mirror images. (Try putting your right shoe on your left foot—it just doesn’t work.) An achiral object is one that can be superimposed on its mirror image, as shown by the superimposed flasks 25.7.1b in the figure below. .

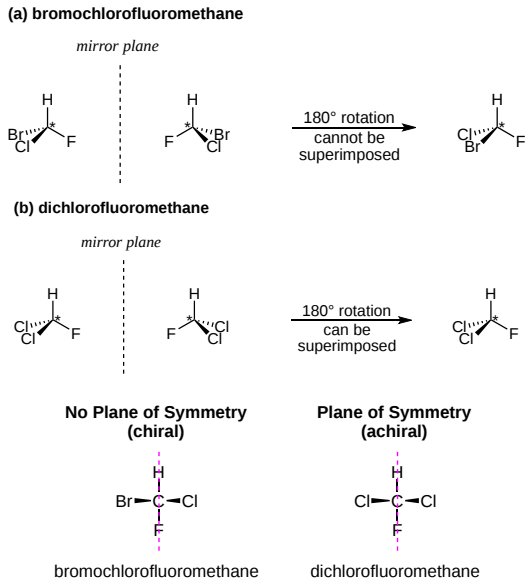


An an important questions is why is one chiral and the other not? The answer is that the flask has a plane of symmetry and your hand does not. A plane of symmetry is a plane or a line through an object which divides the object into two halves that are mirror images of each other. When looking at the flask, a line can be drawn down the middle which separates it into two mirror image halves. However, a similar line down the middle of a hand separates it into two non-mirror image halves. This idea can be used to predict chirality. If an object or molecule has a plane of symmetry it is achiral. If if lacks a plane of symmetry it is chiral.



Symmetry can be used to explain why a carbon bonded to four different substituents is chiral. When a carbon is bonded to fewer than four different substituents it will have a plane of symmetry making it achiral. A carbon atom that is bonded to four different substituents loses all symmetry, and is often referred to as an asymmetric carbon. The lack of a plane of symmetry makes the carbon chiral. The presence of a single chiral carbon atom sufficient to render the molecule chiral, and modern terminology refers to such groupings as chiral centers or stereo centers.

An example is shown in the bromochlorofluoromethane molecule shown in part (a) of the figure below. This carbon, is attached to four different substituents making it chiral. which is often designated by an asterisk in structural drawings. If the bromine atom is replaced by another chlorine to make dichlorofluoromethane, as shown in part (b) below, the molecule and its mirror image can now be superimposed by simple rotation. Thus the carbon is no longer a chiral center. Upon comparison, bromochlorofluoromethane lacks a plane of symmetry while dichlorofluoromethane has a plane of symmetry.

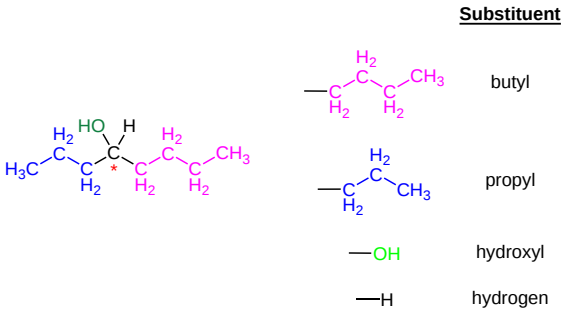


Identifying Chiral carbons

Identifying chiral carbons in a molecule is an important skill for organic chemists. The presence of a chiral carbon presents the possibility of a molecule having multiple stereoisomers. Most of the chiral centers we shall discuss in this chapter are asymmetric carbon atoms, but it should be recognized that other tetrahedral or pyramidal atoms may become chiral centers if appropriately substituted. Also, when more than one chiral center is present in a molecular structure, care must be taken to analyze their relationship before concluding that a specific molecular configuration is chiral or achiral. This aspect of stereoisomerism will be treated later. Because an carbon requires four different substituents to become asymmertric, it can be said, with few exceptions, that sp^2 and sp hybridized carbons involved in multiple bonds are achiral. Also, any carbon with more than one hydrogen, such as a -CH_3 or -CH_2- group, are also achiral.

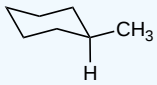
Looking for planes of symmetry in a molecule is useful, but often difficult in practice. It is difficult to illustrate on the two dimensional page, but you will see if you build models of these achiral molecules that, in each case, there is at least one **plane of symmetry**, where one side of the plane is the mirror image of the other. In most cases, the easiest way to decide whether a molecule is chiral or achiral is to look for one or more stereocenters - with a few rare exceptions, the general rule is that molecules with at least one stereocenter are chiral, and molecules with no stereocenters are achiral.

Determining if a carbon is bonded to four distinctly different substituents can often be difficult to ascertain. Remember even the slightest difference makes a substituent unique. Often these difference can be distant from the chiral carbon itself. Careful consideration and often the building of molecular models may be required. A good example is shown below. It may appear that the molecule is achiral, however, when looking at the groups directly attached to the possible chiral carbon, it is clear that they all different. The two alkyl groups are differ by a single -CH_2- group which is enough to consider them different.



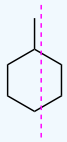
Example 8.2.1

Predict if the following molecule would be chiral or achiral:



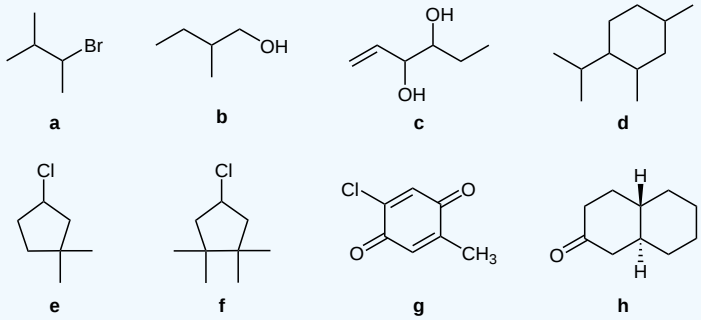
Answer

Achiral. When determining the chirality of a molecule, it best to start by locating any chiral carbons. An obvious candidate is the ring carbon attached to the methyl substituent. The question then becomes: does the ring as two different substituents making the substituted ring carbon chiral? With an uncertainty such as this, it is then helpful try to identify any planes of symmetry in the molecule. This molecule does have a plane of symmetry making the molecule achiral. The plane of symmetry would be easier see if the molecule were view from above. Typically, monosubstituted cycloalkanes have a similar plane of symmetry making them all achiral.

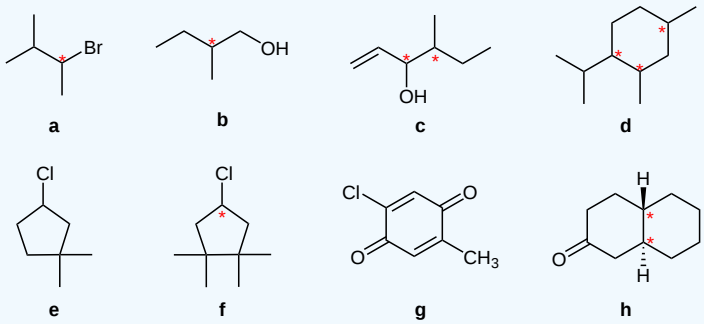


Exercise 8.2.3

Determine if each of the following molecules are chiral or achiral. For chiral molecules indicate any chiral carbons.



Answer

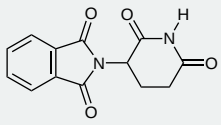


Explanation

Structures F and G are achiral. The former has a plane of symmetry passing through the chlorine atom and bisecting the opposite carbon-carbon bond. The similar structure of compound E does not have such a symmetry plane, and the carbon bonded to the chlorine is a chiral center (the two ring segments connecting this carbon are not identical). Structure G is essentially flat. All the carbons except that of the methyl group are sp^2 hybridized, and therefore trigonal-planar in configuration. Compounds C, D & H have more than one chiral center, and are also chiral.

Note

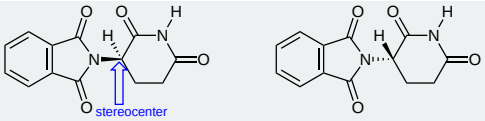
In the 1960's, a drug called thalidomide was widely prescribed in the Western Europe to alleviate morning sickness in pregnant women.



thalidomide

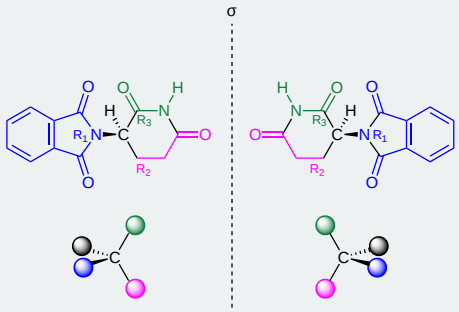
Thalidomide had previously been used in other countries as an antidepressant, and was believed to be safe and effective for both purposes. The drug was not approved for use in the U.S.A. It was not long, however, before doctors realized that something had gone horribly wrong: many babies born to women who had taken thalidomide during pregnancy suffered from severe birth defects.

Researchers later realized the problem lay in the fact that thalidomide was being provided as a mixture of two different isomeric forms.



effective isomer mutagenic isomer

One of the isomers is an effective medication, the other caused the side effects. Both isomeric forms have the same molecular formula and the same atom-to-atom connectivity, so they are not constitutional isomers. Where they differ is in the arrangement in three-dimensional space about one tetrahedral, sp^3-hybridized carbon. These two forms of thalidomide are **stereoisomers**. If you make models of the two stereoisomers of thalidomide, you will see that they too are mirror images, and cannot be superimposed.

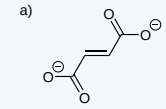


As a historical note, thalidomide was never approved for use in the United States. This was thanks in large part to the efforts of Dr. Frances Kelsey, a Food and Drug officer who, at peril to her career, blocked its approval due to her concerns about the lack of adequate safety studies, particularly with regard to the drug's ability to enter the bloodstream of a developing fetus. Unfortunately, though, at that time clinical trials for new drugs involved widespread and unregulated distribution to doctors and their patients across the country, so families in the U.S. were not spared from the damage caused.

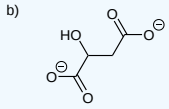
Very recently a close derivative of thalidomide has become legal to prescribe again in the United States, with strict safety measures enforced, for the treatment of a form of blood cancer called multiple myeloma. In Brazil, thalidomide is used in the treatment of leprosy - but despite safety measures, children are still being born with thalidomide-related defects.

Example 5.2.2

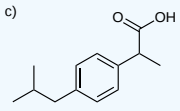
Label the molecules below as chiral or achiral, and locate all stereocenters.



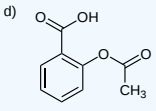
fumarate
(a citric acid cycle intermediate)



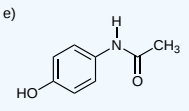
malate
(a citric acid cycle intermediate)



ibuprofen



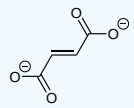
acetylsalicylic acid
(aspirin)



acetaminophen
(active ingredient in Tylenol)

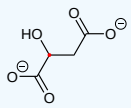
Answer

a)



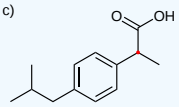
fumarate
(achiral)

b)



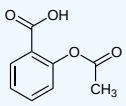
malate
(chiral)

c)



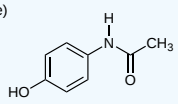
ibuprofen
(chiral)

d)



acetylsalicylic acid
(achiral)

e)

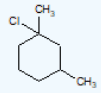


acetaminophen
(achiral)

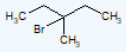
Exercise 8.2.4

1) For the following compounds, star (*) each chiral center, if any.

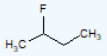
(a)



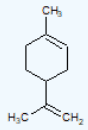
(b)



(c)



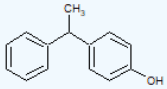
(d)



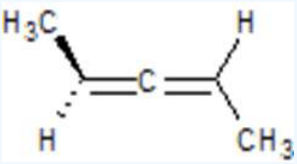
(e)



(f)



2) Explain why the following compound is chiral.



3) Determine which of the following objects is chiral.

a) A Glove.

b) A nail.

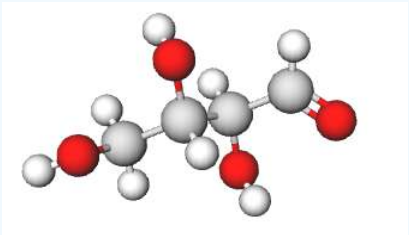
c) A pair of sunglasses.

d) The written word "Chiral".

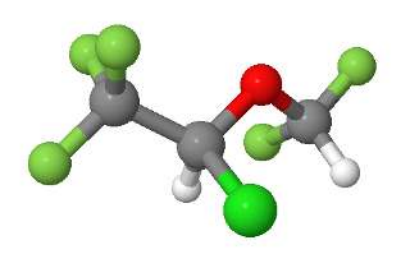
4) Place an "*" by all of the chrial carbons in the following molecules.

a)

Erythrose, a four carbon sugar.

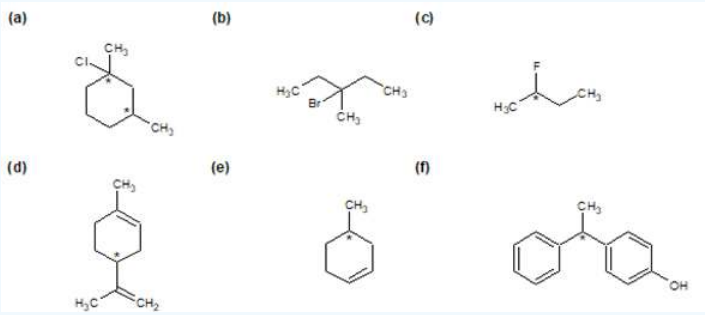


b) Isoflurane, an anestetic. Bright green = Chlorine, Pale green = Fluorine.



Answer

1)



2) Though the molecule does not contain a chiral carbon, it is chiral as it is non-superimposable on its mirror image due to its twisted nature (the twist comes from the structure of the double bonds needing to be at 90° angles to each other, preventing the molecule from being planar).

3)

a) Just as hands are chiral a glove must also be chiral.

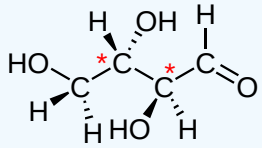
b) A nail has a plane of symmetry which goes down the middle making it a achiral.

c) A pair of sunglasses has a plane of symmetry which goes through the nose making it achiral.

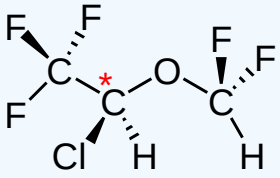
d) Most written words are chiral. Look one in a mirror to confirm this.

4

a)

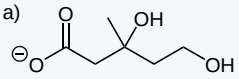


b)

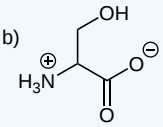


Exercise 8.2.5

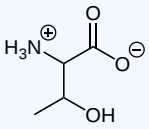
Circle all of the carbon stereocenters in the molecules below.

a) 

mevalonate

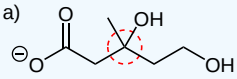
b) 

serine

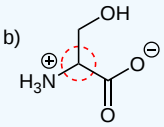
c) 

threonine

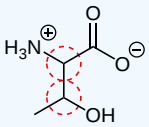
Answer

a) 

mevalonate

b) 

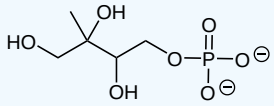
serine

c) 

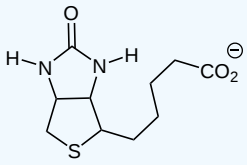
threonine

Exercise 8.2.6

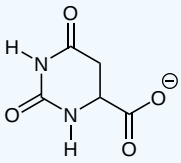
Circle all of the carbon stereocenters in the molecules below.

a) 

2-methylerythritol-4-phopshate

b) 

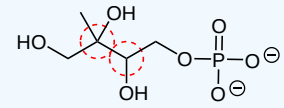
biotin

c) 

dihydroorotate

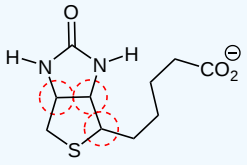
Answer

a)



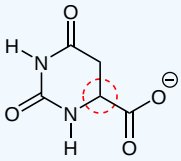
2-methylerythritol-4-phopshate

b)



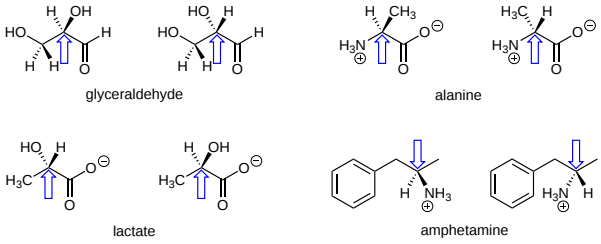
biotin

c)



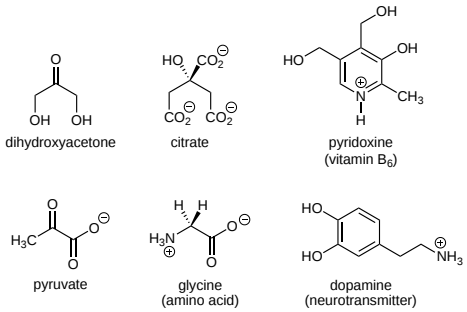
dihydroorotate

Here are some more examples of chiral molecules that exist as pairs of enantiomers. In each of these examples, there is a single stereocenter, indicated with an arrow. (Many molecules have more than one stereocenter, but we will get to that that a little later!)



glyceraldehyde alanine lactate amphetamine

Here are some examples of molecules that are **achiral** (*not* chiral). Notice that none of these molecules has a stereocenter.



dihydroxyacetone citrate pyridoxine (vitamin B_6) pyruvate glycine (amino acid) dopamine (neurotransmitter)

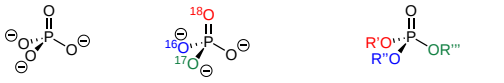
It is difficult to illustrate on the two dimensional page, but you will see if you build models of these achiral molecules that, in each case, there is at least one **plane of symmetry**, where one side of the plane is the mirror image of the other. Chirality is tied conceptually to the idea of asymmetry, and *any molecule that has a plane of symmetry cannot be chiral*. When looking for a plane of symmetry, however, we must consider all possible conformations that a molecule could adopt. Even a very simple molecule like ethane, for example, is asymmetric in many of its countless potential conformations – but it has obvious symmetry in both the eclipsed and staggered conformations, and for this reason it is achiral.

Looking for planes of symmetry in a molecule is useful, but often difficult in practice. In most cases, the easiest way to decide whether a molecule is chiral or achiral is to look for one or more stereocenters - with a few rare exceptions (see section 3.7B), the

general rule is that molecules with at least one stereocenter are chiral, and molecules with no stereocenters are achiral. Carbon stereocenters are also referred to quite frequently as **chiral carbons**.

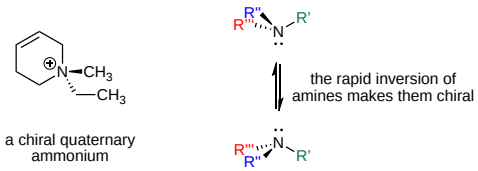
When evaluating a molecule for chirality, it is important to recognize that the question of whether or not the dashed/solid wedge drawing convention is used is irrelevant. Chiral molecules are sometimes drawn without using wedges (although obviously this means that stereochemical information is being omitted). Conversely, wedges may be used on carbons that are not stereocenters – look, for example, at the drawings of glycine and citrate in the figure above. Just because you see dashed and solid wedges in a structure, do not automatically assume that you are looking at a stereocenter.

Other elements in addition to carbon can be stereocenters. The phosphorus center of phosphate ion and organic phosphate esters, for example, is tetrahedral, and thus is potentially a stereocenter.



We will see in chapter 10 how researchers, in order to investigate the stereochemistry of reactions at the phosphate center, incorporated sulfur and/or ^{17}O and ^{18}O isotopes of oxygen (the 'normal' isotope is ^{16}O) to create chiral phosphate groups. Phosphate triesters are chiral if the three substituent groups are different.

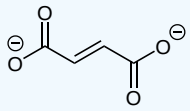
Asymmetric quaternary ammonium groups are also chiral. Amines, however, are not chiral, because they rapidly invert, or turn 'inside out', at room temperature.



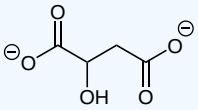
Exercise 8.2.7

Label the molecules below as chiral or achiral, and circle all stereocenters.

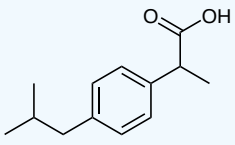
a) fumarate (a citric acid cycle intermediate)



b) malate (a citric acid cycle intermediate)

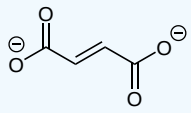


b) malate (a citric acid cycle intermediate)

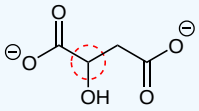


Answer

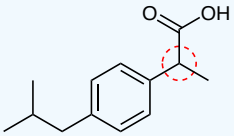
a) achiral (no stereocenters)



b) chiral



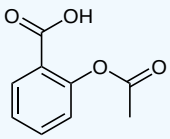
c) chiral



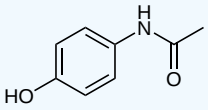
Exercise 8.2.8

Label the molecules below as chiral or achiral, and circle all stereocenters.

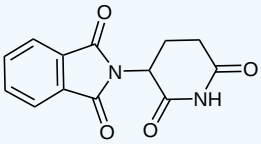
a) acetylsalicylic acid (aspirin)



b) acetaminophen (active ingredient in Tylenol)

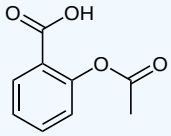


c) thalidomide (drug that caused birth defects in pregnant mothers in the 1960's)

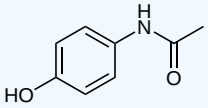


Answer

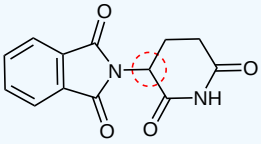
a) achiral (no stereocenters)



b) achiral (no stereocenters)

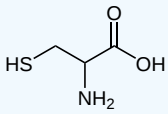


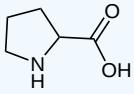
c) chiral



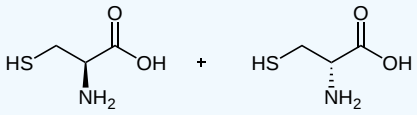
Exercise 8.2.9

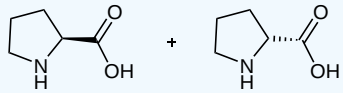
Draw both enantiomers of the following chiral amino acids.

a) Cysteine 

b) Proline 

Answer

a) 

b) 

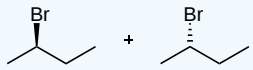
Exercise 8.2.10

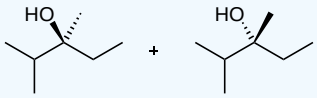
Draw both enantiomers of the following compounds from the given names.

a) 2-bromobutane

b) 2,3-dimethyl-3-pentanol

Answer

a) 

b) 

Exercise 8.2.11

Which of the following body parts are chiral?

a) Hands b) Eyes c) Feet d) Ears

Answer

a) Hands- chiral since the mirror images cannot be superimposed (think of the example in the beginning of the section)

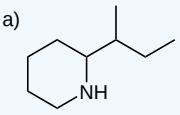
b) Eyes- achiral since mirror images that are superimposable

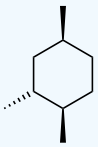
c) Feet- chiral since the mirror images cannot be superimposed (Does your right foot fit in your left shoe?)

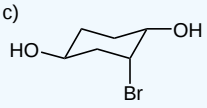
d) Ears- chiral since the mirror images cannot be superimposed

Exercise 8.2.12

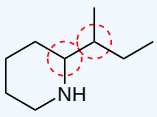
Circle the chiral centers in the following compounds.

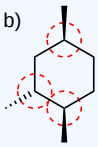
a) 

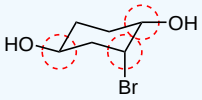
b) 

c) 

Answer

a) 

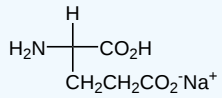
b) 

c) 

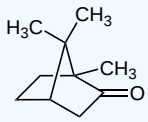
Exercise 8.2.13

Identify the chiral centers in the following compounds.

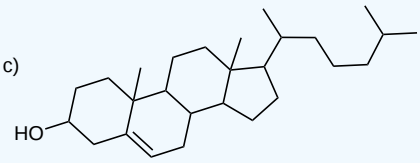
a)



b)

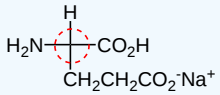


c)

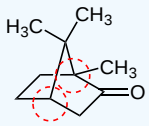


Answer

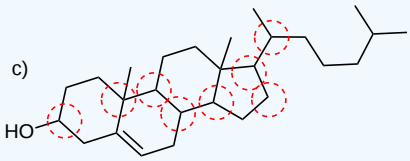
a)



b)



c)



8.2: Chiral Molecules is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **5.1: Enantiomers and the Tetrahedral Carbon** by Dietmar Kennepohl, Jim Clark, Krista Cunningham, Steven Farmer, Tim Soderberg, William Reusch, Zachary Sharrett is licensed CC BY-SA 4.0.
- **3.4: Chirality and stereoisomers** by Tim Soderberg is licensed CC BY-NC-SA 4.0. Original source: https://digitalcommons.morris.umn.edu/chem_facpubs/1/.
- **24.7: Chirality in Organic Chemistry** is licensed CC BY-NC-SA 3.0.
- **5.2: The Reason for Handedness in Molecules - Chirality** by Dietmar Kennepohl, Jim Clark, Krista Cunningham, Layne Morsch, Steven Farmer, Tim Soderberg, William Reusch, Zachary Sharrett is licensed CC BY-SA 4.0.
- **3.5: Naming chiral centers- the R and S system** by Tim Soderberg is licensed CC BY-NC-SA 4.0. Original source: https://digitalcommons.morris.umn.edu/chem_facpubs/1/.

8.3: Optical Activity

Objectives

After completing this section, you should be able to

1. describe the nature of plane-polarized light.
2. describe the features and operation of a simple polarimeter.
3. calculate the specific rotation of a compound, given the relevant experimental data.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- analyzer
- dextrorotatory
- levorotatory
- optically active
- plane-polarized light
- polarimeter
- polarizer
- specific rotation, $[\alpha]_D^{20}$

Study Notes

A *polarizer* is a device through which only light waves oscillating in a single plane may pass. A *polarimeter* is an instrument used to determine the angle through which plane-polarized light has been rotated by a given sample. You will have the opportunity to use a polarimeter in the laboratory component of the course. An *analyzer* is the component of a polarimeter that allows the angle of rotation of plane-polarized light to be determined.

Specific rotations are normally measured at 20°C, and this property may be indicated by the symbol $[\alpha]_D^{20}$. Sometimes the solvent is specified in parentheses behind the specific rotation value, for example,

$$[\alpha]_D^{20} = +12^o \text{ (chloroform)}$$

For liquids, the specific rotation may be obtained using the neat liquid rather than a solution; in such cases the formula is

$$[\alpha]_D^{\text{temp}} \text{ (neat)} = \alpha \times l \times d$$

where α is the observed rotation, l is the path length of the cell (measured in decimetres, dm), and d is the density of the liquid.

Identifying and distinguishing enantiomers is inherently difficult, since their physical and chemical properties are largely identical. Fortunately, a nearly two hundred year old discovery by the French physicist Jean-Baptiste Biot has made this task much easier. This discovery disclosed that the right- and left-handed enantiomers of a chiral compound perturb plane-polarized light in opposite ways. This perturbation is unique to chiral molecules, and has been termed **optical activity**.

Polarimetry

Plane-polarized light is created by passing ordinary light through a polarizing device, which may be as simple as a lens taken from polarizing sun-glasses. Such devices transmit selectively only that component of a light beam having electrical and magnetic field vectors oscillating in a single plane. The plane of polarization can be determined by an instrument called a **polarimeter** (Figure 8.3.1).

Monochromatic (single wavelength) light, is polarized by a fixed polarizer next to the light source. A sample cell holder is located in line with the light beam, followed by a movable polarizer (the analyzer) and an eyepiece through which the light intensity can be observed. In modern instruments an electronic light detector takes the place of the human eye. In the absence of a sample, the light

intensity at the detector is at a maximum when the second (movable) polarizer is set parallel to the first polarizer (α = 0º). If the analyzer is turned 90º to the plane of initial polarization, all the light will be blocked from reaching the detector.

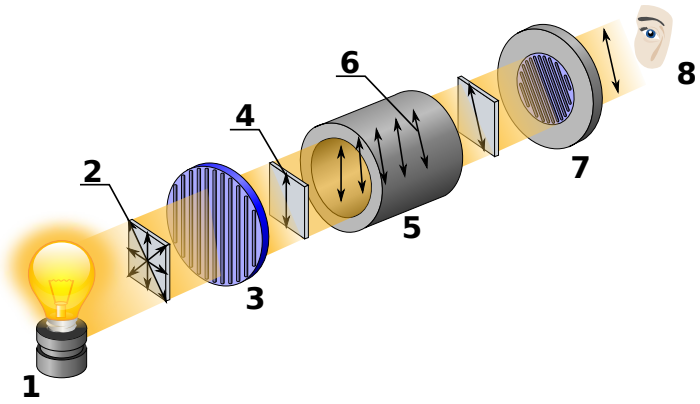


Figure 8.3.1: Operating principle of an optical polarimeter. 1. Light source 2. Unpolarized light 3. Linear polarizer 4. Linearly polarized light 5. Sample tube containing molecules under study 6. Optical rotation due to molecules 7. Rotatable linear analyzer 8. Detector. (CC BY-SA 3.0 Unported; Kaidor via Wikipedia)

Chemists use polarimeters to investigate the influence of compounds (in the sample cell) on plane polarized light. Samples composed only of achiral molecules (e.g. water or hexane), have no effect on the polarized light beam. However, if a single enantiomer is examined (all sample molecules being right-handed, or all being left-handed), the plane of polarization is rotated in either a clockwise (positive) or counter-clockwise (negative) direction, and the analyzer must be turned an appropriate matching angle, **α**, if full light intensity is to reach the detector. In the above illustration, the sample has rotated the polarization plane clockwise by +90º, and the analyzer has been turned this amount to permit maximum light transmission.

The observed rotations (α) of enantiomers are opposite in direction. One enantiomer will rotate polarized light in a clockwise direction, termed **dextrorotatory** or (+), and its mirror-image partner in a counter-clockwise manner, termed **levorotatory** or (–). The prefixes dextro and levo come from the Latin *dexter*, meaning right, and *laevus*, for left, and are abbreviated *d* and *l* respectively. If equal quantities of each enantiomer are examined , using the same sample cell, then the magnitude of the rotations will be the same, with one being positive and the other negative. To be absolutely certain whether an observed rotation is positive or negative it is often necessary to make a second measurement using a different amount or concentration of the sample. In the above illustration, for example, α might be –90º or +270º rather than +90º. If the sample concentration is reduced by 10%, then the positive rotation would change to +81º (or +243º) while the negative rotation would change to –81º, and the correct α would be identified unambiguously.

Since it is not always possible to obtain or use samples of exactly the same size, the observed rotation is usually corrected to compensate for variations in sample quantity and cell length. Thus it is common practice to convert the observed rotation, α, to a **specific rotation**, by the following formula:

$$[\alpha]_D = \frac{\alpha}{lc} \tag{5.3.1}$$

where

- $[\alpha]_D$ is the specific rotation
- l is the cell length in dm
- c is the concentration in g/ml
- D designates that the light used is the 589 line from a sodium lamp

Compounds that rotate the plane of polarized light are termed **optically active**. Each enantiomer of a stereoisomeric pair is optically active and has an equal but opposite-in-sign specific rotation. Specific rotations are useful in that they are experimentally determined constants that characterize and identify pure enantiomers. For example, the lactic acid enantiomers have the following specific rotations:

- Carvone from caraway: $[\alpha]_D^{20} = +62.5^o$ (this isomer may be referred to as (+)-carvone or d-carvone)
- Carvone from spearmint: $[\alpha]_D^{20} = -62.5^o$ (this isomer may be referred to as (–)-carvone or l-carvone)

and carvone enantiomers have the following specific rotations:

- Lactic acid from muscle tissue: $[\alpha]_D^{20} = +2.5^o$ (this isomer may be referred to as (+)-lactic acid or d-lactic acid)
- Lactic acid from sour milk: $[\alpha]_D^{20} = -2.5^o$ (this isomer may be referred to as (–)-lactic acid or l-lactic acid)

A 50:50 mixture of enantiomers has no observable optical activity. Such mixtures are called **racemates** or racemic modifications, and are designated (±). When chiral compounds are created from achiral compounds, the products are racemic unless a single enantiomer of a chiral co-reactant or catalyst is involved in the reaction. The addition of HBr to either cis- or trans-2-butene is an example of racemic product formation (the chiral center is colored red).

$$CH_3CH{=}CHCH_3 + HBr \longrightarrow (\pm)CH_3CH_2\color{red}{C}HBrCH_3$$

Chiral organic compounds isolated from living organisms are usually optically active, indicating that one of the enantiomers predominates (often it is the only isomer present). This is a result of the action of chiral catalysts we call enzymes, and reflects the inherently chiral nature of life itself. Chiral synthetic compounds, on the other hand, are commonly racemates, unless they have been prepared from enantiomerically pure starting materials.

There are two ways in which the condition of a chiral substance may be changed:

1. A racemate may be separated into its component enantiomers. This process is called **resolution**.
2. A pure enantiomer may be transformed into its racemate. This process is called **racemization**.

Enantiomeric Excess

The "optical purity" is a comparison of the optical rotation of a pure sample of unknown stereochemistry versus the optical rotation of a sample of pure enantiomer. It is expressed as a percentage. If the sample only rotates plane-polarized light half as much as expected, the optical purity is 50%.

$$\%\ \text{optical purity} = \frac{\text{specific rotation of mixture}}{\text{specific rotation of pure enantiomer}} \times 100\%$$

Because *R* and *S* enantiomers have equal but opposite optical activity, it naturally follows that a 50:50 racemic mixture of two enantiomers will have no observable optical activity. If we know the specific rotation for a chiral molecule, however, we can easily calculate the ratio of enantiomers present in a mixture of two enantiomers, based on its measured optical activity. When a mixture contains more of one enantiomer than the other, chemists often use the concept of **enantiomeric excess (ee)** to quantify the difference. Enantiomeric excess can be expressed as:

$$ee = \frac{(\%\ \text{more abundant enantiomer} - 50) \times 100\%}{50}$$

For example, a mixture containing 60% *R* enantiomer (and 40% *S* enantiomer) has a 20% enantiomeric excess of R: ((60-50) x 100) / 50 = 20 %.

? Exercise 8.3.1

The specific rotation of (*S*)-carvone is (+)61°, measured 'neat' (pure liquid sample, no solvent). The optical rotation of a neat sample of a mixture of *R* and *S* carvone is measured at (-)23°. Which enantiomer is in excess, and what is its ee? What are the percentages of (*R*)- and (*S*)-carvone in the sample?

Answer

The observed rotation of the mixture is levorotary (negative, counter-clockwise), and the specific rotation of the pure *S* enantiomer is given as dextrorotary (positive, clockwise), meaning that the pure *R* enantiomer must be levorotary, and the mixture must contain more of the *R* enantiomer than of the *S* enantiomer.

Rotation (*R*/*S* Mix) = [Fraction(*S*) × Rotation (*S*)] + [Fraction(*R*) × Rotation (*R*)]

Let Fraction (*S*) = x, therefore Fraction (*R*) = 1 – x.

Rotation (*R*/*S* Mix) = x[Rotation (*S*)] + (1 – x)[Rotation (*R*)].

–23 = x(+61) + (1 – x)(–61)

Solve for x: x = 0.3114 and (1 – x) = 0.6885

Therefore the percentages of (*R*)- and (*S*)-carvone in the sample are 68.9% and 31.1%, respectively.

ee = [(% more abundant enantiomer – 50) × 100]/50. = [68.9 – 50) × 100]/50 = 37.8%.

Chiral molecules are often labeled according to the sign of their specific rotation, as in (S)-(+)-carvone and (R)-(-)-carvone, or (±)-carvone for the racemic mixture. However, there is no relationship whatsoever between a molecule's R/S designation and the sign of its specific rotation. Without performing a polarimetry experiment or looking in the literature, we would have no idea that (-)-carvone has the R configuration and (+)-carvone has the S configuration

Chiral molecules are often labeled according to the sign of their specific rotation, as in (S)-(+)-carvone and (R)-(-)-carvone, or (±)-carvone for the racemic mixture. However, there is no relationship whatsoever between a molecule's R/S designation and the sign of its specific rotation. Without performing a polarimetry experiment or looking in the literature, we would have no idea that (-)-carvone has the R configuration and (+)-carvone has the S configuration.

Separation of Chiral Compounds

As noted earlier, chiral compounds synthesized from achiral starting materials and reagents are generally racemic (i.e. a 50:50 mixture of enantiomers). Separation of racemates into their component enantiomers is a process called resolution. Since enantiomers have identical physical properties, such as solubility and melting point, resolution is extremely difficult. Diastereomers, on the other hand, have different physical properties, and this fact is used to achieve resolution of racemates. Reaction of a racemate with an enantiomerically pure chiral reagent gives a mixture of diastereomers, which can be separated. For example, if a racemic mixture of a chiral alcohol is reacted with a enantiomerically pure carboxylic acid, the result is a mixture of diastereomers: in this case, because the pure (R) entantiomer of the acid was used, the product is a mixture of (R-R) and (R-S) diastereomeric esters, which can, in theory, be separated by their different physical properties. Subsequent hydrolysis of each separated ester will yield the 'resolved' (enantiomerically pure) alcohols. The used of this technique is known as chiral resolution.

? Exercise 8.3.2

A 3.20 g sample of morphine ($[\alpha]_D$ = -132) was dissolved in 10.0 mL of acetic acid ($[\alpha]_D$ = 0). If it is put into a sample tube with a path length of 2.00 cm, what would be its observed rotation (α)?

Answer

The specific rotation, $[\alpha]_D$ = (observed rotation, α (degrees))/ [(pathlength, *l* (dm)) x (concentration, c (g/cm^3))] = α/(*l* x c)

Solving for α, α = $[\alpha]_D$ x *l* x c

($[\alpha]_D$ = -132) x (*l* = 2.00 cm = 0.200 dm) x (c = 3.20 g / 10.0 cm^3 = 0.320 g/cm^3)

α = -132 x 0.200 dm x 0.320 g/cm^3 = -8.45 °

? Exercise 8.3.3

Is the morphine in the previous excercise dextrorotatory or levorotatory?

Answer

Since morphine has a (-) rotation, it indicates that it rotates light to the left (counterclockwise) and morphine is levorotatory.

? Exercise 8.3.4

Label the following compounds as dextrorotatory or levorotatory.

a. sucrose ($[\alpha]_D$ = + 66.7)
b. cholesterol ($[\alpha]_D$ = - 31.5)
c. cocaine ($[\alpha]_D$ = - 16)
d. chloroform ($[\alpha]_D$ = 0)

Answer

a. sucrose ($[\alpha]_D$ = + 66.7) dextrorotatory

b. cholesterol ($[\alpha]_D$ = - 31.5) levorotatory
c. cocaine ($[\alpha]_D$ = - 16) levorotatory
d. chloroform ($[\alpha]_D$ = 0) neither, not optically active

? Exercise 8.3.5a

The specific rotation of (*S*)-carvone is (+) 61^o when measured neat (pure liquid sample with no solvent). The optical rotation of a neat sample of a mixture of R and S carvone is measured at (-) 23 ^{o}.

a) Which enantiomer is in excess?

Answer

Since the pure *S* enantiomer ((+) 61^o) is dextrorotatory (positive, clockwise), the *R* enantiomer must be levorotatory. The observed rotation of the mixture is levorotatory since its negative (counterclockwise). This means the mixture must contain more of the *R* enantiomer than the *S* enantiomer.

? Exercise 8.3.5b

b) What are the percentages of (*S*)- and (*R*)- carvone in the sample mixture?

Answer

Optical rotation (α) of the (*R*/*S* mixture) = [fraction (*S*) x $[\alpha]_D$ (*S*)] + [fraction (*R*) x $[\alpha]_D$ (*R*)]

To determine the fraction of S and R, we make y = fraction (*S*) and 1 – y = fraction (*R*)

-23^o = y x (61^o) + (1 – y) x (-61^o) solving for y: y = 0.3114 and (1-y) = 0.6885

Therefore the percentage of (*S*)-carvone is 31.1 % and (*R*)-carvone is 68.9 %

? Exercise 8.3.5c

c) What is the ee (enantiomeric excess)?

Answer

ee = [(% more abundant isomer – 50) x 100]/50 = [(68.9 – 50) x100]/50 = 37.8 % ee

? Exercise 8.3.6a

Determine the ee's of the following from the percentages

- 95 % (*R*)- tartaric acid and 5.0 % (*S*)- tartaric acid

Answer

[(95 – 50) x 100] / 50 = 90 % ee (*R*)-tartaric acid

? Exercise 8.3.6b

Determine the ee's of the following from the percentages

- 75 % (*S*)- limonene and 25 % (*R*)- limonene

Answer

[(75 – 50) x 100] / 50 = 50 % ee (*S*)- limonene

Exercise 8.3.6c

Determine the ee's of the following from the percentages

- 85 % (*R*) cysteine

Answer

(85 – 50) x 100] / 50 = 70 % ee (*R*)-cysteine

Exercise 8.3.6d

Determine the ee's of the following from the percentages

- 50 % (*S*) alanine

Answer

(50 – 50) x 100] / 50 = 0 % ee, racemic mixture

8.3: Optical Activity is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **5.3: Optical Activity** by Dietmar Kennepohl, Krista Cunningham, Steven Farmer, Tim Soderberg, Zachary Sharrett is licensed CC BY-SA 4.0.

8.4: Absolute Configuration- R-S Sequence Rules

Objectives

After completing this section, you should be able to

1. assign Cahn-Ingold-Prelog priorities to a given set of substituents.
2. determine whether a given wedge-and-broken-line structure corresponds to an *R* or an *S* configuration, with or without the aid of molecular models.
3. draw the wedge-and-broken-line structure for a compound, given its IUPAC name, complete with *R* or *S* designation.
4. construct a stereochemically accurate model of a given enantiomer from either a wedge-and-broken-line structure or the IUPAC name of the compound, complete with *R* or *S* designation.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- absolute configuration
- *R* configuration
- *S* configuration

Study Notes

When designating a structure as *R* or *S*, you must ensure that the atom or group with the lowest priority is pointing away from you, the observer. The easiest way to show this is to use the wedge-and-broken-line representation. You can then immediately determine whether you are observing an *R* configuration or an *S* configuration.

To name the enantiomers of a compound unambiguously, their names must include the "handedness" of the molecule. The method for this is formally known as *R*/*S* nomenclature.

Introduction

The method of unambiguously assigning the handedness of molecules was originated by three chemists: R.S. Cahn, C. Ingold, and V. Prelog and, as such, is also often called the Cahn-Ingold-Prelog rules. In addition to the Cahn-Ingold system, there are two ways of experimentally determining the absolute configuration of an enantiomer:

1. X-ray diffraction analysis. Note that there is no correlation between the sign of rotation and the structure of a particular enantiomer.
2. Chemical correlation with a molecule whose structure has already been determined via X-ray diffraction.

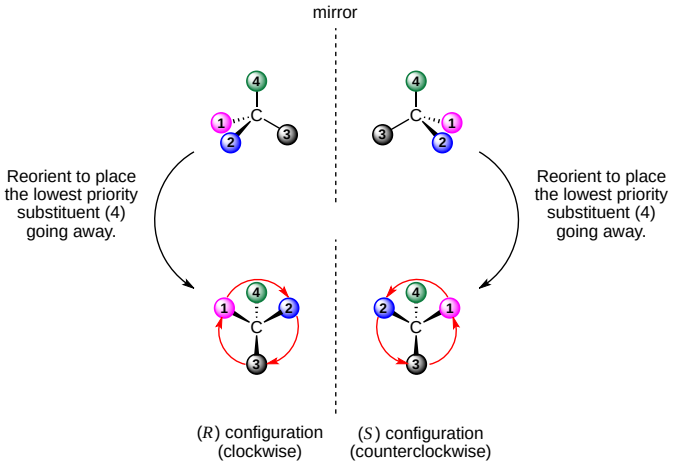
However, for non-laboratory purposes, it is beneficial to focus on the (*R*)/(*S*) system. The sign of optical rotation, although different for the two enantiomers of a chiral molecule,at the same temperature, **cannot** be used to establish the absolute configuration of an enantiomer; this is because the sign of optical rotation for a particular enantiomer may change when the temperature changes.

Stereocenters are labeled (*R*) or (*S*)

The "right hand" and "left hand" nomenclature is used to name the enantiomers of a chiral compound. The stereocenters are labeled as (*R*) or (*S*).

The **Cahn-Ingold-Prelog** rules of assign priorities the groups directly bonded to the chiral carbon. Having ranked the four groups attached to a chiral carbon, we describe the stereochemical configuration around the carbon by orienting the molecule so that the group with the lowest ranking (4) is given a dash bond to indicate it points directly away from us. We then look at the three remaining substituents, which now appear to radiate toward us which is shown by using wedge bonds. If a curved arrow drawn from the highest to second-highest to third-highest ranked substituent is clockwise, we say that the chirality center has the (R) configuration (Latin rectus, meaning “right”). If an arrow from is counterclockwise, the chirality center has the (S) configuration (Latin sinister, meaning “left”). To remember these assignments, think of a car’s steering wheel when making a Right (clockwise) turn. Note, the (R) or (S) configurations represent the two enantiomers of a chiral molecule. The (R) or (S) configuration is often

added as a prefix, in parenthesis, to a chiral molecule's name to indicate which enantiomer is being discussed (e.g., (R)-2-bromobutane). If more than chiral carbon is present in a chiral molecule, each carbon's number is included before the (R) or (S) configuration. Ex: (2R,4S,6R)-2-bromo-6-chloro-4-methylheptane.



Sequence Rules to Assign Priorities to Substituents

Before applying the (*R*) and (*S*) nomenclature to a stereocenter, the substituents must be prioritized according to the following rules:

Rule 1

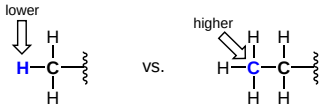
First, examine at the atoms directly attached to the stereocenter of the compound. A atom with a higher atomic number takes precedence over a atom with a lower atomic number. Hydrogen is the lowest possible priority atom, because it has the lowest atomic number.

1. The atom with higher atomic number has higher priority (I > Br > Cl > S > P > F > O > N > C > H).
2. When comparing isotopes, the atom with the higher mass number has higher priority [^{18}O > ^{16}O or ^{15}N > ^{14}N or ^{13}C > ^{12}C or T (^{3}H) > D (^{2}H) > H].

Rule 2

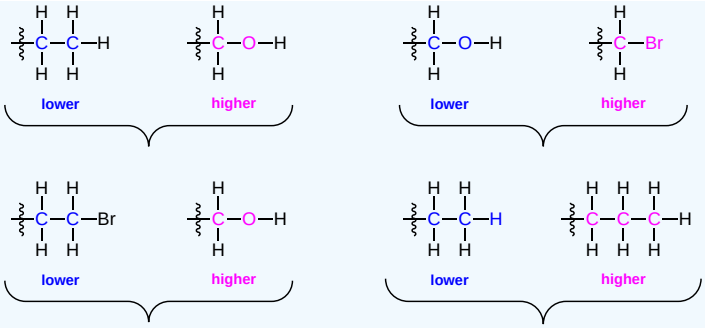
If there are two or more substituents which have the same element directly attached to chiral carbon, proceed along the substituent chains until a point of difference is found. Determine which of the chains has the first connection to an atom with the highest priority (the highest atomic number). That chain has the higher priority.

For example: an ethyl substituent takes priority over a methyl substituent. At the connectivity of the stereocenter, both have a carbon atom, which are equal in rank. Going down the chains, a methyl has only has hydrogen atoms attached to it, whereas the ethyl has two hydrogen atoms and a carbon atom. The carbon atom on the ethyl is the first point of difference and has a higher atomic number than hydrogen; therefore the ethyl takes priority over the methyl.



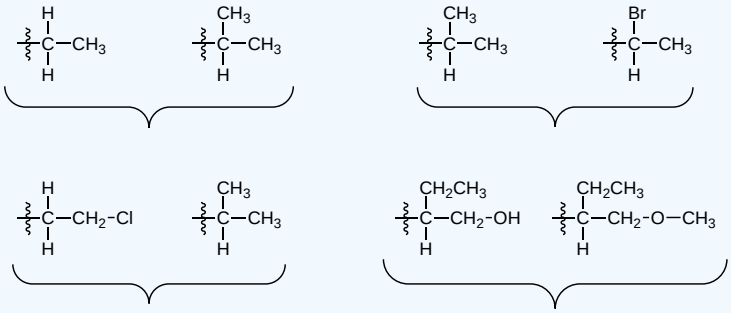
The "-H" (left) ranks lower than the "C-" (right) based on the relative molecular weights at the first point of difference.

Example 8.4.1



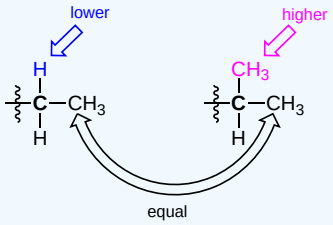
Worked Exercise 8.4.1

For the following pairs of substituents, determine which would have the higher and lower priority based on the **Cahn-Ingold-Prelog** rules. Explain your answer.



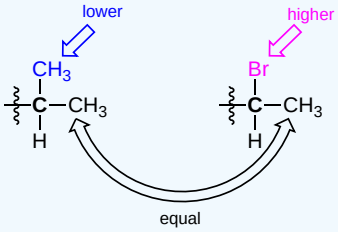
Answer

A 1-methylethyl substituent takes precedence over an ethyl substituent. Connected to the first carbon atom, ethyl only has one other carbon, whereas the 1-methylethyl has two carbon atoms attached to the first; this is the first point of difference. Therefore, 1-methylethyl ranks higher in priority than ethyl, as shown below:



The "C-" (right) ranks higher than the "H-" (left) based on the first point of difference and their relative atomic numbers.

However:

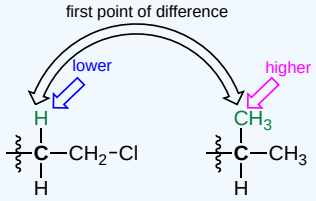


In this case, even though the bold carbon on the right structure has two connections to a non-hydrogen atom (C), it is the lower priority. This is because one of the atoms attached to the bold carbon on the left molecule

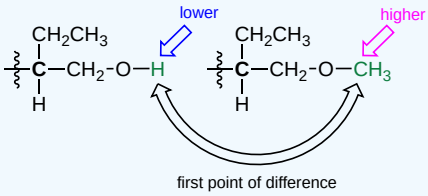
ranks higher than any of the atoms attached to the bold carbon on the right structure, since Br has a higher atomic number than C.

Caution!!

Keep in mind that priority is determined by the **first** point of difference along the two similar substituent chains. After the first point of difference, the rest of the chain is irrelevant.

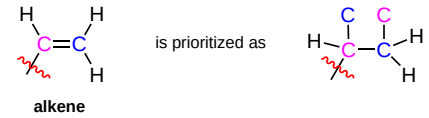


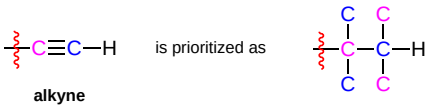
When looking for the first point of difference on similar substituent chains, one may encounter branching. If there is branching, choose the branch that is higher in priority. If the two substituents have similar branches, rank the elements within the branches until a point of difference.

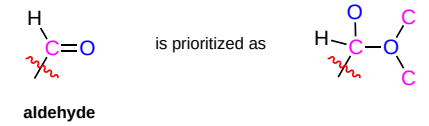


Rule 3

For assigning priority, multiple bonds are treated as if each bond of the multiple bond is bonded to a unique atom. For example, an alkene substituent (CH_2=CH-) has higher priority than an ethyl substituent (CH_3CH_2-). The alkene carbon priority is "two" bonds to carbon atoms and one bond to a hydrogen atom compared with the ethyl carbon that has only one bond to a carbon atom and two bonds to two hydrogen atoms. Similarly, alkyne substituent (HCC-) would have an even higher priority because the alkyne carbon is treated as if it is bonded to three carbons. This method remains the same with compounds containing a carbonyl (C=O) group. The carbon of an aldehyde substituent (O=CH-) is treated as if it is bonded to a hydrogen and two oxygen atoms.

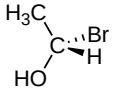






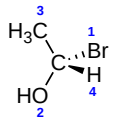
Determining (*R*) or (*S*) Configuration Using a Molecular Model

In order to demonstrate how to determine the (*R*)/(*S*) configuration of the chiral carbon in the following molecule using molecular models, first construct a model of the bromoethanol structure:

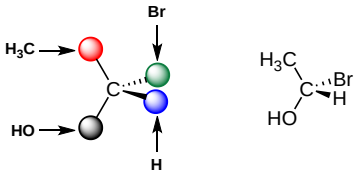


First make a molecular model of a tetrahedral carbon with four different substituents. In many cases, this will appear as a carbon with four bonds with a different colored ball attached to each bond.

For the molecule in question, determine the location of the chiral carbon and assign CIP priorities to the substituents. In this case, Br gets the highest priority because it has the highest atomic number. The O in the OH substituent gets priority 2 and the C in CH_3 gets priority 3. Lastly, H gets the lowest priority, 4, because it has the smallest atomic number.



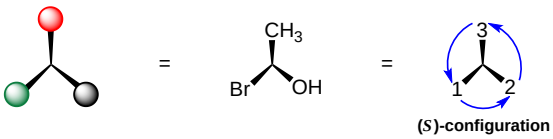
Now take your molecular model and orientate it to match the molecule in question. Remember in the dash/wedge representation, two regular bonds are in the plane of the page. The wedge bond is coming toward you and the dashed bond is going away from you. If you were to hold a piece of paper directly in front of you, the substituents with the regular bond should both be touching the piece of paper. The dashed bond should be pointing behind the piece of paper and the wedge bond should be pointing in front.



In this structure, the bromine is going away from you, the hydrogen is coming toward you and the hydroxide and methyl groups are in the plane of the page.

Then based on the position, assign each substituent on the chiral carbon a colored ball on your molecular model. In this case, bromine is going away so it is assigned the green ball. The hydrogen is coming toward you so it is assigned the blue ball. The last two substituents are in the plane of the page, however, the CH_3 is positioned higher so it is assigned the red ball which leaves OH being assigned the black ball.

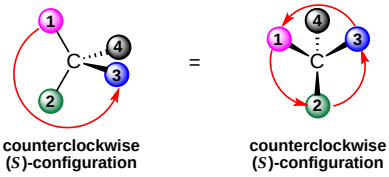
Lastly, grab onto the ball for the lowest priority substitutent, in this case the blue one, and point the other three substituents towards you. The three bonds should be angled towards you as if they all have wedge bonds. Assign the original substituents and their corresponding CIP priorities to the three colored balls. The green ball was assigned to bromine which was given priority one. The OH was assigned to the black ball and given priority two. The CH_3 was assigned to the red ball and given priority three. In this case the priorities are going counter clockwise so the chiral carbon has an ***(S)*** configuration.



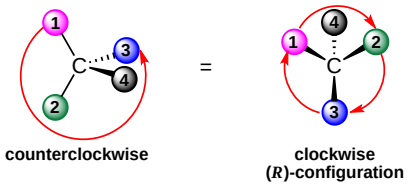
Determining (*R*) or (*S*) Configuration Without a Molecular Model

If a molecular model cannot be used there are a couple of simple methods which can be applied if the dash/wedge bond system is being used.

After assigning CIP priorities, if the lowest priority substituent (4) is on the dash bond the configuration of substituents 1-3 can be assigned directly. As shown in the figure below, the configuration of substituents 1-3 does not change when moving to sight down the bond of substituent 4. In both cases, substituents 1-3 are ordered in a counterclockwise fashion which gives the chiral carbon an (*S*) configuration.



The opposite is true if the lowest priority substituent (4) is on the wedge bond. As shown in the figure below, the configuration of substituents 1-3 is inverted when moving to sight down the bond of substituent 4. When the lowest priority substituent is on the wedge bond, the configuration of substituents 1-3 can be assigned directly only if the direction is inverted. i.e. clockwise = (*S*) and counterclockwise = (*R*).

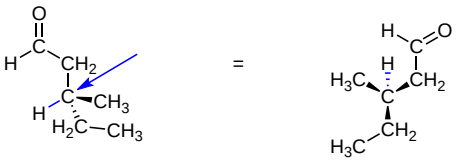


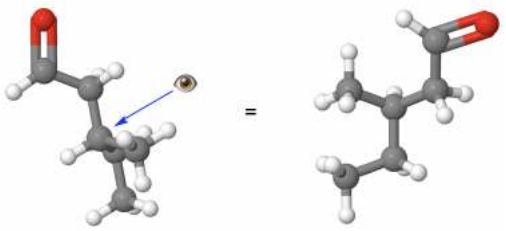
With the lowest priority group in front, drawing an arc from 1 to 2 to 3 gives the reverse of the configuration.

However, if the lowest priority substituent is on one of the regular bonds when the dash/wedge system is being used then configurations are best assigned by changing perspectives. This method can also be used if the three-dimensional configuration of the chiral carbon is represented. First, locate the chiral carbon and assign CIP priorities to its substituents. Then while perceiving the drawn molecule as a three-dimensional image, mentally change your perspective such that you are looking down the bond between the chiral carbon and the lowest CIP ranked substituent (#4). If done correctly, the bonds for substituents 1-3 should be coming towards you as wedge bonds. You can then follow the direction of the CIP priority numbers to determine the (*R*)/(*S*) configuration of the chiral carbon.



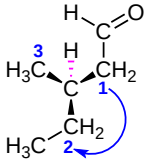
Locate the chiral carbon and assign CIP priorities to its substituents.





Mentally sight down the bond between the chiral carbon and the lowest CIP ranked substituent.

This bond is shown in magenta.



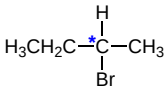
clockwise
(*R*)-configuration

Follow the direction of the CIP priority numbers to determine the (*R*)/(*S*) configuration.

Drawing the Structure of a Chiral Molecule from its Name

Draw the structure of (*S*)-2-Bromobutane:

1) Draw the basic structure of the molecule and determine the location of the chiral carbon.



2) Determine the chiral carbon's substituents and assign them a CIP priority.

-H (Priority 4)

-CH_3 (Priority 3)

-CH_2CH_3 (Priority 2)

-Br (Priority 1)

3) Draw the chiral carbon in a dash/wedge form and add the lowest priority substituent to the dash bond. In this case, the lowest priority substituent is -H.



4) Add the remaining substituents in a clockwise fashion for (*R*) and a counterclockwise fashion for (*S*).



clockwise
(*R*)-configuration

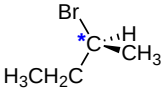


counterclockwise
(*S*)-configuration

The molecule posed in this question has an (*S*) configuration so the remaining substituents are added in a counterclockwise fashion.



counterclockwise
(*S*)-configuration



(*S*)-2-bromobutane

? Exercise 8.4.1

1) Orient the following so that the least priority (4) atom is paced behind, then assign stereochemistry ((*R*) or (*S*)).



2) Draw (*R*)-2-bromobutan-2-ol.

3) Assign (*R*)/(*S*) to the following molecule.



4) Which in the following pairs would have a higher CIP priority?

a. -H or -Cl
b. -Br or -I
c. $-CH_2OH$ or $-OCH_3$
d. $-CH_2CH_3$ or $-CH=CH_2$
e. $-NH_2$ or -OH

5) Rank the following substituents in order of their CIP priority:

a. -H, $-OCH_3$, $-CH_2OH$, -OH
b. -OH, $-CO_2H$, -CH=O, $-CH_2OH$
c. -CN, $-NH_2$, -CH=O, $-NHCH_3$
d. -SH, $-SCH_3$, -OH, $-OOCH_3$

6) Determine if the chiral carbon in the following molecules have an (*R*) or (*S*) configuration. Red = Oxygen & Blue = Nitrogen.

a)

b)

Answer

1) A is (*S*) and B is (*R*).



2)



3) The stereocenter is (*R*).

4)

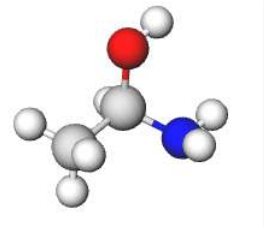
a. -Cl
b. -I
c. $-OCH_3$
d. $-CH=CH_2$
e. -OH

5) Rank the following substituents in order of their CIP priority:

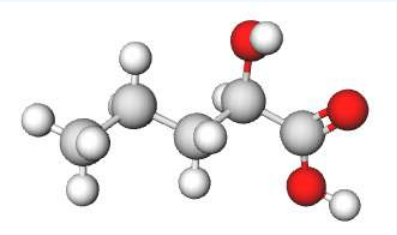
a. $-OCH_3$, -OH, $-CH_2OH$, -H,
b. -OH, $-CO_2H$, -CH=O, $-CH_2OH$
c. $-NHCH_3$, $-NH_2$, -CH=O, -CN
d. $-SCH_3$, -SH, $-OOCH_3$, -OH

6)

a) The chiral carbon is (*R*). The four substituents of the chiral carbon are -OH (1), $-NH_2$ (2), $-CH_3$ (3), and -H (4). Then looking down the lowest priority bond, you should roughly see what appears in the picture below. The substituents with priorities 1-3 are ordered in a clockwise fashion so the chiral carbon is (*R*).



b) The chiral carbon is (*S*). The four substituents of the chiral carbon are -CO_2H (1), -OH (2), -$CH_2CH_2CH_3$ (3), and -H (4). Then looking down the lowest priority bond, you should roughly see what appears in the picture below. The substituents with priorities 1-3 are ordered in a counterclockwise fashion so the chiral carbon is (*S*).



Exercise 8.4.2

Identify which substituent in the following sets has a higher ranking.

a. -H or -CH_3
b. -$CH_2CH_2CH_3$ or CH_2CH_3
c. -CH_2Cl or CH_2OH

Answer

a. **-CH_3**
b. **-$CH_2CH_2CH_3$**
c. **-CH_2Cl**

Exercise 8.4.3

Identify which substituent in the following sets has a higher ranking.

a. -NH_2 or -N=NH
b. -CH_2CH_2OH or -CH_2OH
c. -$CH=CH_2$ or -CH_2CH_3

Answer

a) **-N=NH**

b) **-CH_2OH**

c) **-$CH=CH_2$**

Exercise 8.4.4

Place the following sets of substituents in each group in order of lowest priority (1^{st}) to highest priority (4^{th})

a. -NH_2, -F, -Br, -CH_3
b. -SH, -NH_2, -F, -H

Answer

a) $-CH_3 < -NH_2 < -F, < -Br$

b) $-H < -NH_2 < -F, < -SH$

Exercise 8.4.5

Place the following sets of substituents in each group in order of lowest priority (1st) to highest priority (4th)

a. $-CH_2CH_3$, -CN, $-CH_2CH_2OH$, $-CH_2CH_2CH_2OH$
b. $-CH_2NH_2$, $-CH_2SH$, $-C(CH_3)_3$, -CN

Answer

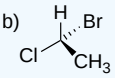
a) $-CH_2CH_3 < -CH_2CH_2OH < -CH_2CH_2CH_2OH, < -CN$

b) $-C(CH_3)_3 < -CH_2NH_2 < -CN < -CH_2SH$

Exercise 8.4.6

Assign the following chiral centers as (*R*) or (*S*).

a) 

b) 

c) 

Answer

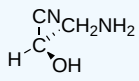
a) **(*S*)**: I > Br > F > H. The lowest priority substituent is going backwards so following the highest priority, it goes left (counterclockwise).

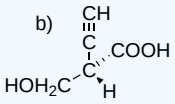
b) **(*R*)**: Br > Cl > CH_3 > H. Using a model kit, you need to rotate the H to the back position where the Br is. This causes the priority to go to the left (clockwise) when looking at it with the H in the back position. Alternatively, if you do not have a model kit, you can imagine the structure 3-dimensionally and since the lowest priority (H) is facing up (as drawn), if you look at it from below, starting with Br (1st priority) and moving towards Cl (2nd priority), you are moving right (clockwise) which represents (*R*) stereochemistry.

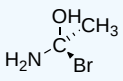
c) **Neither (*R*) or (*S*)**: Since there are two identical substituents (H's) the molecule is achiral and cannot be assigned (*R*) or (*S*).

Exercise 8.4.7

Assign the following chiral centers as (*R*) or (*S*).

a) 

b) 

c) 

Answer

a) **(*R*)**: OH > CN (C triple bonded to N) > CH_2NH_2 > H. The H needs to be moved to the back position which causes the priority to go to the right (clockwise) which indicates (*R*).

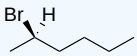
b) **(*S*)**: COOH > CH_2OH > C CH > H. Since the H is coming forward, you can assign the priority and it goes to the right (clockwise which would be (*R*)) but since the lowest priority is forward, you have to switch it to (*S*). Alternatively, you can rotate the molecule to put the lowest priority to the back and you'll see that it rotates left (or counterclockwise) for (*S*).

c) **(*S*)**: Br > OH > NH_2 > CH_3. Since the lowest priority is going back, you can follow the priority and see that it is going left (counterclockwise) and therefore (*S*).

Exercise 8.4.8

Draw the structure of (*R*)-2-bromohexane.

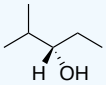
Answer



Exercise 8.4.9

Draw the structure of (*S*)-2-methyl-3-pentanol.

Answer



References

1. Schore and Vollhardt. *Organic Chemistry Structure and Function.* New York:W.H. Freeman and Company, 2007.
2. McMurry, John and Simanek, Eric. *Fundamentals of Organic Chemistry*. 6th Ed. Brooks Cole, 2006.

8.4: Absolute Configuration- R-S Sequence Rules is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **5.5: Sequence Rules for Specifying Configuration** by Dietmar Kennepohl, Ekta Patel, Ifemayowa Aworanti, Krista Cunningham, Layne Morsch, Steven Farmer, Zachary Sharrett is licensed CC BY-SA 4.0.

SECTION OVERVIEW

8.5: Stereochemistry of the Alkenes

8.5.1: Cis-Trans Isomerism in Alkenes

8.5.2: Sequence Rules - The E,Z Designation

8.5: Stereochemistry of the Alkenes is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

8.5.1: Cis-Trans Isomerism in Alkenes

Objectives

After completing this section, you should be able to

- discuss the formation of carbon-carbon double bonds using the concept of sp^2 hybridization.
- describe the geometry of compounds containing carbon-carbon double bonds.
- compare the molecular parameters (bond lengths, strengths and angles) of a typical alkene with those of a typical alkane.
- explain why free rotation is not possible about a carbon-carbon double bond.
- explain why the lack of free rotation about a carbon-carbon double bond results in the occurrence of cis-trans isomerism in certain alkenes.
- decide whether or not cis-trans isomerism is possible for a given alkene, and where such isomerism is possible, draw the Kekulé structure of each isomer.

Key Terms

Make certain that you can define, and use in context, the key term below.

- cis-trans stereoisomers

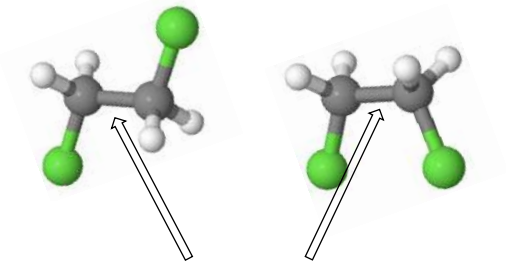
Study Notes

Your previous studies in chemistry may have prepared you to discuss the nature of a carbon-carbon double bond. If not, you should review Section 1.8 of this course before beginning the present section. It is particularly important that you make molecular models of some simple alkenes to gain insight into the geometry of these compounds.

Geometric isomerism (also known as cis-trans isomerism or E-Z isomerism) is a form of stereoisomerism. Isomers are molecules that have the same molecular formula, but have a different arrangement of the atoms in space. That excludes any different arrangements which are simply due to the molecule rotating as a whole, or rotating about particular bonds. Where the atoms making up the various isomers are joined up in a different order, this is known as structural isomerism. Structural isomerism is **not** a form of stereoisomerism, and is dealt with in a separate Module.

Geometric (cis / trans) isomerism

These isomers occur where you have restricted rotation somewhere in a molecule. At an introductory level in organic chemistry, examples usually just involve the carbon-carbon double bond - and that's what this page will concentrate on. Think about what happens in molecules where there is **un**restricted rotation about carbon bonds - in other words where the carbon-carbon bonds are all single. The next diagram shows two possible configurations of 1,2-dichloroethane.

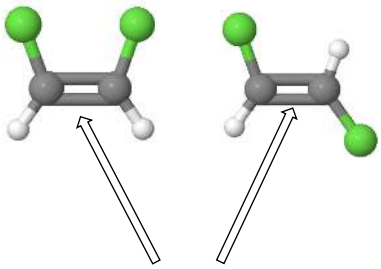


free rotation about carbon-carbon single bond

These two models represent exactly the same molecule. You can get from one to the other just by twisting around the carbon-carbon single bond. These molecules are *not* isomers. If you draw a structural formula instead of using models, you have to bear in mind the possibility of this free rotation about single bonds. You must accept that these two structures represent the same molecule:



But what happens if you have a carbon-carbon double bond - as in 1,2-dichloroethene?



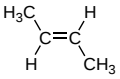
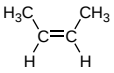
These two molecules are not the same. The carbon-carbon double bond won't rotate and so you would have to take the models to pieces in order to convert one structure into the other one. That is a simple test for isomers. If you have to take a model to pieces to convert it into another one, then you've got isomers. If you merely have to twist it a bit, then you haven't!

Drawing structural formulae for the last pair of models gives two possible isomers:

1. In one, the two chlorine atoms are locked on opposite sides of the double bond. This is known as the ***trans*** isomer. (*trans* : from latin meaning "across" - as in transatlantic).
2. In the other, the two chlorine atoms are locked on the same side of the double bond. This is know as the ***cis*** isomer. (*cis* : from latin meaning "on this side")

	
trans-1,2-dichloroethene	*cis*-1,2-dichloroethene

The most likely example of geometric isomerism you will meet at an introductory level is but-2-ene. In one case, the CH_3 groups are on opposite sides of the double bond, and in the other case they are on the same side.

	
trans-but-2-ene	*cis*-but-2-ene

The importance of drawing geometric isomers properly

It's very easy to miss geometric isomers in exams if you take short-cuts in drawing the structural formulae. For example, it is very tempting to draw but-2-ene as

$$CH_3CH{=}CHCH_3$$

If you write it like this, you will almost certainly miss the fact that there are geometric isomers. If there is even the slightest hint in a question that isomers might be involved, always draw compounds containing carbon-carbon double bonds showing the correct bond angles (120°) around the carbon atoms at the ends of the bond. In other words, use the format shown in the last diagrams above.

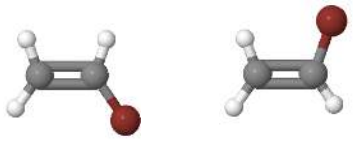
How to recognize the possibility of geometric isomerism

You obviously need to have restricted rotation somewhere in the molecule. Compounds containing a carbon-carbon double bond have this restricted rotation. (Other sorts of compounds may have restricted rotation as well, but we are concentrating on the case

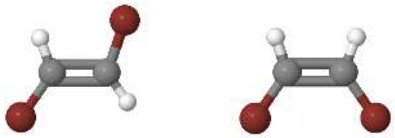
you are most likely to meet when you first come across geometric isomers.) If you have a carbon-carbon double bond, you need to think carefully about the possibility of geometric isomers.

What needs to be attached to the carbon-carbon double bond?

Think about this case:



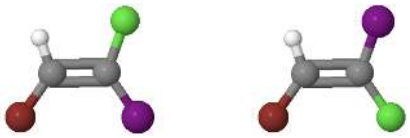
Although we've swapped the right-hand groups around, these are still the same molecule. To get from one to the other, all you would have to do is to turn the whole model over. You won't have geometric isomers if there are two groups the same on one end of the bond - in this case, the two pink groups on the left-hand end. So there must be two different groups on the left-hand carbon and two different groups on the right-hand one. The cases we've been exploring earlier are like this:



But you could make things even more different and still have geometric isomers:

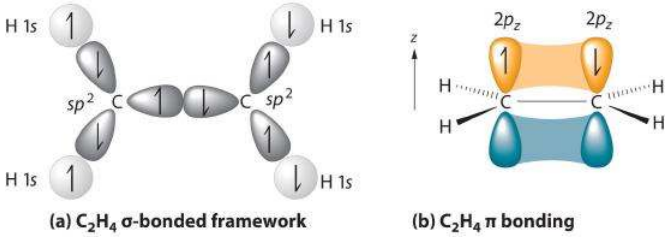


Here, the blue and green groups are either on the same side of the bond or the opposite side. Or you could go the whole hog and make everything different. You still get geometric isomers, but by now the words *cis* and *trans* are meaningless. This is where the more sophisticated *E-Z* notation comes in.



Rigidity of C=C Bonds

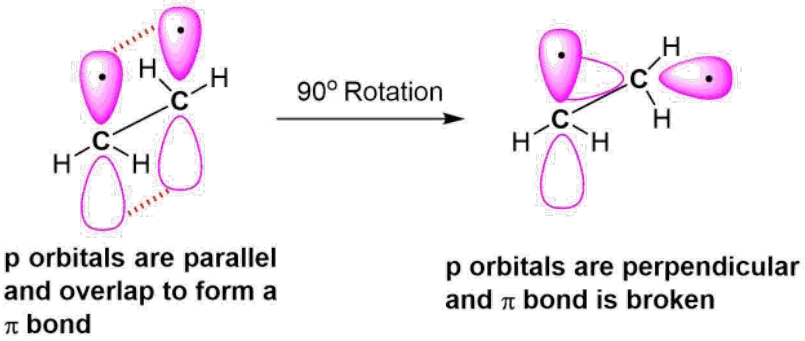
As discussed in Section 1.8 the double bond in the molecule ethene ($H_2C=CH_2$) is created by the overlap of two different sets of orbitals. The C-C σ bond is formed when an sp^2 orbital from each carbon atom overlaps end to end. Also, the C-C pi bond is created by the side-to-side overlap of a p_z orbital from each carbon atom.



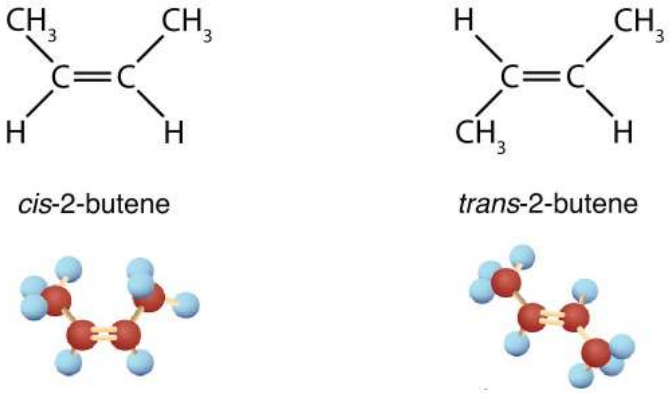
(a) C_2H_4 σ-bonded framework (b) C_2H_4 π bonding

Because they are the result of side-by-side overlap (rather then end-to-end overlap like a sigma bond), *pi bonds are not free to rotate.* If rotation about this bond were to occur, it would involve disrupting the side-by-side overlap between the two $2p_z$ orbitals that make up the pi bond. If free rotation were to occur the p-orbitals would have to go through a phase where they are 90° from each other, which would break the pi bond because there would be no overlap. Since the pi bond is essential to the structure of

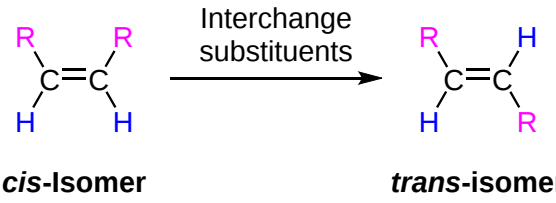
ethene it must not break, so there can be no free rotation about the carbon-carbon sigma bond. The presence of the pi bond thus 'locks' the six atoms of ethene into the same plane.



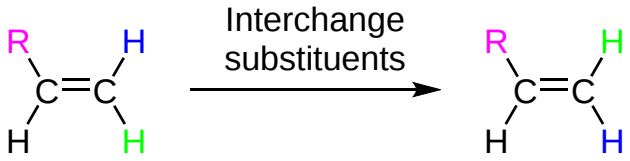
Restricted rotation about the double bond means that the relative positions of substituent groups above or below the double bond become significant. This leads to a special kind of isomerism in double bonds. Consider the alkene with the condensed structural formula $CH_3CH{=}CHCH_3$. We could name it 2-butene, but there are actually two such compounds due to this isomerism. The isomer in which the two methyl (CH_3) groups lie on the same side of the molecule is called the cis isomer (Latin *cis*, meaning "on this side") and is named cis-2-butene. The isomer with the two (CH_3) groups on opposite sides of the molecule is the trans isomer (Latin *trans*, meaning "across") and is named *trans*-2-butene. These two compounds are *cis-trans* isomers (or geometric isomers), compounds that have different configurations (groups permanently in different places in space) because of the presence of a rigid structure in their molecule. In general these isomers have different physical, chemical, and physiological properties.



It is important to note that the presence of a double bond does **not** necessarily lead to *cis-trans* isomerism. Being able to tell if a double bond has the possibility of isomerism is a very important skill. *Cis-trans* can occur whenever both double-bond carbons are directly attached to a carbon and a hydrogen. In this case, interchanging the substituents on one of the double-bond carbons creates a different isomer.



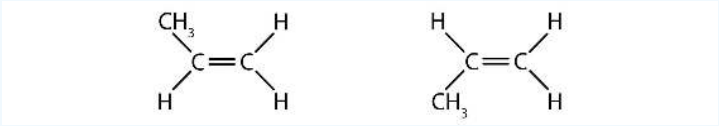
If one of the double-bond carbons of an alkene is attached to two identical groups, *cis-trans* isomerism is not possible. Here, interchanging the substituents on one of the double-bond carbons forms an identical molecule.



These two molecules are identical

Worked Example 8.5.1.1

Are the following molecules *cis-trans* isomers?



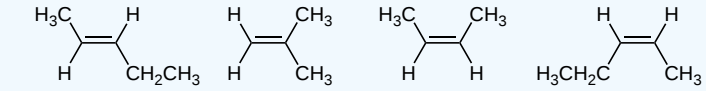
Answer

Although the two molecules *are seemingly* different propenes, these two structures are not really different from each other. Because the one of the double-bond carbons is attached to two identical groups (hydrogens) it is incapable of forming *cis-trans* isomers. The interchange of two substituents seen here does not create a new isomer. If either molecule were flipped over top to bottom, the two would you would look identical.

Exercise 8.5.1.1

Classify each compound as a *cis* isomer, a *trans* isomer, or neither.

a) b) c) d)



Answer

a) trans isomer

b) neither

c) cis isomer

d) cis isomer

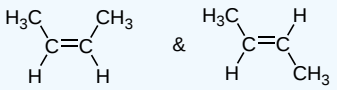
Exercise 8.5.1.2

Which of the following compounds could exist as cis/trans isomers? Draw (& label) both of the isomers for the ones that can.

a. $CH_3CH{=}CHCH_3$
b. $(CH_3)_2C{=}CHCH_3$
c. $H_2C{=}CHCH_3$
d. $CH_3CH_2CH{=}CHBr$

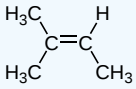
Answer

a)



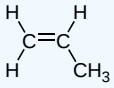
cis isomer & trans isomer

b)



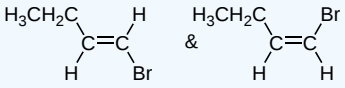
no cis/trans isomers

c)



no cis/trans isomers

d)



trans isomer & cis isomer

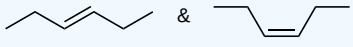
Exercise 8.5.1.3

Draw (& label) the cis and trans isomer for each of the following compound names. If no cis/trans isomerism is possible, write none.

a. 3-hexene
b. 1-hexene
c. 4-methylpent-2-ene (4-methyl-2-pentene)
d. 1,1-dibromobut-2-ene (1,1-dibromo-2-butene)

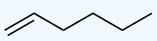
Answer

a)



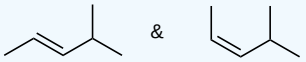
trans isomer & cis isomer

b)



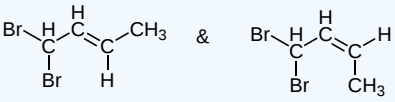
no cis/trans isomers

c)



trans isomer & cis isomer

d)

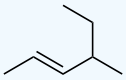


trans isomer & cis isomer

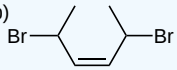
Exercise 8.5.1.4

Name the following compounds using cis/trans nomenclature

a)



b)



Answer

a) *trans*-4-methylhex-2-ene (*trans*-4-methyl-2-hexene)

b) *cis*-2,5-dibromohex-3-ene (*cis*-2,5-dibromo-3-hexene)

8.5.1: Cis-Trans Isomerism in Alkenes is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Jim Clark, Steven Farmer, Dietmar Kennepohl, Zachary Sharrett, Krista Cunningham, & Krista Cunningham.

- **7.5: Cis-Trans Isomerism in Alkenes** by Dietmar Kennepohl, Jim Clark, Krista Cunningham, Steven Farmer, Zachary Sharrett is licensed CC BY-SA 4.0.

8.5.2: Sequence Rules - The E,Z Designation

Objectives

After completing this section, you should be able to

1. illustrate, by means of a suitable example, the limitations of the terms *cis* and *trans* in naming isomeric alkenes.
2. use the *E*/*Z* designation to describe the geometry of a given alkene structure.
3. incorporate the *E*/*Z* designation into the IUPAC name of a given alkene.
4. draw the correct Kekulé, condensed or shorthand structure of an alkene, given its *E*/*Z* designation plus other necessary information (e.g., molecular formula, IUPAC name).

Key Terms

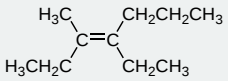
Make certain that you can define, and use in context, the key term below.

- sequence rules (Cahn-Ingold-Prelog rules)

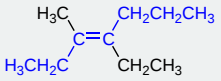
Study Notes

The limitations of the *cis/trans* system are illustrated in the examples given below.

1. From your study of the IUPAC system, you should be able to identify this compound as 4-ethyl-3-methyl-3-heptene, but is it *cis* or *trans*?



At first you might say *cis*, because it appears that two ethyl groups appear on the same side of the double bond. However, the correct answer is *trans*. The rule is that the designation *cis* or *trans* must correspond to the configuration of the *longest* carbon chain. Tracing out the seven-carbon chain in the compound shown above, you change sides as you pass through the double bond:

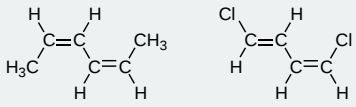


So, the full name for this compound is *trans*-4-ethyl-3methyl-3-heptene.

2. The *cis*/*trans* system breaks down completely in a compound such as that shown below. The *E*/*Z* system, which is the subject of this section, is designed to accommodate such situations.



In cases where two or more double bonds are present, you must be prepared to assign an *E* or *Z* designation to each of the double bonds. For example:

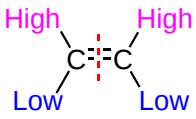


Another use for these sequence rules will be part of the discussion of optical isomerism in Section 9.5.

E/*Z* nomenclature

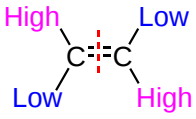
When each carbon in a double bond is attached to a hydrogen and and a non-hydrogen substituent, the geometric isomers can be identified by using the *cis-trans* nomenclature discussed in the previous section. However, when a double bond is attached to three or four non-hydrogen substituents there are some examples where *cis-trans* nomenclature is ineffective in describing the

substituents orientation in geometric isomers. In these situations the rigorous IUPAC system for naming alkene isomers, called the E/Z system, is used. The E/Z system analyzes the two substituents attached to each carbon in the double bond and assigns each either a high or low priority. If the higher priority group on both carbons in the double bond the **same** side the alkene is said to have a **Z isomer** (from German zusammen = together). You could think of Z as Zame Zide to help memorize it. If the higher priority group on **opposite** sides the alkene has an **E isomer** (from German entgegen = opposite).



Z Configuration

High priority substituents are on the same side of the double bond



E Configuration

High priority substituents are on opposide sides of the double bond

Note, if both substituents an a double bond carbon are exactly the same there is no E/Z isomerizem is possible. Also, if E/Z isomerism is possible, interchanging the substituents attached on double-bond carbon converts one isomer to the other.

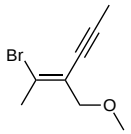
Substituent priority for the E,Z system is assigned using the Cahn–Ingold–Prelog (CIP) sequence rules. These are the same rules used to assign R/S configurations to chiral centers in **Section 5.5**. A brief overview of using CIP rules to determine alkene configuration is given here but CIP rules are discussed in greater detail in **Section 5.5**.

> **Note**
>
> The priority rules are often called the Cahn-Ingold-Prelog (CIP) rules, after the chemists who developed the system

Rule 1: The "first point of difference" rule

First, determine the two substituents on each double-bond carbon separately. Rank these substituents based on **the atom** which directly attached to the double-bond carbon. The substituent whose atom has a higher atomic number takes precedence over the substituent whose atom has a lower atomic number.

Which is higher priority, by the CIP rules: a C with an O and 2 H attached to it or a C with three C? The first C has one atom of high priority but also two atoms of low priority. How do these "balance out"? Answering this requires a clear understanding of how the ranking is done. The simple answer is that the first point of difference is what matters; the O wins.



To illustrate this, consider the molecule at the left. Is the double bond here *E* or *Z*? At the left end of the double bond, Br > C. But the right end of the double bond requires a careful analysis.

At the right hand end, the first atom attached to the double bond is a C at each position. A tie, so we look at what is attached to this first C. For the upper C, it is CCC (since the triple bond counts three times). For the lower C, it is OHH -- listed in order from high priority atom to low. OHH is higher priority than CCC, because of the first atom in the list. That is, the O of the lower group beats the C of the upper group. In other words, the O is the highest priority atom of any in this comparison; thus the O "wins".

Therefore, the high priority groups are "up" on the left end (the -Br) and "down" on the right end (the -CH_2-O-CH_3). This means that the isomer shown is opposite = entgegen = *E*. And what is the name? The "name" is (E)-2-Bromo-3-(methoxymethyl)hex-2-en-4-yne.

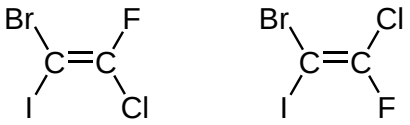
Rule 2

If the first atom on both substituents are the identical, then proceed along both substituent chains until the first point of difference is determined.

Rule 3

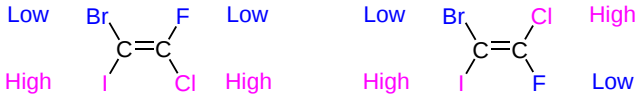
Remember that atoms involved in multiple bonds are considered with a specific set of rules. These atoms are treated as if they have the same number of single-bond atoms as they have attached to multiply bonded atoms.

An easy example which shows the necessity of the E/Z system is the alkene, 1-bromo-2-chloro-2-fluoro-1-iodoethene, which has four different substituents attached to the double bond. The figure below shows that there are two distinctly different geometric isomers for this molecule neither of which can be named using the *cis-trans* system.



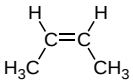
Consider the left hand structure. On the double bond carbon on the left, the two atoms attached to the double bond are Br and I. By the CIP priority rules, I is higher priority than Br (higher atomic number). Now look at carbon on the right. The attached atoms are Cl and F, with Cl having the higher atomic number and the higher priority.

When considering the relative positions of the higher priority groups, the higher priority group is "down" on the left double bond carbon and "down" at right double bond carbon. Since the two higher priority groups are both on the **same** side of the double bond ("down", in this case), they are zusammen = together. Therefore, this is the (Z) isomer. Similarly, the right hand structure is (E).

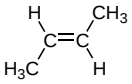


Z Configuration **E Configuration**

Example 8.5.2.1



cis-2-butene
(*Z*)-2-butene



trans-2-butene
(*E*)-2-butene

The Figure above shows the two isomers of 2-butene. You should recognize them as *cis* and *trans*. Let's analyze them to see whether they are *E* or *Z*. Start with the left hand structure (the cis isomer). On C2 (the left end of the double bond), the two atoms attached to the double bond are C and H. By the CIP priority rules, C is higher priority than H (higher atomic number). Now look at C3 (the right end of the double bond). Similarly, the atoms are C and H, with C being higher priority. We see that the higher priority group is "down" at C2 and "down" at C3. Since the two priority groups are both on the **same** side of the double bond ("down", in this case), they are zusammen = together. Therefore, this is (*Z*)-2-butene.

Now look at the right hand structure (the *trans* isomer). In this case, the priority group is "down" on the left end of the double bond and "up" on the right end of the double bond. Since the two priority groups are on **opposite** sides of the double bond, they are entgegen = opposite. Therefore, this is (*E*)-2-butene.

E/*Z* will work – even when *cis*/*trans* fails

In simple cases, such as 2-butene, *Z* corresponds to *cis* and *E* to *trans*. However, that is **not** a rule. This section and the following one illustrate some idiosyncrasies that happen when you try to compare the two systems. The real advantage of the *E*/*Z* system is that it will always work. In contrast, the *cis*/*trans* system breaks down with many ambiguous cases.

Example 8.5.2.2

The following figure shows two isomers of an alkene with four different groups on the double bond, 1-bromo-2-chloro-2-fluoro-1-iodoethene.



(*Z*)-1-bromo-2-chloro-2-fluoro-1-iodoethene

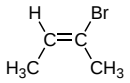


(*E*)-1-bromo-2-chloro-2-fluoro-1-iodoethene

It should be apparent that the two structures shown are distinct chemicals. However, it is impossible to name them as *cis* or *trans*. On the other hand, the *E*/*Z* system works fine... Consider the left hand structure. On C1 (the left end of the double bond), the two atoms attached to the double bond are Br and I. By the CIP priority rules, I is higher priority than Br (higher atomic number). Now look at C2. The atoms are Cl and F, with Cl being higher priority. We see that the higher priority group is "down" at C1 and "down" at C2. Since the two priority groups are both on the **same** side of the double bond ("down", in this case), they are zusammen = together. Therefore, this is the (*Z*) isomer. Similarly, the right hand structure is (*E*).

E/*Z* will work, but may not agree with *cis*/*trans*

Consider the molecule shown below. This is 2-bromo-2-butene -- ignoring the geometric isomerism for now. *Cis* or *trans*? This molecule is clearly *cis*. The two methyl groups are on the same side. More rigorously, the "parent chain" is *cis*.



E or *Z*? There is a methyl at each end of the double bond. On the left, the methyl is the high priority group -- because the other group is -H. On the right, the methyl is the low priority group -- because the other group is -Br. That is, the high priority groups are -CH_3 (left) and -Br (right). Thus the two priority groups are on opposite sides = entgegen = *E*.

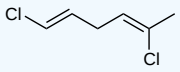
Note

This example should convince you that *cis* and *Z* are not synonyms. *Cis*/*trans* and *E*/*Z* are determined by distinct criteria. There may seem to be a simple correspondence, but it is not a rule. Be sure to determine *cis*/*trans* or *E*/*Z* separately, as needed.

Multiple double bonds

If the compound contains more than one double bond, then each one is analyzed and declared to be *E* or *Z*.

Example 8.5.2.3

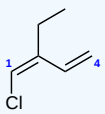


The configuration at the left hand double bond is *E*; at the right hand double bond it is *Z*. Thus this compound is (1*E*,4*Z*)-1,5-dichloro-1,4-hexadiene.

The double-bond rule in determining priorities

Example 8.5.2.4

Consider the compound below

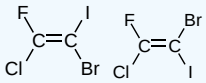


This is 1-chloro-2-ethyl-1,3-butadiene -- ignoring, for the moment, the geometric isomerism. There is no geometric isomerism at the second double bond, at 3-4, because it has 2 H at its far end.

What about the first double bond, at 1-2? On the left hand end, there is H and Cl; Cl is higher priority (by atomic number). On the right hand end, there is $-CH_2-CH_3$ (an ethyl group) and $-CH=CH_2$ (a vinyl or ethenyl group). Both of these groups have C as the first atom, so we have a tie so far and must look further. What is attached to this first C? For the ethyl group, the first C is attached to C, H, and H. For the ethenyl group, the first C is attached to a C twice, so we count it twice; therefore that C is attached to C, C, H. CCH is higher than CHH; therefore, the ethenyl group is higher priority. Since the priority groups, Cl and ethenyl, are on the same side of the double bond, this is the *Z*-isomer; the compound is (*Z*)-1-chloro-2-ethyl-1,3-butadiene.

Example 8.5.2.5

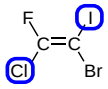
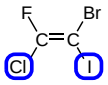
The configuration about double bonds is undoubtedly best specified by the *cis*/*trans* notation when there is no ambiguity involved. Unfortunately, many compounds cannot be described adequately by the *cis*/*trans* system. Consider, for example, configurational isomers of 1-fluoro-1-chloro-2-bromo-2-iodo-ethene, 9 and 10. There is no obvious way in which the *cis*/*trans* system can be used:



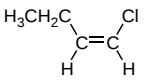
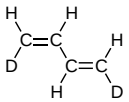
9 **10**

A system that is easy to use and which is based on the sequence rules already described for the *R*,*S* system works as follows:

1. An order of precedence is established for the two atoms or groups attached to each end of the double bond according to the sequence rules of Section 19-6. When these rules are applied to 1-fluoro- 1-chloro-2-bromo-2- iodoethene, the priority sequence is:
    - at carbon atom 1, C1 > F
    - at carbon atom 2, I > Br
2. Examination of the two configurations shows that the two priority groups- one on each end- are either on the same side of the double bond or on opposite sides:

 priority groups on opposite sides (*E*) configuration	 priority groups on same side (*Z*) configuration

The *Z* isomer is designated as the isomer in which the top priority groups are on the same side (*Z* is taken from the German word zusammen- together). The *E* isomer has these groups on opposite sides (*E*, German for entgegen across). Two further examples show how the nomenclature is used:

 (*Z*)-1-chloro-1-butene	 (1*Z*,3*E*)-1,3-butadiene-1,4-*d*2

Exercises

Exercise 8.5.2.1

Which of the following sets has a higher ranking?

a. $-CH_3$ or $-CH_2Br$
b. -Br or -Cl
c. $-CH=CH_2$ or -CH=O

Answer

a) $-CH_2Br$

b) -Br

c) -CH=O

Exercise 8.5.2.2

Place the following sets of substituents in each group in order of lowest priority (1^{st}) to highest priority (4^{th})

a. $-CH(CH_3)_2$, $-CH_2CH_3$, $-C(CH_3)_3$, $-CH_3$
b. $-NH_2$, -F, -Br, $-CH_3$
c. -SH, $-NH_2$, -F, -H

Answer

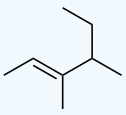
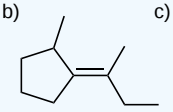
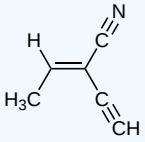
a) (lowest priority) $-CH_3 < -CH_2CH_3 < -CH(CH_3)_2 < -C(CH_3)_3$ (highest priority)

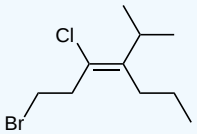
b) (lowest priority) $-CH_3 < -NH_2 < -F < -Br$ (highest priority)

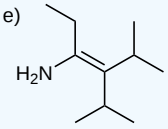
c) (lowest priority) $-H < -NH_2 < -F < -SH$ (highest priority)

Exercise 8.5.2.3

Label the following alkenes as E, Z, or neither.

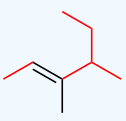
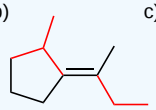
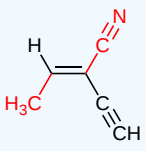
a) 
b) 
c) 

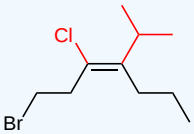
d) 

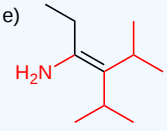
e) 

Answer

The higher priority group is highlighted in red.

a) 
b) 
c) 

d) 

e) 

a) E

b) E

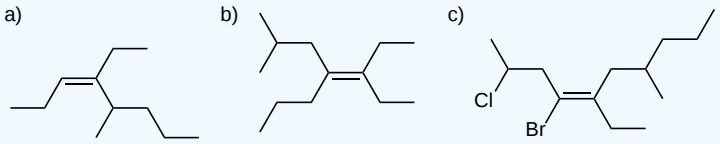
c) E

d) Z

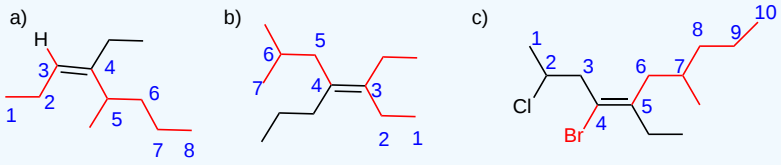
e) neither (both isopropyls on the right have the same priority)

Exercise 8.5.2.4

Name the following alkenes.



Answer



The higher priority group is highlighted in red.

a. (Z)-4-ethyl-5-methyloct-3-ene or (Z)-4-ethyl-5-methyl-3-octene
b. 3-ethyl-6-methyl-4-propylhept-3-ene or 3-ethyl-6-methyl-4-propyl-3-heptene
c. (E)-4-bromo-2-chloro-5-ethyl-7-methyldec-4-ene or (E)-4-bromo-2-chloro-5-ethyl-7-methyl-4-decene

8.5.2: Sequence Rules - The E,Z Designation is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Steven Farmer, Dietmar Kennepohl, Zachary Sharrett, Krista Cunningham, John Roberts, Marjorie C. Caserio, Robert Bruner, & Robert Bruner.

- **7.6: Sequence Rules - The E,Z Designation** by Dietmar Kennepohl, John Roberts, Krista Cunningham, Marjorie C. Caserio, Robert Bruner, Steven Farmer, Zachary Sharrett is licensed CC BY-SA 4.0.

8.6: Study Guide

8: Organic Chemistry II - Stereochemistry

Key Topics for TRU students taking CHEM1500

- Conformations of alkanes and cycloalkanes
- staggered/eclipsed/anti/gauche conformations
- torsional energy barriers
- ring angle strain
- steric strain
- cyclohexane and substituted cyclohexanes conformations
- axial and equatorial bonds

Key Learning Outcomes (Examples)

- draw the various possible significant conformations of organic compounds with a straight-chain or ring-structure carbon atoms

8.6: Study Guide is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

9: Organic Chemistry III - Conformational Analysis

9.1: Rotation about Single Bonds- Conformations
9.2: Rotation in Substituted Ethanes
9.3: Ring Strain and the Structure of Cycloalkanes
9.4: Cyclohexane- A Strain-Free Cycloalkane
9.5: Substituted Cyclohexanes
9.S: Study Guide

9: Organic Chemistry III - Conformational Analysis is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

9.1: Rotation about Single Bonds- Conformations

Objectives

After completing this section, you should be able to

1. explain the concept of free rotation about a carbon-carbon single bond.
2. explain the difference between conformational isomerism and structural isomerism.
3. draw the conformers of ethane using both sawhorse representation and Newman projection.
4. sketch a graph of energy versus bond rotation for ethane, and discuss the graph in terms of torsional strain.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- conformation (conformer, conformational isomer)
- dihedral angle
- eclipsed conformation
- Newman projection
- staggered conformation
- strain energy
- torsional strain (eclipsing strain)

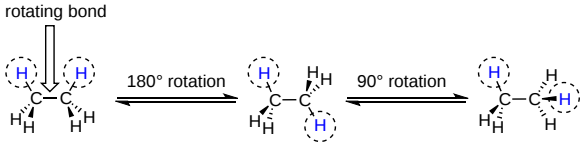
Study Notes

You should be prepared to sketch various conformers using both sawhorse representations and Newman projections. Each method has its own advantages, depending upon the circumstances. Notice that when drawing the Newman projection of the eclipsed conformation of ethane, you cannot clearly draw the rear hydrogens exactly behind the front ones. This is an inherent limitation associated with representing a 3-D structure in two dimensions.

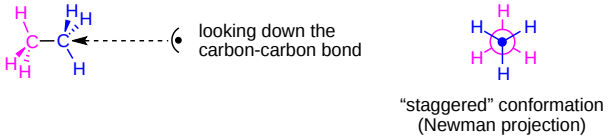
Conformational isomerism involves rotation about sigma bonds, and does not involve any differences in the connectivity of the atoms or geometry of bonding. Two or more structures that are categorized as conformational isomers, or **conformers**, are really just two of the exact same molecule that differ only in rotation of one or more sigma bonds.

Ethane Conformations

Although there are seven sigma bonds in the ethane molecule, rotation about the six carbon-hydrogen bonds does not result in any change in the shape of the molecule because the hydrogen atoms are essentially spherical. Rotation about the carbon-carbon bond, however, results in many different possible molecular conformations.



In order to better visualize these different conformations, it is convenient to use a drawing convention called the **Newman projection**. In a Newman projection, we look lengthwise down a specific bond of interest – in this case, the carbon-carbon bond in ethane. We depict the 'front' atom as a dot, and the 'back' atom as a larger circle.



The six carbon-hydrogen bonds are shown as solid lines protruding from the two carbons at 120°angles, which is what the actual tetrahedral geometry looks like when viewed from this perspective and flattened into two dimensions.

Figure 3.6.1: A 3D Model of Staggered Ethane.

The lowest energy conformation of ethane, shown in the figure above, is called the ‘staggered’ conformation. In the staggered conformation, all of the C-H bonds on the front carbon are positioned at an angle of 60° relative to the C-H bonds on the back carbon. This angle between a sigma bond on the front carbon compared to a sigma bond on the back carbon is called the dihedral angle. In this conformation, the distance between the bonds (and the electrons in them) is maximized. Maximizing the distance between the electrons decreases the electrostatic repulsion between the electrons and results in a more stable structure.

If we now rotate the front CH_3 group 60° clockwise, the molecule is in the highest energy ‘eclipsed' conformation, and the hydrogens on the front carbon are as close as possible to the hydrogens on the back carbon.



“eclipsed” conformation

This is the highest energy conformation because of unfavorable electrostatic repulsion between the electrons in the front and back C-H bonds. The energy of the eclipsed conformation is approximately 3 kcal/mol (12 kJ/mol) higher than that of the staggered conformation. **Torsional strain** (or eclipsing strain) is the name give to the energy difference caused by the increased electrostatic repulsion of eclipsing bonds.

Another 60° rotation returns the molecule to a second staggared conformation. This process can be continued all around the 360° circle, with three possible eclipsed conformations and three staggered conformations, in addition to an infinite number of variations in between. We will focus on the staggered and eclipsed conformers since they are, respectively, the lowest and highest energy conformers.

Unhindered (Free) Rotations Do Not Exist in Ethane

The carbon-carbon bond is not *completely* free to rotate – the 3 kcal/mol torsional strain in ethane creates a barrier to rotation that must be overcome for the bond to rotate from one staggered conformation to another. This rotational barrier is not large enough to prevent rotation except at extremely cold temperatures. So at normal temperatures, the carbon-carbon bond is constantly rotating. However, at any given moment the molecule is more likely to be in a staggered conformation - one of the rotational ‘energy valleys’ - than in any other conformer. The potential energy associated with the various conformations of ethane varies with the dihedral angle of the bonds, as shown in Figure 3.6.2.

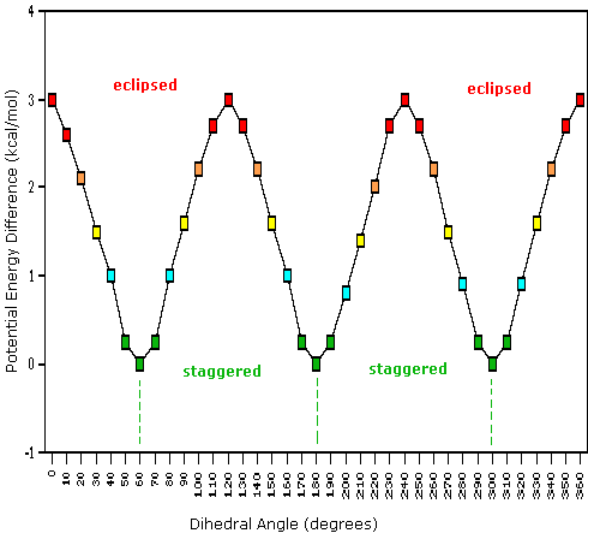


Figure 3.6.2: The potential energy associated with the various conformations of ethane varies with the dihedral angle of the bonds. Valleys in the graph represent the low energy staggered conformers, while peaks represent the higher energy eclipsed conformers.

Although the conformers of ethane are in rapid equilibrium with each other, the 3 kcal/mol energy difference leads to a substantial preponderance of staggered conformers (> 99.9%) at any given time. The animation below illustrates the relationship between ethane's potential energy and its dihedral angle

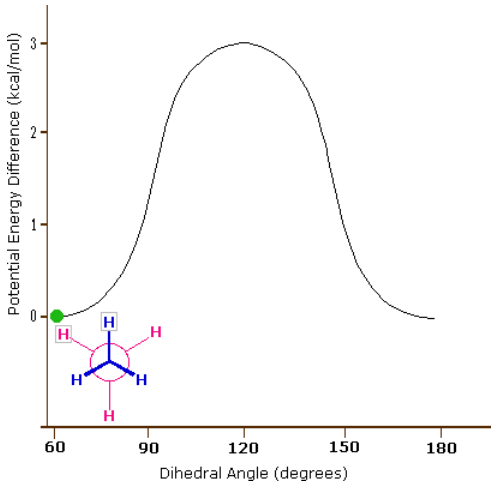


Figure 3.6.2: Animation of potential energy vs. dihedral angle in ethane

Exercises

1) What is the most stable rotational conformation of ethane and explain why it is preferred over the other conformation?

Solutions

1) Staggered, as there is less repulsion between the hydrogen atoms.

Questions

Q3.6.1

What is the most stable rotational conformation of ethane and explain why it is preferred over the other conformation?

Solutions

S3.6.1

Staggered, as there is less repulsion between the hydrogen atoms.

9.1: Rotation about Single Bonds- Conformations is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **3.6: Conformations of Ethane** by Dietmar Kennepohl, Krista Cunningham, Steven Farmer, William Reusch is licensed CC BY-SA 4.0.

9.2: Rotation in Substituted Ethanes

Objectives

After completing this section, you should be able to

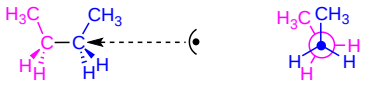
1. depict the staggered and eclipsed conformers of propane (or a similar compound) using sawhorse representations and Newman projections.
2. sketch a graph of energy versus bond rotation for propane (or a similar compound) and discuss the graph in terms of torsional strain.
3. depict the anti, gauche, eclipsed and fully eclipsed conformers of butane (or a similar compound), using sawhorse representations and Newman projections.
4. sketch a graph of energy versus C_2-C_3 bond rotation for butane (or a similar compound), and discuss it in terms of torsional and steric repulsion.
5. assess which of two (or more) conformers of a given compound is likely to predominate at room temperature from a semi-quantitative knowledge of the energy costs of the interactions involved.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- anti conformation
- gauche conformation
- eclipsed conformation
- steric repulsion (strain)

In butane, there are three rotating carbon-carbon sigma bonds to consider, but we will focus on the middle bond between C_2 and C_3. Below are two representations of butane in a conformation which puts the two CH_3 groups (C_1 and C_4) in the eclipsed position.

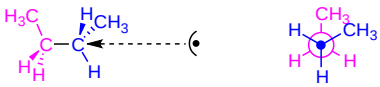


"eclipsed" (A)

Eclipsed interaction	Energy (kcal/mol)	Energy (kJ/mol)
H-H	1.0	4.0
H-CH_3	1.4	6.0
CH_3-CH_3	2.6	11.0

The CH_3-CH_3 groups create the significantly larger eclipsed interaction of 11.0 kJ/mol. There are also two H-H eclipsed interactions at 4.0 kJ/mol each to create a total of 2(4.0 kJ/mol) + 11.0 kJ/mol = 19.0 kJ/mol of strain. This is the highest energy conformation for butane, due to torsional strain caused by the electrostatic repulsion of electrons in the eclipsed bonds, but also because of another type of strain called '**steric repulsion'**, between the two rather bulky methyl groups. Steric strain comes about when two large groups, such as two methyl groups, try to occupy the same space. What results is a repulsive non-covalent interaction caused by their respective electron densities.

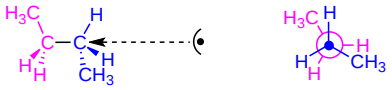
If we rotate the front, (blue) carbon by 60°clockwise, the butane molecule is now in a staggered conformation.



gauche

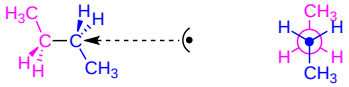
This is more specifically referred to as the '**gauche'** conformation of butane. Notice that although they are staggered, the two methyl groups are not as far apart as they could possibly be. There is still significant steric repulsion between the two bulky groups.

A further rotation of 60° gives us a second eclipsed conformation (B) in which both methyl groups are lined up with hydrogen atoms.



"eclipsed" (B)

Due to steric repulsion between methyl and hydrogen substituents, this eclipsed conformation B is higher in energy than the gauche conformation. However, because there is no methyl-to-methyl eclipsing, it is lower in energy than eclipsed conformation A. One more 60° rotation produces the **'anti'** conformation, where the two methyl groups are positioned opposite each other and steric repulsion is minimized.



anti

The anti conformation is the lowest energy conformation for butane. The diagram below summarizes the relative energies for the various eclipsed, staggered, and gauche conformations.

Figure* 9.2.1:* A 3D Structure of the Anti Butane Conformer.

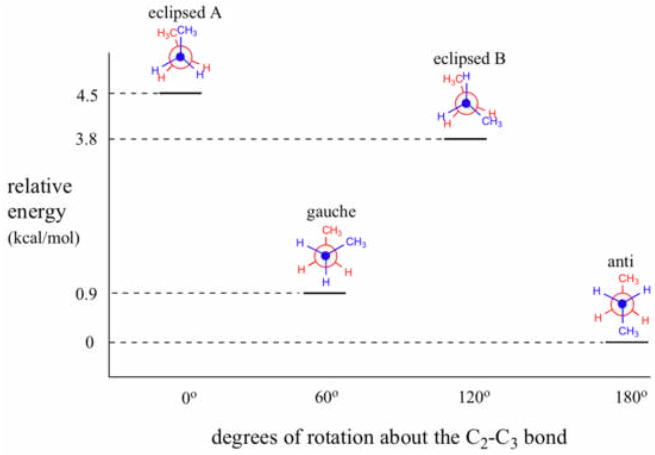


Figure 9.2.2: Potential curve vs dihedral angle of the C_2-C_3 bond of butane.

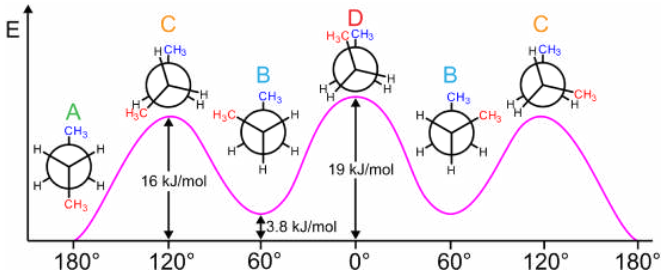
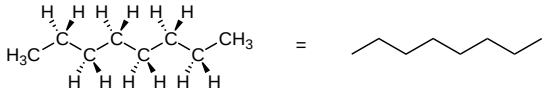


Figure 9.2.2: Newman projections of butane conformations & their relative energy differences (not total energies). Conformations form when butane rotates about one of its single covalent bond. Torsional/dihedral angle is shown on x-axis. Torsional/dihedral angle is shown on x-axis. Conformation names (according to IUPAC): **A**: anti-periplanar, anti or trans **B**: synclinal or gauche **C**: anticlinal or eclipsed **D**: syn-periplanar or cis. Source for conformation names & conformer classification: Pure & Appl. Chem., Vol. 68, No. 12, pp. 2193-2222, 1996. (Public Domain; Keministi).

At room temperature, butane is most likely to be in the lowest-energy anti conformation at any given moment in time, although the energy barrier between the anti and eclipsed conformations is not high enough to prevent constant rotation except at very low temperatures. For this reason (and also simply for ease of drawing), it is conventional to draw straight-chain alkanes in a zigzag form, which implies the anti conformation at all carbon-carbon bonds. For example octane is commonly drawn as:



octane

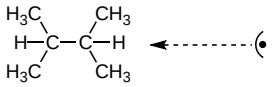
Drawing Newman Projections

Newman projections are a valuable method for viewing the relative positions of groups within molecule. Being able to draw the Newman projection for a given molecule is a valuable skill and will be used repeatedly throughout organic chemistry. Because organic molecules often contain multiple carbon-carbon bonds it is important to precisely know which bond and which direction is being sighted for the Newman projection. The details of the Newman projection change given the molecule but for typical alkanes a full conformational analysis involves a full 360^o rotation in 60^o increments. This will produce three staggered conformers and three eclipsed conformers. Typically, the staggered conformers are more stable and the eclipsed conformers are less stable. The least stable conformer will have the largest groups eclipsed while the most stable conformer will have the largest groups anti (180^o) to each other.

Example

Draw the Newman projection of 2,3 dimethylbutane along the C_2-C_3 bond. Then determine the least stable conformation.

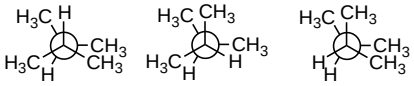
First draw the molecule and locate the indicated bond:



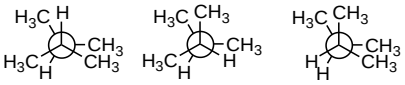
Because the question asks for the least stable conformation, focus on the three possible eclipsed Newman projections. Draw out three eclipsed Newman projections as a template. Because it is difficult to draw a true staggered Newman projection, it is common to show the bonds slightly askew.



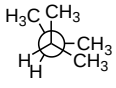
Place the substituents attached to the second carbon (C_3) on the back bonds of all three Newman projections. In this example they are 2 CH_3s and an H. Place the substituents in the same position on all three Newman projections.



Then place the substituents attached to the first carbon (C_2) on the front bonds of the Newman projection. In this example, the substituents are also 2 CH_3s and an H. Move the substituents through two 60^o rotations to create the remaining two eclipsed Newman projections. Leave the substituents on the back carbon in place. Attempting to rotate the front and back carbons simultaneously is a common mistake and often leads to incorrect Newman projections.



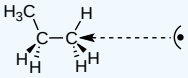
Compare the Newman projections by looking the eclipsed interactions. Remember that the order of torsional strain interactions are CH_3-CH_3 > CH_3-H > H-H. The third structure has two CH_3-CH_3 torsional interactions which will make it the least stable conformer of 2,3 dimethyl butane.



Example 9.2.1

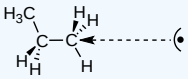
Draw Newman projections of the eclipsed and staggered conformations of propane, as if viewed down the C_1-C_2 bond.

Answer





highest energy
(eclipsed)

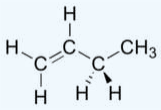




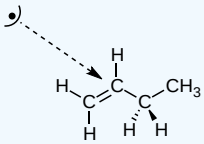
lowest energy
(staggered)

Example 9.2.2

Draw a Newman projection, looking down the C_2-C_3 bond, of 1-butene in the conformation shown below.



Answer





Exercises

9.2: Rotation in Substituted Ethanes is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **3.7: Conformations of Other Alkanes** by Dietmar Kennepohl, Jim Clark, Krista Cunningham, Steven Farmer, Tim Soderberg, William Reusch is licensed CC BY-SA 4.0.

9.3: Ring Strain and the Structure of Cycloalkanes

Objectives

After completing this section, you should be able to:

- Describe the Baeyer strain theory.
- Describe how the measurement of heats of combustion provides information about the amount of strain present in a cycloalkane ring.
- Determine the relative stability of cyclic compounds, by assessing such factors as angle strain, torsional strain and steric strain.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- angle strain
- steric strain
- torsional strain
- ring strain
- heat of combustion

Heat of Combustion as a Measure of Bond Strength

The combustion of carbon compounds, especially hydrocarbons, has been the most important source of heat energy for human civilizations throughout recorded history. The practical importance of this reaction cannot be denied, but the massive and uncontrolled chemical changes that take place in combustion make it difficult to deduce mechanistic paths. Using the combustion of propane as an example, we see from the following equation that every covalent bond in the reactants has been broken and an entirely new set of covalent bonds have formed in the products. No other common reaction involves such a profound and pervasive change, and the mechanism of combustion is so complex that chemists are just beginning to explore and understand some of its elementary features.

$$\mathrm{CH_3CH_2CH_3 + 5\,O_2 \longrightarrow 3\,CO_2 + 4\,H_2O + heat}$$

Since all the covalent bonds in the reactant molecules are broken, the quantity of heat evolved in this reaction, and any other combustion reaction, is related to the strength of these bonds (and, of course, the strength of the bonds formed in the products). Precise heat of combustion measurements can provide useful information about the structure of molecules and their relative stability.

For example, heat of combustion is useful in determining the relative stability of isomers. Pentane has a heat of combustion of -782 kcal/mol, while that of its isomer, 2,2-dimethylpropane (neopentane), is –777 kcal/mol. These values indicate that 2,3-dimethylpentane is 5 kcal/mol more stable than pentane, since it has a lower heat of combustion.

Ring Strain

Table 9.3.1 lists the heat of combustion data for some simple cycloalkanes. These cycloalkanes do not have the same molecular formula, so the heat of combustion per each CH_2 unit present in each molecule is calculated (the fourth column) to provide a useful comparison. From the data, cyclopropane and cyclobutane have significantly higher heats of combustion per CH_2, while cyclohexane has the lowest heat of combustion. This indicates that cyclohexane is more stable than cyclopropane and cyclobutane, and in fact, that cyclohexane has a same relative stability as long chain alkanes that are not cyclic. This difference in stability is seen in nature where six membered rings are by far the most common. What causes the difference in stability or the strain in small cycloalkanes?

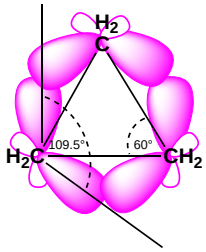
Table 9.3.1: Heats of combustion of select hydrocarbons

Cycloalkane $(CH_2)_n$	CH_2 Units n	ΔH^{25° kcal/mol	ΔH^{25° per CH_2 Unit	Ring Strain kcal/mol

Cycloalkane $(CH_2)_n$	CH_2 Units n	ΔH^{25° kcal/mol	ΔH^{25° per CH_2 Unit	Ring Strain kcal/mol
Cyclopropane	n = 3	468.7	156.2	27.6
Cyclobutane	n = 4	614.3	153.6	26.4
Cyclopentane	n = 5	741.5	148.3	6.5
Cyclohexane	n = 6	882.1	147.0	0.0
Cycloheptane	n = 7	1035.4	147.9	6.3
Cyclooctane	n = 8	1186.0	148.2	9.6
Cyclononane	n = 9	1335.0	148.3	11.7
Cyclodecane	n = 10	1481	148.1	11.0
$CH_3(CH_2)_mCH_3$	m = large	—	147.0	0.0

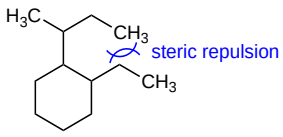
The Baeyer Theory on the Strain in Cycloalkane Rings

In 1890, the famous German organic chemist, A. Baeyer, suggested that cyclopropane and cyclobutane are less stable than cyclohexane, because the the smaller rings are more "strained". There are many different types of strain that contribute to the overall ring strain in cycloalkanes, including angle strain, torsional strain, and steric strain. **Torsional strain** and **steric strain** were previously defined in the discussion of conformations of butane. **Angle Strain** occurs when the sp^3 hybridized carbons in cycloalkanes do not have the expected ideal bond angle of 109.5º, causing an increase in the potential energy. An example of angle strain can be seen in the diagram of cyclopropane below in which the bond angle is 60º between the carbons. The compressed bond angles causes poor overlap of the hybrid orbitals forming the carbon-carbon sigma bonds which in turn creates destabilization.



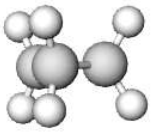
The C-C-C bond angles in cyclopropane (diagram above) (60º) and cyclobutane (90º) are much different than the ideal bond angle of 109.5º. This bond angle causes cyclopropane and cyclobutane to be less stable than molecules such as cyclohexane and cyclopentane, which have a much lower ring strain because the bond angle between the carbons is much closer to 109.5º. Changes in chemical reactivity as a consequence of angle strain are dramatic in the case of cyclopropane, and are also evident for cyclobutane.

In addition to angle strain, there is also steric (transannular) strain and torsional strain in many cycloalkanes. Transannular strain exists when there is steric repulsion between atoms.



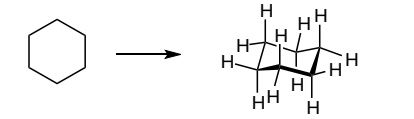
transannular strain

Because cycloalkane lack the ability to freely rotate, torsional (eclipsing) strain exists when a cycloalkane is unable to adopt a staggered conformation around a C-C bond. Torsional strain is especially prevalent in small cycloalkanes, such as cyclopropane, whose structures are nearly planar.



The Eclipsed C-H Bonds in Cyclopropane

Larger rings like cyclohexane, deal with torsional strain by forming conformers in which the rings are not planar. A conformer is a stereoisomer in which molecules of the same connectivity and formula exist as different isomers, in this case, to reduce ring strain. The ring strain is reduced in conformers due to the rotations around the sigma bonds, which decreases the angle and torsional strain in the ring. The non-planar structures of cyclohexane are very stable compared to cyclopropane and cyclobutane, and will be discussed in more detail in the next section.



The Types of Strain Which Contribute to Ring Strain in Cycloalkanes

- Angle Strain - The strain caused by the increase or reduction of bond angles
- Torsional Strain - The strain caused by eclipsing bonds on adjacent atoms
- Steric Strain - The strain caused by the repulsive interactions of atoms trying to occupy the same space

Exercise 9.3.1

trans-1,2-Dimethylcyclobutane is more stable than *cis*-1,2-dimethylcyclobutane. Explain this observation.

Answer

The trans form does not have eclipsing methyl groups, therefore lowering the energy within the molecule. It does however have hydrogen-methyl eclipsing interactions which are not as high in energy as methyl-methyl interactions.

Exercise 9.3.2

Cyclobutane has more torsional stain than cyclopropane. Explain this observation.

Answer

Cyclobutane has 4 CH_2 groups while cyclopropane only has 3. More CH2 groups means cyclobutane has more eclipsing H-H interactions and therefore has more torsional strain.

Exercises

1. *Trans*-1,2-Dimethylcyclobutane is more stable than *cis*-1,2-dimethylcyclobutane. Explain this observation.
2. The trans form does not have eclipsing methyl groups, therefore lowering the energy within the molecule. It does however have hydrogen-methyl interactions, but are not as high in energy than methyl-methyl interactions.

Objectives

After completing this section, you should be able to

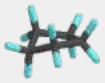
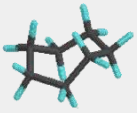
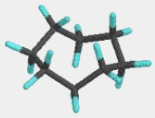
1. describe, and sketch the conformation of cyclopropane, cyclobutane, and cyclopentane.
2. describe the bonding in cyclopropane, and use this to account for the high reactivity of this compound.

3. analyze the stability of cyclobutane, cyclopentane and their substituted derivatives in terms of angular strain, torsional strain and steric interactions.

Study Notes

Notice that in both cyclobutane and cyclopentane, torsional strain is reduced at the cost of increasing angular (angle) strain.

Although the customary line drawings of simple cycloalkanes are geometrical polygons, the actual shape of these compounds in most cases is very different.

cyclopropane	cyclobutane	cyclopentane	cyclohexane	cycloheptane	cyclooctane
					

Cyclopropane is necessarily planar (flat), with the carbon atoms at the corners of an equilateral triangle. The 60º bond angles are much smaller than the optimum 109.5º angles of a normal tetrahedral carbon atom, and the resulting angle strain dramatically influences the chemical behavior of this cycloalkane. Cyclopropane also suffers substantial eclipsing strain, since all the carbon-carbon bonds are fully eclipsed. Cyclobutane reduces some bond-eclipsing strain by folding (the out-of-plane dihedral angle is about 25º), but the total eclipsing and angle strain remains high. Cyclopentane has very little angle strain (the angles of a pentagon are 108º), but its eclipsing strain would be large (about 40 kJ/mol) if it remained planar. Consequently, the five-membered ring adopts non-planar puckered conformations whenever possible.

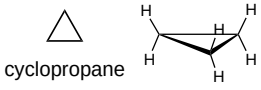
Rings larger than cyclopentane would have angle strain if they were planar. However, this strain, together with the eclipsing strain inherent in a planar structure, can be relieved by puckering the ring. Cyclohexane is a good example of a carbocyclic system that virtually eliminates eclipsing and angle strain by adopting non-planar conformations. Cycloheptane and cyclooctane have greater strain than cyclohexane, in large part due to transannular crowding (steric hindrance by groups on opposite sides of the ring).

Cyclic systems are a little different from open-chain systems. In an open chain, any bond can be rotated 360º, going through many different conformations. That complete rotation isn't possible in a cyclic system, because the parts that would be trying to twist away from each other would still be connected together. Thus cyclic systems have fewer "degrees of freedom" than aliphatic systems; they have "restricted rotation".

Because of the restricted rotation of cyclic systems, most of them have much more well-defined shapes than their aliphatic counterparts. Let's take a look at the basic shapes of some common rings. Many biologically important compounds are built around structures containing rings, so it's important that we become familiar with them. In nature, three- to six-membered rings are frequently encountered, so we'll focus on those.

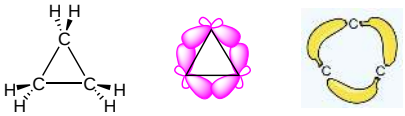
Cyclopropane

A three membered ring has no rotational freedom whatsoever. A plane is defined by three points, so the three carbon atoms in cyclopropane are all constrained to lie in the same plane. This lack of flexibility does not allow cyclopropane to form more stable conformers which are non-planar.



The main source of ring strain in cyclopropane is angle strain. All of the carbon atoms in cyclopropane are tetrahedral and would prefer to have a bond angle of 109.5^{o} The angles in an equilateral triangle are actually 60^{o}, about half as large as the optimum angle. The large deviation from the optimal bond angle means that the C-C sigma bonds forming the cyclopropane ring are bent. Maximum bonding occurs when the overlapping orbitals are pointing directly toward each other. The severely strained bond angles in cyclopropane means that the orbitals forming the C-C bonds overlap at a slight angle making them weaker. This strain is

partially overcome by using so-called “banana bonds”, where the overlap between orbitals is no longer directly in a line between the two nuclei, as shown here in three representations of the bonding in cyclopropane:



The constrained nature of cyclopropane causes neighboring C-H bonds to all be held in eclipsed conformations. Cyclopropane is always at maximum torsional strain. This strain can be illustrated in a Newman projections of cyclopropane as shown from the side.



Newman Projection of cyclopropane

Cyclopropane isn't large enough to introduce any steric strain. Steric strain does not become a factor until we reach six membered rings. Before that point, rings are not flexible enough to allow for two ring substituents to interact with each other.

The combination of torsional and angle strain creates a large amount of ring strain in cyclopropane which weakens the C-C ring bonds (255 kJ/mol) when compared to C-C bonds in open-chain propane (370 kJ/mol).

Cyclobutane

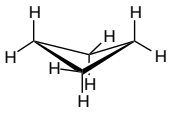
Cyclobutane is a four membered ring. The larger number of ring hydrogens would cause a substantial amount of torsional strain if cyclobutane were planar.



cyclobutane

In three dimensions, cyclobutane is flexible enough to buckle into a "puckered" shape which causes the C-H ring hydrogens to slightly deviate away from being completely eclipsed. This conformation relives some of the torsional strain but increases the angle strain because the ring bond angles decreases to 88^{o}.

In a line drawing, this butterfly shape is usually shown from the side, with the near edges drawn using darker lines.



The deviation of cyclobutane's ring C-H bonds away from being fully eclipsed can clearly be seen when viewing a Newman projections signed down one of the C-C bond.



Newman projection of cyclobutane

- With bond angles of 88^{o} rather than 109.5^{o} degrees, cyclobutane has significant amounts of angle strain, but less than in cyclopropane.
- Although torsional strain is still present, the neighboring C-H bonds are not exactly eclipsed in the cyclobutane's puckered conformation.
- Steric strain is very low. Cyclobutane is still not large enough that substituents can reach around to cause crowding.
- Overall the ring strain in cyclobutane (110 kJ/mol) is slightly less than cyclopropane (115 kJ/mol).

Cyclopentane

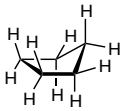
Cyclopentanes are even more stable than cyclobutanes, and they are the second-most common cycloalkane ring in nature, after cyclohexanes. Planar cyclopentane has virtually no angle strain but an immense amount of torsional strain. To reduce torsional

strain, cyclopentane addops a non-planar conformation even though it slightly increases angle strain.



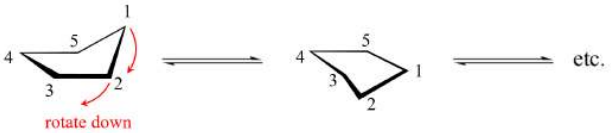
cyclopentane

The lowest energy conformation of cyclopentane is known as the ‘envelope’, with four of the ring atoms in the same plane and one out of plane (notice that this shape resembles an envelope with the flap open). The out-of-plane carbon is said to be in the ***endo*** position (‘*endo*’ means ‘inside’). The envelope removes torsional strain along the sides and flap of the envelope. However, the neighboring carbons are eclipsed along the "bottom" of the envelope, away from the flap.

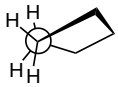


3D structure of cyclopentane (notice that the far top right carbon is the endo position).

At room temperature, cyclopentane undergoes a rapid bond **rotation** process in which each of the five carbons takes turns being in the *endo* position.



Cyclopentane distorts only very slightly into an "envelope" shape in which one corner of the pentagon is lifted up above the plane of the other four. The envelope removes torsional strain along the sides and flap of the envelope by allowing the bonds to be in an almost completely staggered position. However, the neighboring bonds are eclipsed along the "bottom" of the envelope, away from the flap. Viewing a Newman projections of cyclopentane signed down one of the C-C bond show the staggered C-H bonds.

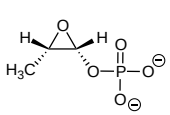


Newman projection of cyclopentane

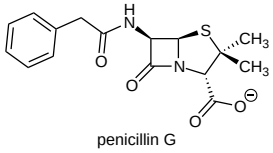
- The angle strain in the envelope conformation of cyclopentane is low. The ideal angle in a regular pentagon is about 107^{o}, very close to the preferred 109.5^{o} tetrahedral bond angle.
- There is some torsional strain in cyclopentane. The envelope conformation reduces torsional strain by placing some bonds in nearly staggered positions. However, other bonds are still almost fully eclipsed.
- Cyclopentane is not large enough to allow for steric strain to be created.
- Overall, cyclopentane has very little ring strain (26 kJ/mol) when compared to cyclopropane and cyclobutane.

C_3-C_5 Cycloalkanes in Nature

If one of the carbon-carbon bonds is broken in cyclopropane or cyclobutane, the ring will ‘spring’ open, releasing energy as the bonds reassume their preferred tetrahedral geometry. The effectiveness of two antibiotic drugs, fosfomycin and penicillin, is due in large part to the high reactivity of the three- and four-membered rings in their structures.

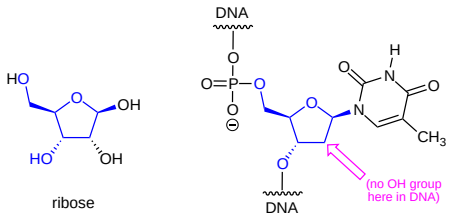


fosfomycin

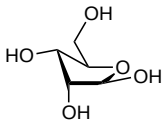


penicillin G

One of the most important five-membered rings in nature is a sugar called ribose – DNA and RNA are both constructed upon ‘backbones’ derived from ribose. Pictured below is one thymidine (T) deoxy-nucleotide from a stretch of DNA. Since the ribose has lost one of the OH groups (at carbon 2 of the ribose ring), this is part of a deoxyribonucleic acid (DNA). If the OH at carbon 2 of the ribose ring was present, this would be part of a ribonucleic acid (RNA).



The lowest-energy conformations for ribose are envelope forms in which either C_3 or C_2 are *endo*, on the same side as the C_5 substituent.



? Exercise 9.3.1

If cyclobutane were to be planar, how many H-H eclipsing interactions would there be? Assuming 4 kJ/mol per H-H eclipsing interaction what would the strain be on this “planar” molecule?

Answer

There are eight eclipsing interactions (two per C-C bond). The extra strain on this molecule would be 32 kJ/mol (4 kJ/mol x 8).

? Exercise 9.3.1

In the two conformations of *trans*-1,2-Dimethylcyclopentane one is more stable than the other. Explain why this is.



Answer

The first conformation is more stable. Even though the methyl groups are *trans* in both models, they are anti to one another in the first structure (which is lower energy) while they are gauche in the second structure increasing strain within the molecule.

? Exercise 9.3.3

In methylcyclopentane, which carbon would most likely be in the *endo* position?

Answer

The ring carbon attached to the methyl group would most likely be the endo carbon. The large methyl group would create the most torsional strain if eclipsed. Being in the *endo* position would place the bonds is a more staggered position which would reduce strain.

? Exercise 9.3.4

If cyclobutane were to be planar how many H-H eclipsing interactions would there be, and assuming 4 kJ/mol per H-H eclipsing interaction what is the strain on this “planar” molecule?

Answer

There are eight eclipsing interactions (two per C-C bond). The extra strain on this molecule would be 32 kJ/mol (4 kJ/mol x 8).

? Exercise 9.3.5

In the two conformations of *trans*-cyclopentane one is more stable than the other. Explain why this is.



Answer

The first conformation is more stable. Even though the methyl groups are *trans* in both models, in the second structure they are eclipsing one another, therefore increasing the strain within the molecule compared to the first structure where the larger methyl groups are anti to one another.

9.3: Ring Strain and the Structure of Cycloalkanes is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **4.3: Stability of Cycloalkanes - Ring Strain** by Dietmar Kennepohl, Kelly Matthews, Krista Cunningham, Steven Farmer, Tim Soderberg, William Reusch is licensed CC BY-SA 4.0.
- **4.4: Conformations of Cycloalkanes** by Chris Schaller, Dietmar Kennepohl, Krista Cunningham, Layne Morsch, Steven Farmer, William Reusch is licensed CC BY-SA 4.0.

9.4: Cyclohexane- A Strain-Free Cycloalkane

Objectives

After completing this section, you should be able to

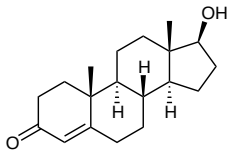
1. explain why cyclohexane rings are free of angular strain.
2. draw the structure of a cyclohexane ring in the chair conformation.

Key Terms

Make certain that you can define, and use in context, the key terms below.

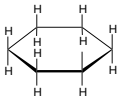
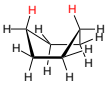
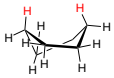
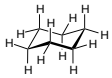
- chair conformation
- twist-boat conformation

We will find that cyclohexanes tend to have the least angle strain and consequently are the most common cycloalkanes found in nature. A wide variety of compounds including, hormones, pharmaceuticals, and flavoring agents have substituted cyclohexane rings.



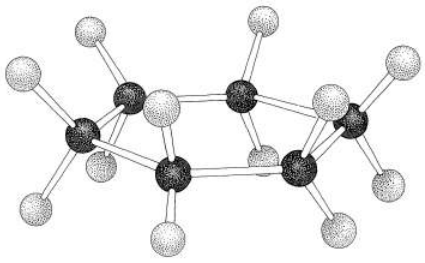
testosterone, which contains three cyclohexane rings and one cyclopentane ring

Rings larger than cyclopentane would have angle strain if they were planar. However, this strain, together with the eclipsing strain inherent in a planar structure, can be relieved by puckering the ring. Cyclohexane is a good example of a carbocyclic system that virtually eliminates eclipsing and angle strain by adopting non-planar conformations. Cycloheptane and cyclooctane have greater strain than cyclohexane, in large part due to transannular crowding (steric hindrance by groups on opposite sides of the ring). Cyclohexane has the possibility of forming multiple conformations each of which have structural differences which lead to different amounts of ring strain.

			
planar structure severe angle strain (120°) severe eclipsing strain (all bonds) small steric strain	**boat conformation** slight angle strain eclipsing strain at two bonds steric crowding of two hydrogens	**twist boat conformation** slight angle strain small eclipsing strain small steric strain	**chair conformation** no angle strain no eclipsing strain small steric strain

Conformations of Cyclohexane

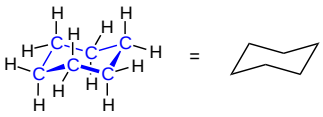
A planar structure for cyclohexane is clearly improbable. The bond angles would necessarily be 120º, 10.5º larger than the ideal tetrahedral angle. Also, every carbon-hydrogen bond in such a structure would be eclipsed. The resulting angle and eclipsing strains would severely destabilize this structure. The ring strain of planar cyclohexane is in excess of 84 kJ/mol so it rarely discussed other than in theory.



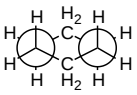
Cyclohexane in the strained planar configuration showing how the hydrogens become eclipsed.

Chair Conformation of Cyclohexane

The flexibility of cyclohexane allows for a conformation which is almost free of ring strain. If two carbon atoms on opposite sides of the six-membered ring are bent out of the plane of the ring, a shape is formed that resembles a reclining beach chair. This **chair conformation** is the lowest energy conformation for cyclohexane with an overall ring strain of 0 kJ/mol. In this conformation, the carbon-carbon ring bonds are able to assume bonding angles of ~111^{o} which is very near the optimal tetrahedral 109.5^{o} so angle strain has been eliminated.

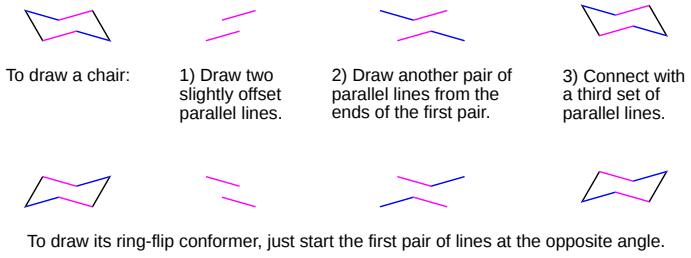


Also, the C-H ring bonds are staggered so torsional strain has also been eliminated. This is clearly seen when looking at a Newman projection of chair cyclohexane sighted down the two central C-C bonds.



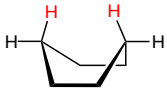
Newman projection of cyclohexane

How to Draw the Chair Conformation



Boat Conformation of Cyclohexane

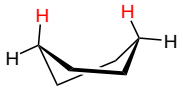
The **Boat Conformation** of cyclohexane is created when two carbon atoms on opposite sides of the six-membered ring are both lifted up out of the plane of the ring creating a shape which slightly resembles a boat. The boat conformation is less stable than the chair form for two major reasons. The boat conformation has unfavorable steric interactions between a pair of 1,4 hydrogens (the so-called "flagpole" hydrogens) that are forced to be very close together (1.83Å). This steric hindrance creates a repulsion energy of about 12 kJ/mol. An additional cause of the higher energy of the boat conformation is that adjacent hydrogen atoms on the 'bottom of the boat' are forced into eclipsed positions. For these reasons, the boat conformation about 30 kJ/mol less stable than the chair conformation.



A boat structure of cyclohexane (the interfering "flagpole" hydrogens are shown in red)

Twist-Boat Conformation of Cyclohexane

The boat form is quite flexible and by twisting it at the bottom created the **twist-boat conformer**. This conformation reduces the strain which characterized the boat conformer. The flagpole hydrogens move farther apart (the carbons they are attached to are shifted in opposite directions, one forward and one back) and the eight hydrogens along the sides become largely but not completely staggered. Though more stable than the boat conformation, the twist-boat (sometimes skew-boat) conformation is roughly 23 kJ/mol less stable than the chair conformation.



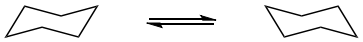
A twist-boat structure of cyclohexane

Half Chair Conformation of Cyclohexane

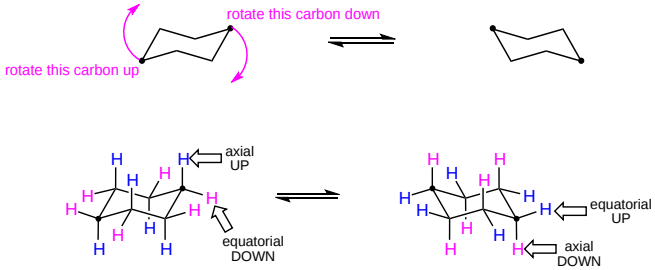
Cyclohexane can obtain a partially plane conformation called "half chair" but with only with excessive amounts of ring strain. The half chair conformation is formed by taking planar cyclohexane and lifting one carbon out of the plane of the ring. The half chair conformation has much of the same strain effects predicted by the fully planar cyclohexane. In the planar portion of half chair cyclohexane the C-C bond angles are forced to 120º which creates significant amounts of angle strain. Also, the corresponding C-H bonds are fully eclipsed which create torsional strain. The out-of-plane carbon allows for some of the ring's bond angles to reach 109.5º and for some of C-H bonds to not be fully eclipsed. Overall, the half chair conformation is roughly 45 kJ/mol less stable than the chair conformation.

Conformation Changes in Cyclohexane - "Ring Flips"

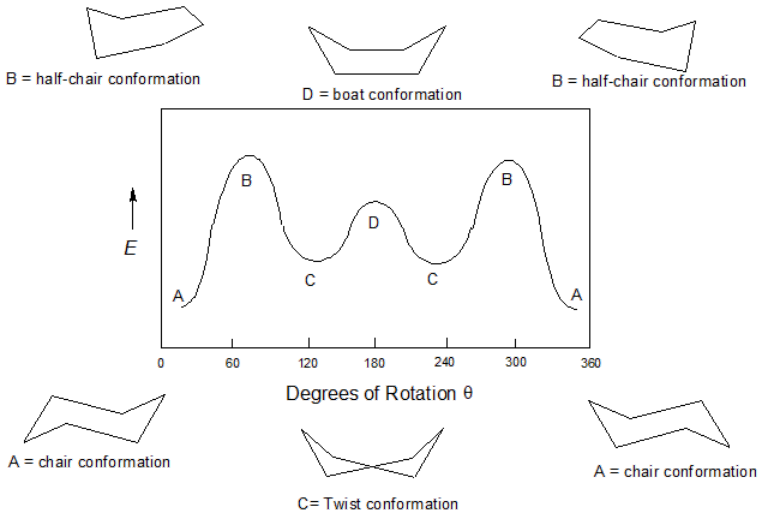
Cyclohexane is rapidly rotating between the two most stable conformations known as the chair conformations in what is called the "ring flip" shown below. The importance of the ring flip will be discussed in the next section.



"Ring flip" describes the rapid equilibrium of cyclohexane rings between the two chair conformations



It is important to note that one chair does not immediately become the other chair, rather the ring must travel through the higher energy conformations as transitions. At room temperature the energy barrier created by the half chair conformation is easily overcome allowing for equilibration between the two chair conformation on the order of 80,000 times per second. Although cyclohexane is continually converting between these different conformations, the stability of the chair conformation causes it to comprises more than 99.9% of the equilibrium mixture at room temperature.



1" id="MathJax-Element-12-Frame" role="presentation" style="position:relative;" tabindex="0">Image of energy diagram of cyclohexane conformations

1" role="presentation" style="position:relative;" tabindex="0">

Exercises

1) Consider the conformations of cyclohexane: half chair, chair, boat, twist boat. Order them in increasing ring strain in the molecule.

Solutions

1) Chair < Twist Boat < Boat < half chair (most ring strain)

Questions

Q4.5.1

Consider the conformations of cyclohexane, chair, boat, twist boat. Order them in increasing strain in the molecule.

Solutions

S4.5.1

Chair < Twist Boat < Boat (most strain)

Objectives

After completing this section, you should be able to

1. Draw the chair conformation of cyclohexane, with axial and equatorial hydrogen atoms clearly shown and identified.
2. identify the axial and equatorial hydrogens in a given sketch of the cyclohexane molecule.
3. explain how chair conformations of cyclohexane and its derivatives can interconvert through the process of ring flip.

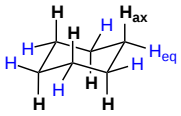
Key Terms

Make certain that you can define, and use in context, the key terms below.

- axial position
- equatorial position
- ring flip

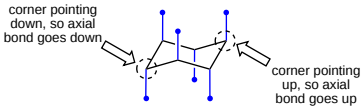
Axial and Equatorial Positions in Cyclohexane

Careful examination of the chair conformation of cyclohexane, shows that the twelve hydrogens are not structurally equivalent. Six of them are located about the periphery of the carbon ring, and are termed **equatorial**. The other six are oriented above and below the approximate plane of the ring (three in each location), and are termed **axial** because they are aligned parallel to the symmetry axis of the ring.

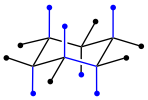


In the figure above, the equatorial hydrogens are colored blue, and the axial hydrogens are black. Since there are two equivalent chair conformations of cyclohexane in rapid equilibrium, all twelve hydrogens have 50% equatorial and 50% axial character.

How To Draw Axial and Equatorial Bonds

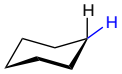


Draw axial bonds **straight up** or **straight down.**



Draw equatorial bonds **up and out** or **down and out.**

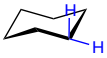
How **not** to draw the chair:



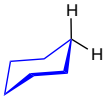
Incorrect. Equatorial bond should be **down** and **out**.



Incorrect. Axial bond should be **straight up**.



Incorrect. Axial bond should be **straight down,** equatorial bond should be **up** and **out**.



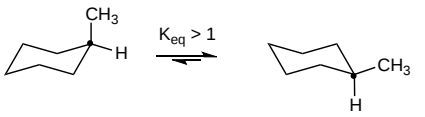
Incorrect. Ring should be tilted slightly.

Aside from drawing the basic chair, the key points are:

- Axial bonds alternate up and down, and are shown "vertical".
- Equatorial groups are approximately horizontal, but actually somewhat distorted from that (slightly up or slightly down), so that the angle from the axial group is a bit more than a right angle -- reflecting the common 109.5º bond angle.
- Each carbon has an axial and an equatorial bond.
- Each face of the cyclohexane ring has three axial and three equatorial bonds.
- Each face alternates between axial and equatorial bonds. Then looking at the "up" bond on each carbon in the cyclohexane ring they will alternate axial-equatorial-axial ect.
- When looking down at a cyclohexane ring:
  - the equatorial bonds will form an "equator" around the ring.
  - The axial bonds will either face towards you or away. These will alternate with each axial bond. The first axial bond will be coming towards with the next going away. There will be three of each type.
- Note! The terms cis and trans in regards to the stereochemistry of a ring are not directly linked to the terms axial and equatorial. It is very common to confuse the two. It typically best not to try and directly inter convert the two naming systems.

Axial vs. Equatorial Substituents

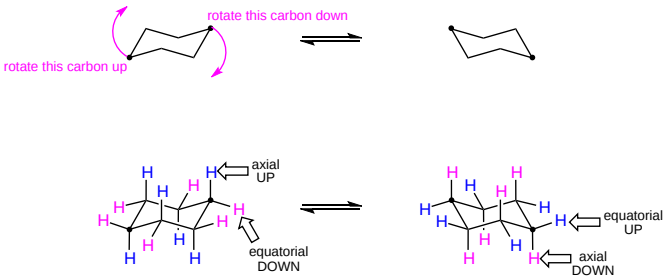
When a substituent is added to cyclohexane, the ring flip allows for two distinctly different conformations. One will have the substituent in the axial position while the other will have the substituent in the equatorial position. In the next section will discuss the energy differences between these two possible conformations. Below are the two possible chair conformations of methylcyclohexane created by a ring-flip. Although the conformation which places the methyl group in the equatorial position is more stable by 7 kJ/mol, the energy provided by ambient temperature allows the two conformations to rapidly interconvert.



methyl group axial

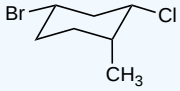
methyl group equatorial
(more stable by **7 kJ/mol**)

The figure below illustrates how to convert a molecular model of cyclohexane between two different chair conformations - this is something that you should practice with models. Notice that a 'ring flip' causes equatorial groups to become axial, and vice-versa.



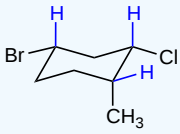
Example 9.4.1

For the following please indicate if the substituents are in the axial or equatorial positions.



Solution

Due to the large number of bonds in cyclohexane it is common to only draw in the relevant ones (leaving off the hydrogens unless they are involved in a reaction or are important for analysis). It is still possible to determine axial and equatorial positioning with some thought. With problems such as this it is important to remember that each carbon in a cyclohexane ring has one axial and one equatorial bond. Also, remember that axial bonds are perpendicular with the ring and appear to be going either straight up or straight down. Equatorial bonds will be roughly in the plane of the cyclohexane ring (only slightly up or down). Sometimes it is valuable to draw in the additional bonds on the carbons of interest.



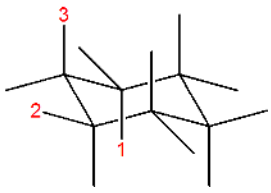
With this it can be concluded that the bromine and chlorine substituents are attached in equatorial positions and the CH_3 substituent is attached in an axial position.

Exercises

1) Draw two conformations of cyclohexyl amine ($C_6H_{11}NH_2$). Indicate axial and equatorial positions.

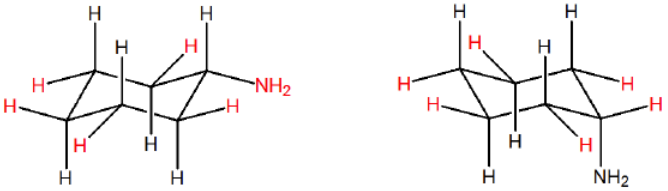
2) Draw the two isomers of 1,4-dihydroxylcyclohexane, identify which are equatorial and axial.

3) In the following molecule, label which are equatorial and which are axial, then draw the chair flip (showing labels 1,2,3).



Solutions

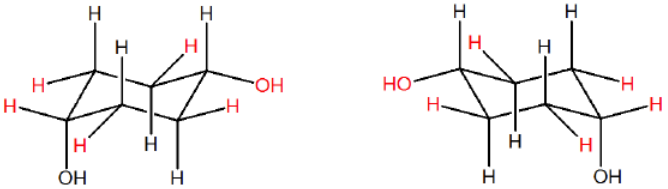
1)



Axial

Equatorial

2)

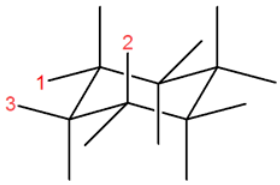


Axial

Equatorial

3) Original conformation: 1 = axial, 2 = equatorial, 3 = axial

Flipped chair now looks like this.



Questions

Q4.6.1

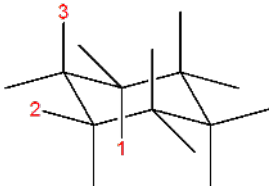
Draw two conformations of cyclohexyl amine ($C_6H_{11}NH_2$). Indicate axial and equatorial positions.

Q4.6.2

Draw the two isomers of 1,4-dihydroxylcyclohexane, identify which are equatorial and axial.

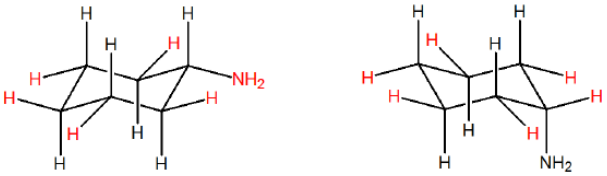
Q4.6.3

In the following molecule, label which are equatorial and which are axial, then draw the chair flip (showing labels 1,2,3).



Solutions

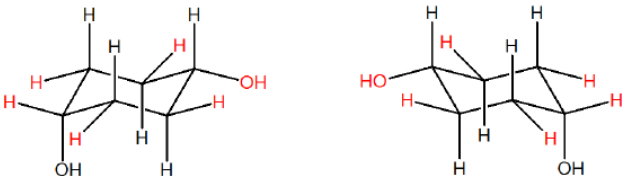
S4.6.1



Axial

Equatorial

S4.6.2



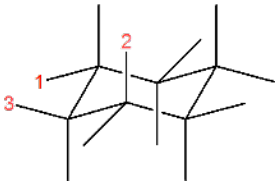
Axial

Equatorial

S4.6.3

Original conformation: 1 = axial, 2 = equatorial, 3 = axial

Flipped chair now looks like this.



9.4: Cyclohexane- A Strain-Free Cycloalkane is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **4.5: Conformations of Cyclohexane** by Dietmar Kennepohl, Krista Cunningham, Layne Morsch, Robert Bruner, Steven Farmer, William Reusch is licensed CC BY-SA 4.0.
- **4.6: Axial and Equatorial Bonds in Cyclohexane** by Dietmar Kennepohl, Kelly Matthews, Krista Cunningham, Layne Morsch, Steven Farmer, Tim Soderberg is licensed CC BY-SA 4.0.

9.5: Substituted Cyclohexanes

Objectives

After completing this section, you should be able to

1. account for the greater stability of the equatorial conformers of monosubstituted cyclohexanes compared to their axial counterparts, using the concept of 1,3-diaxial interaction.
2. compare the gauche interactions in butane with the 1,3-diaxial interactions in the axial conformer of methylcyclohexane.
3. arrange a given list of substituents in increasing or decreasing order of 1,3-diaxial interactions.

Key Terms

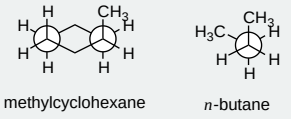
Make certain that you can define, and use in context, the key term below.

- 1,3-diaxial interaction

Study Notes

1,3-Diaxial interactions are steric interactions between an axial substituent located on carbon atom 1 of a cyclohexane ring and the hydrogen atoms (or other substituents) located on carbon atoms 3 and 5.

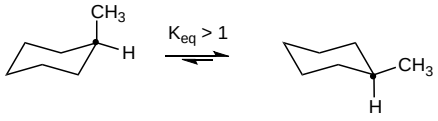
Be prepared to draw Newman-type projections for cyclohexane derivatives as the one shown for methylcyclohexane. Note that this is similar to the Newman projections from chapter 3 such as *n*-butane.



methylcyclohexane *n*-butane

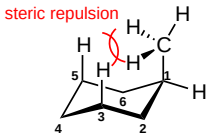
Newman projections of methylcyclohexane and *n*-butane

When a substituent is added to a cyclohexane ring, the two possible chair conformations created during a ring flip are not equally stable. In the example of methylcyclohexane the conformation where the methyl group is in the equatorial position is more stable than the axial conformation by 7.6 kJ/mol at 25º C. The percentages of the two different conformations at equilibrium can be determined by solving the following equation for K (the equilibrium constant): $\Delta E = -RT\ln K$. In this equation ΔE is the energy difference between the two conformations, R is the gas constant (8.314 J/mol•K), T is the temperature in Kelvin, and K is the equilibrium constant for the ring flip conversion. Using this equation, we can calculate a K value of 21 which means about 95% methylcyclohexane molecules have the methyl group in the equatorial position at 25º C.

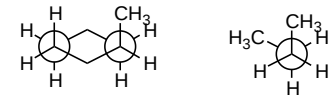


methyl group axial methyl group equatorial (more stable by **7 kJ/mol**)

The energy difference between the two conformations comes from strain, called 1,3-diaxial interactions, created when the axial methyl group experiences steric crowding with the two axial hydrogens located on the same side of the cyclohexane ring. Because axial bonds are parallel to each other, substituents larger than hydrogen experience greater steric crowding when they are oriented axial rather than equatorial. Consequently, ***substituted cyclohexanes will preferentially adopt conformations in which the larger substituents are in the equatorial orientation***. When the methyl group is in the equatorial position this strain is not present which makes the equatorial conformer more stable and favored in the ring flip equilibrium.



Actually, 1,3-diaxial steric strain is directly related to the steric strain created in the gauche conformer of butane discussed in Section: 3-7. When butane is in the gauche conformation 3.8 kJ/mol of strain was created due the steric crowding of two methyl group with a 60° dihedral angle. When looking at the a Newman projection of axial methylcyclohexane the methyl group is at a 60° dihedral angle with the ring carbon in the rear. This creates roughly the same amount of steric strain as the gauche conformer of butante. Given that there is actually two such interactions in axial methylcyclohexane, it makes sense that there is 2(3.8 kJ/mol) = 7.6 kJ/mol of steric strain in this conformation. The Newman projection of equatorial methylcyclohexane shows no such interactions and is therefore more stable.



methylcyclohexane *n*-butane

Newman projections of methyl cyclohexane and butane showing similarity of 1,3-diaxial and gauche interactions.

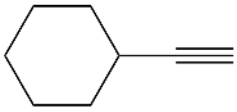
Strain values for other cyclohexane substituents can also be considered. The relative steric hindrance experienced by different substituent groups oriented in an axial versus equatorial location on cyclohexane determined the amount of strain generated. The strain generated can be used to evaluate the relative tendency of substituents to exist in an equatorial or axial location. Looking at the energy values in this table, it is clear that as the size of the substituent increases, the 1,3-diaxial energy tends to increase, also. Note that it is the size and not the molecular weight of the group that is important. Table 4.7.1 summarizes some of these strain values values.

Table 4.7.1: A Selection of ΔG° *Values for the Change from Axial to Equatorial Orientation of Substituents for Monosubstituted Cyclohexanes*

Substituent	-ΔG° (kcal/mol)	Substituent	-ΔG° (kcal/mol)
CH_3-	1.7	O_2N-	1.1
CH_2H_5-	1.8	$N\equiv C-$	0.2
$(CH_3)_2CH-$	2.2	CH_3O-	0.5
$(CH_3)_3C-$	≥ 5.0	HO_2C-	0.7
$F-$	0.3	$H_2C=CH-$	1.3
$Cl-$	0.5	C_6H_5-	3.0
$Br-$	0.5		
$I-$	0.5		

Exercises

1) In the molecule, cyclohexyl ethyne there is little steric strain, why?



2) Calculate the energy difference between the axial and equatorial conformations of bromocyclohexane?

3) Using your answer from Question 2) estimate the percentages of axial and equatorial conformations of bromocyclohexane at 25° C.



Bromo group axial   Bromo group equitorial

4) There very little in 1,3-diaxial strain when going from a methyl substituent (3.8 kJ/mol) to an ethyl substituent (4.0 kJ/mol), why? It may help to use molecular model to answer this question.

Solutions

1) The ethyne group is linear and therefore does not affect the hydrogens in the 1,3 positions to say to the extent as a bulkier or a bent group (e.g. ethene group) would. This leads to less of a strain on the molecule.



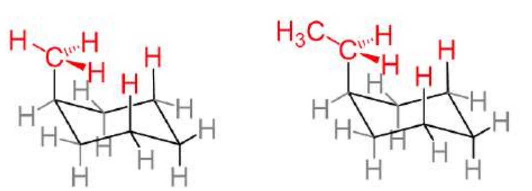
2) The equatorial conformation of bromocyclohexane will have two 1,3 diaxial interactions. The table above states that each interaction accounts for 1.2 kJ/mol of strain. The total strain in equatorial bromocyclohexane will be 2(1.2 kJ/mol) = 2.4 kJ/mol.

3) Remembering that the axial conformation is higher in energy, the energy difference between the two conformations is ΔE = (E equatorial - E axial) = (0 - 2.4 kJ/mol) = -2.4 kJ/mol. After converting ^{o}C to Kelvin and kJ/mol to J/mol we can use the equation ΔE = -RT lnK to find that -ΔE/RT = lnK or (2.4 x 10^{3} J/mol) / (8.313 kJ/mol K • 298 K) = lnK. From this we calculate that K = 2.6. Because the ring flip reaction is an equilibrium we can say that K = [Equatorial] / [Axial]. If assumption is made that [Equatorial] = X then [Axial] must be 1-X. Plugging these values into the equilibrium expression produces K = [X] / [1-X]. After plugging in the calculated value for K, X can be solved algebraically. 2.6 = [X] / [1-X] → 2.6 - 2.6X = X → 2.6 = 3.6X → 2.6/3.6 = X = 0.72. This means that bromocyclohexane is in the equatorial position 72% of the time and in the axial position 28% of the time.



Bromo group axial   Bromo group equitorial

4) The fact that C-C sigma bonds can freely rotate allows the ethyl subsistent to obtain a conformation which places the bulky CH_3 group away from the cyclohexane ring. This forces the ethyl substituent to have only have 1,3- diaxial interactions between hydrogens, which only provides a slight difference to a methyl group.



Methylcyclohexane   Ethylcyclohexane

Exercises

Objective

After completing this section, you should be able to use conformational analysis to determine the most stable conformation of a given disubstituted cyclohexane.

Key Terms

Make certain that you can define, and use in context, the key term below.

- conformational analysis

Study Notes

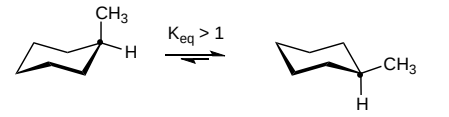
When faced with the problem of trying to decide which of two conformers of a given disubstituted cyclohexane is the more stable, you may find the following generalizations helpful.

1. A conformation in which both substituents are equatorial will always be more stable than a conformation with both groups axial.
2. When one substituent is axial and the other is equatorial, the most stable conformation will be the one with the bulkiest substituent in the equatorial position. Steric bulk decreases in the order

   tert-butyl > isopropyl > ethyl > methyl > hydroxyl > halogens

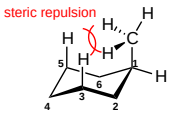
Monosubstituted Cyclohexanes

In the previous section, it was stated that the chair conformation in which the methyl group is equatorial is more stable because it minimizes steric repulsion, and thus the equilibrium favors the more stable conformer. This is true for all monosubstituted cyclohexanes. The chair conformation which places the substituent in the equatorial position will be the most stable and be favored in the ring flip equilibrium.



methyl group axial

methyl group equatorial
(more stable by **7 kJ/mol**)



Disubstituted Cyclohexanes

Determining the more stable chair conformation becomes more complex when there are two or more substituents attached to the cyclohexane ring. To determine the stable chair conformation, the steric effects of each substituent, along with any additional steric interactions, must be taken into account for both chair conformations.

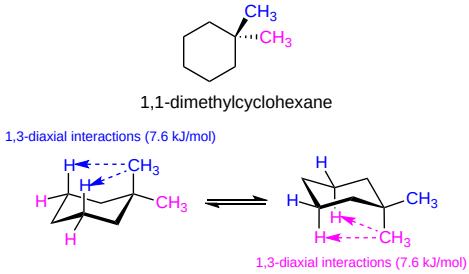
In this section, the effect of conformations on the relative stability of disubstituted cyclohexanes is examined using the two principles:

i. Substituents prefer equatorial rather than axial positions in order to minimize the steric strain created of 1,3-diaxial interactions.
ii. The more stable conformation will place the larger substituent in the equatorial position.

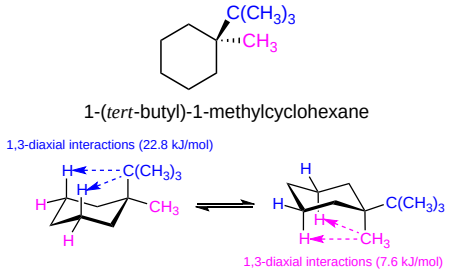
1,1-Disubstituted Cyclohexanes

The more stable chair conformation can often be determined empirically or by using the energy values of steric interactions previously discussed in this chapter. Note, in some cases there is no discernable energy difference between the two chair conformations which means they are equally stable.

1,1-dimethylcyclohexane does not have *cis* or *trans* isomers, because both methyl groups are on the same ring carbon. Both chair conformers have one methyl group in an axial position and one methyl group in an equatorial position giving both the same relative stability. The steric strain created by the 1,3-diaxial interactions of a methyl group in an axial position (versus equatorial) is 7.6 kJ/mol (from Table 4.7.1), so both conformers will have equal amounts of steric strain. Thus, the equilibrium between the two conformers does not favor one or the other. Note, that both methyl groups cannot be equatorial at the same time without breaking bonds and creating a different molecule.

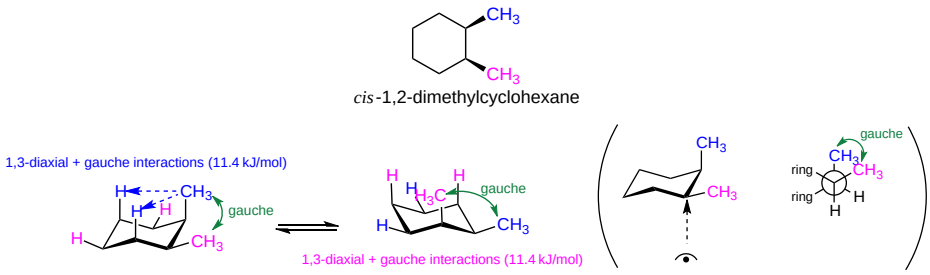


However, if the two groups are different, as in 1-*tert*-butyl-1-methylcyclohexane, then the equilibrium favors the conformer in which the larger group (*tert*-butyl in this case) is in the more stable equatorial position. The energy cost of having one tert-butyl group axial (versus equatorial) can be calculated from the values in table 4.7.1 and is approximately 22.8 kJ/mol. The conformer with the *tert*-butyl group axial is approximately 15.2 kJ/mol (22.8 kJ/mol - 7.6 kJ/mol) less stable then the conformer with the *tert*-butyl group equatorial. Solving for the equilibrium constant K shows that the equatorial is preferred about 460:1 over axial. This means that 1-*tert*-butyl-1-methylcyclohexane will spend the majority of its time in the more stable conformation, with the *tert*-butyl group in the equatorial position.

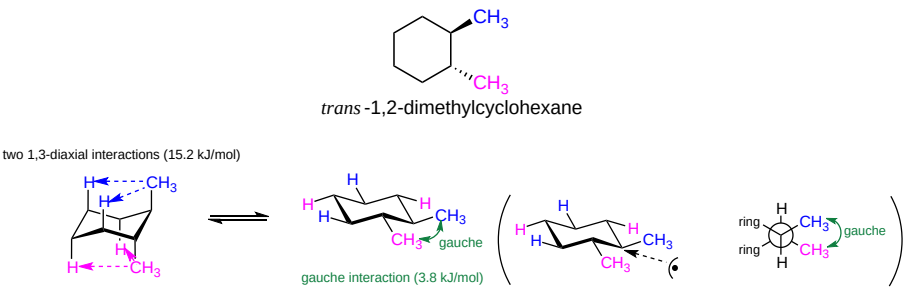


Cis and *trans* stereoisomers of 1,2-dimethylcyclohexane

In *cis*-1,2-dimethylcyclohexane, both chair conformations have one methyl group equatorial and one methyl group axial. As previously discussed, the axial methyl group creates 7.6 kJ/mol of steric strain due to 1,3-diaxial interactions. It is important to note, that both chair conformations also have an additional 3.8 kJ/mol of steric strain created by a gauche interaction between the two methyl groups. Overall, both chair conformations have 11.4 kJ/mol of steric strain and are of equal stability.

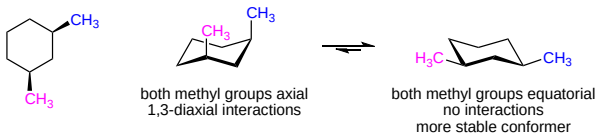


In *trans*-1,2-dimethylcyclohexane, one chair conformer has both methyl groups axial and the other conformer has both methyl groups equatorial. The conformer with both methyl groups equatorial has no 1,3-diaxial interactions however there is till 3.8 kJ/mol of strain created by a gauche interaction. The conformer with both methyl groups axial has four 1,3-Diaxial interactions which creates 2 x 7.6 kJ/mol (15.2 kJ/mol) of steric strain. This conformer is (15.2 kJ/mol -3.8 kJ/mol) 11.4 kJ/mol less stable than the other conformer. The equilibrium will therefore favor the conformer with both methyl groups in the equatorial position.

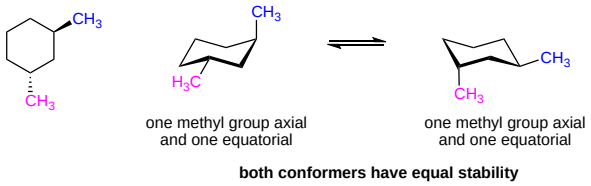


Cis and *trans* stereoisomers of 1,3-dimethylcyclohexane

A similar conformational analysis can be made for the *cis* and *trans* stereoisomers of 1,3-dimethylcyclohexane. For *cis*-1,3-dimethylcyclohexane one chair conformation has both methyl groups in axial positions creating 1,3-diaxial interactions. The other conformer has both methyl groups in equatorial positions thus creating no 1,3-diaxial interaction. Because the methyl groups are not on adjacent carbons in the cyclohexane rings gauche interactions are not possible. Even without energy calculations it is simple to determine that the conformer with both methyl groups in the equatorial position will be the more stable conformer.



For *trans*-1,3-dimethylcyclohexane both conformations have one methyl axial and one methyl group equatorial. Each conformer has one methyl group creating a 1,3-diaxial interaction so both are of equal stability.



Summary of Disubstitued Cyclohexane Chair Conformations

When considering the conformational analyses discussed above a pattern begins to form. There are only two possible relationships which can occur between ring-flip chair conformations:

1) AA/EE: One chair conformation places both substituents in axial positions creating 1,3-diaxial interactions. The other conformer places both substituents in equatorial positions creating no 1,3-diaxial interactions. This diequatorial conformer is the more stable regardless of the substituents.

2) AE/EA: Each chair conformation places one substituent in the axial position and one substituent in the equatorial position. If the substituents are the same, there will be equal 1,3-diaxial interactions in both conformers making them equal in stability. However, if the substituents are different then different 1,3-diaxial interactions will occur. The chair conformation which places the larger substituent in the equatorial position will be favored.

Substitution type	Chair Conformation Relationship
cs-1,2-disubstituted cyclohexanes	AE/EA
trans-1,2-disubstituted cyclohexanes	AA/EE
cis-1,3-disubstituted cyclohexanes	AA/EE
trans-1,3-disubstituted cyclohexanes	AE/EA
cis-1,4-disubstituted cyclohexanes	AE/EA
trans-1,4-disubstituted cyclohexanes	AA/EE

Example 9.5.1

For *cis*-1-chloro-4-methylcyclohexane, draw the most stable chair conformation and determine the energy difference between the two chair conformers.

Solution

Based on the table above, *cis*-1,4-disubstitued cyclohexanes should have two chair conformations each with one substituent axial and one equatorial. Based on this, we can surmise that the energy difference of the two chair conformations will be based on the difference in the 1,3-diaxial interactions created by the methyl and chloro substituents.



As predicted, each chair conformer places one of the substituents in the axial position. Because the methyl group is larger and has a greater 1,3-diaxial interaction than the chloro, the most stable conformer will place it the equatorial position, as shown in the structure on the right. Using the 1,3-diaxial energy values given in the previous sections we can calculate that the conformer on the right is (7.6 kJ/mol - 2.0 kJ/mol) 5.6 kJ/mol more stable than the other.

Example 9.5.2

For *trans*-1-chloro-2-methylcyclohexane, draw the most stable chair conformation and determine the energy difference between the two chair conformers.

Solution

Based on the table above, *trans*-1,2-disubstitued cyclohexanes should have one chair conformation with both substituents axial and one conformation with both substituents equatorial. Based on this, we can predict that the conformer which places both substituents equatorial will be the more stable conformer. The energy difference of the two chair conformations will be based on the 1,3-diaxial interactions created by both the methyl and chloro substituents.

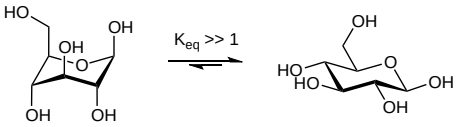


As predicted, one chair conformer places both substituents in the axial position and other places both substituents equatorial. The more stable conformer will place both substituents in the equatorial position, as shown in the structure on the right. Using the 1,3-diaxial energy values given in the previous sections we can calculate that the conformer on the right is (7.6 kJ/mol + 2.0 kJ/mol) 9.6 kJ/mol more stable than the other.

Conformational Analysis of Complex Six Membered Ring Structures

Cyclohexane can have more than two substituents. Also, there are multiple six membered rings which contain atoms other than carbon. All of these systems usually form chair conformations and follow the same steric constraints discussed in this section. Because the most commonly found rings in nature are six membered, conformational analysis can often help in understanding the usual shapes of some biologically important molecules. In complex six membered ring structures a direct calculation of 1,3-diaxial energy values may be difficult. In these cases a determination of the more stable chair conformer can be made by empirically applying the principles of steric interactions.

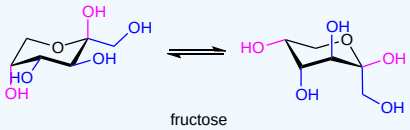
A later chapter will discuss how many sugars can exist in cyclic forms which are often six remembered rings. When in an aqueous solution the six carbon sugar, glucose, is usually a six membered ring adopting a chair conformation. When looking at the two possible ring-clip chair conformations, one has all of the substituents axial and the other has all the substutents equatorial. Even without a calculation, it is clear that the conformation with all equatorial substituents is the most stable and glucose will most commonly be found in this conformation.



glucose
(β-glucopyranose form)

Example 9.5.3

The six carbon sugar, fructose, in aqueous solution is also a six-membered ring in a chair conformation. Which of the two possible chair conformations would be expected to be the most stable?



fructose
(β-fructopyranose form)

Solution

The lower energy chair conformation is the one with three of the five substituents (including the bulky $–CH_2OH$ group) in the equatorial position (pictured on the right). The left structure has 3 equatorial substituents while the structure on the right only has two equatorial substituents.

Exercises

1. Draw the two chair conformations for *cis*-1-ethyl-2-methylcyclohexane using bond-line structures and indicate the more energetically favored conformation.

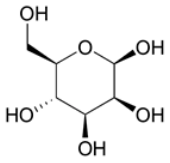
2. Draw the most stable conformation for *trans*-1-ethyl-3-methylcyclohexane using bond-line structures.

3. Draw the most stable conformation for trans-1-*t*-butyl-4-methylcyclohexane using bond-line structures.

4. Draw the most stable conformation fo *trans*-1-isopropyl-3-methylcyclohexane.

5. Can a 'ring flip' change a *cis*-disubstituted cyclohexane to *trans*? Explain.

6. Draw the two chair conformations of the six-carbon sugar mannose, being sure to clearly show each non-hydrogen substituent as axial or equatorial. Predict which conformation is likely to be more stable, and explain why.

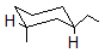


mannose

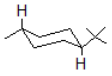
Solutions

1. 

larger ethyl group in equatorial position is favored

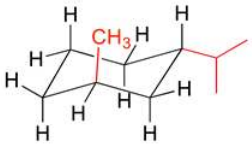
2. 

larger ethyl group in equatorial position is favored

3. 

both alkyl groups in equatorial position

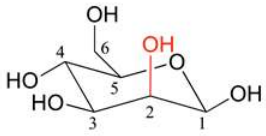
4.



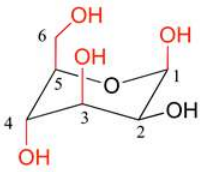
The bulkier isopropyl groups is in the equatorial position.

5. No. In order to change the relationship of two substituents on a ring from *cis* to *trans*, you would need to break and reform two covalent bonds. Ring flips involve only *rotation* of single bonds.

6.



major chair form of mannose
(only one substituent axial)



minor chair form of mannose
(four substituents axial)

Exercises

9.5: Substituted Cyclohexanes is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **4.7: Conformations of Monosubstituted Cyclohexanes** by Dietmar Kennepohl, Krista Cunningham, Layne Morsch, Robert Bruner, Steven Farmer, Tim Soderberg is licensed CC BY-SA 4.0.
- **4.8: Conformations of Disubstituted Cyclohexanes** by Dietmar Kennepohl, Jim Clark, Kelly Matthews, Krista Cunningham, Layne Morsch, Robert Bruner, Steven Farmer, Tim Soderberg is licensed CC BY-SA 4.0.

9.S: Study Guide

9: Organic Chemistry III - Conformational Analysis

Key Topics for TRU students taking CHEM1500

- Configurational isomers
- cis/trans
- E/Z
- stereogenic centres and R/S systems
- compounds with more than one stereogenic centre
- meso compounds
- resolution of racemic mixtures
- examples of stereochemistry using amino acids
- peptides and carbohydrates

Key Learning Outcomes (Examples)

- designate the stereochemistry for carbon-carbon double bonds as E or Z and for stereogenic C atoms as R or S
- identify stereogenic carbon atoms from the molecular structures of organic molecules including some common pharmaceuticals and bio-chemical substances
- categorize different types of isomers for organic compounds including “real world” applications to pharmaceuticals and bio-chemical substances

9.S: Study Guide is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

Index

A

A values
7.5.1: Naming Alkanes
accuracy
1.1.5: Measurement Uncertainty, Accuracy, and Precision
Actinide
1.2.6: The Periodic Table
3.1: The Periodic Table
alkali metal
1.2.6: The Periodic Table
3.1: The Periodic Table
alkaline earth metal
1.2.6: The Periodic Table
3.1: The Periodic Table
alkanes
7.5.1: Naming Alkanes
alpha particle
1.2.3: Evolution of Atomic Theory
amplitude
2.1: Electromagnetic Energy
anion
1.2.4: Atomic Structure and Symbolism
atom
1.1.2: Phases and Classification of Matter
atomic mass
1.2.4: Atomic Structure and Symbolism
atomic mass unit
1.2.4: Atomic Structure and Symbolism
atomic number
1.2.4: Atomic Structure and Symbolism
atomization enthalpy
4.2: Lattice Enthalpies and Born Haber Cycles
aufbau principle
2.6: Electronic Structure of Atoms (Electron Configurations)
axial position
5.1: Molecular Structure and Polarity

B

binary acid
1.2.8: Chemical Nomenclature
binary compound
1.2.8: Chemical Nomenclature
blackbody
2.1: Electromagnetic Energy
bond angle
5.1: Molecular Structure and Polarity
bond dipole moment
5.1: Molecular Structure and Polarity
bond distance
5.1: Molecular Structure and Polarity
bond energy
4.6: Strengths of Ionic and Covalent Bonds
bond length
4.3: Covalent Bonding
bonding molecular orbital
7.1.9: Describing Chemical Bonds- Molecular Orbital Theory

C

cation
1.2.4: Atomic Structure and Symbolism
Celsius
1.1.4: Measurements
chalcogen
1.2.6: The Periodic Table
3.1: The Periodic Table
chemical change
1.1.3: Physical and Chemical Properties
chemical property
1.1.3: Physical and Chemical Properties
chemical symbol
1.2.4: Atomic Structure and Symbolism
chemistry
1.1.1: Chemistry in Context
compound
1.1.2: Phases and Classification of Matter
conformational isomers
8.1: Types of Isomers
continuous spectrum
2.1: Electromagnetic Energy
conversion factors
1.1.6: Mathematical Treatment of Measurement Results
core electron
2.6: Electronic Structure of Atoms (Electron Configurations)
covalent bond
1.2.7: Molecular and Ionic Compounds
4.3: Covalent Bonding
covalent compound
1.2.7: Molecular and Ionic Compounds
covalent radius
3.2: Periodic Variations in Element Properties
cubic centimeter
1.1.4: Measurements
cubic meter
1.1.4: Measurements
cycloalkanes
7.5.2: Naming Cycloalkanes

D

Dalton unit
1.2.4: Atomic Structure and Symbolism
Dalton's Atomic Theory
1.2.2: Early Ideas in Atomic Theory
density
1.1.4: Measurements
dimensional analysis
1.1.6: Mathematical Treatment of Measurement Results
dipole moment
5.1: Molecular Structure and Polarity
dispersion
6.1: Intermolecular Forces
double bond
4.4: Lewis Symbols and Structures

E

E,Z Notation
8.5.2: Sequence Rules - The E,Z Designation
effective nuclear charge
3.2: Periodic Variations in Element Properties
electromagnetic radiation
2.1: Electromagnetic Energy
electromagnetic spectrum
2.1: Electromagnetic Energy
electron
1.2.3: Evolution of Atomic Theory
electron affinity
3.2: Periodic Variations in Element Properties
electron configuration
2.6: Electronic Structure of Atoms (Electron Configurations)
electronegativity
4.3: Covalent Bonding
element
1.1.2: Phases and Classification of Matter
empirical formula
1.2.5: Chemical Formulas
epimers
8.1: Types of Isomers
equatorial position
5.1: Molecular Structure and Polarity
ethane
7.1.5: sp³ Hybrid Orbitals and the Structure of Ethane
ethylene
7.1.5: sp³ Hybrid Orbitals and the Structure of Ethane
exact number
1.1.5: Measurement Uncertainty, Accuracy, and Precision
extensive property
1.1.3: Physical and Chemical Properties

F

Fahrenheit
1.1.6: Mathematical Treatment of Measurement Results
formal charge
4.5: Formal Charges and Resonance
free radical
4.4: Lewis Symbols and Structures
frequency
2.1: Electromagnetic Energy
functional group
7.3: Functional Groups
fundamental unit of charge
1.2.4: Atomic Structure and Symbolism

G

gas
1.1.2: Phases and Classification of Matter
goiter
1.2.4: Atomic Structure and Symbolism
group
1.2.6: The Periodic Table
3.1: The Periodic Table

H

halogen
1.2.6: The Periodic Table
3.1: The Periodic Table
hertz
2.1: Electromagnetic Energy
heterogeneous mixture
1.1.2: Phases and Classification of Matter
homogeneous mixture
1.1.2: Phases and Classification of Matter
Hund's rule
2.6: Electronic Structure of Atoms (Electron Configurations)

hybrid orbital
5.3: Hybrid Atomic Orbitals
hybrid orbitals
7.1.4: sp³ Hybrid Orbitals and the Structure of Methane
hybridization
5.3: Hybrid Atomic Orbitals
hydrogen bonding
6.1: Intermolecular Forces
hypervalent molecule
4.4: Lewis Symbols and Structures
hypothesis
1.1.1: Chemistry in Context

I

induced dipole
6.1: Intermolecular Forces
inert gas
1.2.6: The Periodic Table
3.1: The Periodic Table
inert pair effect
4.1: Ionic Bonding
inner transition metal
1.2.6: The Periodic Table
3.1: The Periodic Table
instantaneous dipole
6.1: Intermolecular Forces
intensity
2.1: Electromagnetic Energy
intensive property
1.1.3: Physical and Chemical Properties
interference pattern
2.1: Electromagnetic Energy
intermolecular force
6.1: Intermolecular Forces
International System of Units
1.1.4: Measurements
ion
1.2.4: Atomic Structure and Symbolism
ionic bond
1.2.7: Molecular and Ionic Compounds
4.1: Ionic Bonding
ionic compound
1.2.7: Molecular and Ionic Compounds
ionization energy
3.2: Periodic Variations in Element Properties
isoelectronic
3.2: Periodic Variations in Element Properties
isomerism
8.1: Types of Isomers
isomers
1.2.5: Chemical Formulas
isotope
1.2.3: Evolution of Atomic Theory

K

Kelvin
1.1.4: Measurements
kilogram
1.1.4: Measurements

L

lanthanide
1.2.6: The Periodic Table
3.1: The Periodic Table
Lattice Energy
4.6: Strengths of Ionic and Covalent Bonds
lattice enthalpy
4.2: Lattice Enthalpies and Born Haber Cycles
law
1.1.1: Chemistry in Context
law of conservation of matter
1.1.2: Phases and Classification of Matter
law of constant composition
1.2.2: Early Ideas in Atomic Theory
Law of Definite Proportions
1.2.2: Early Ideas in Atomic Theory
law of multiple proportions
1.2.2: Early Ideas in Atomic Theory
length
1.1.4: Measurements
Lewis structure
4.4: Lewis Symbols and Structures
Lewis symbol
4.4: Lewis Symbols and Structures
line spectrum
2.1: Electromagnetic Energy
linear
5.1: Molecular Structure and Polarity
liquid
1.1.2: Phases and Classification of Matter
liter
1.1.4: Measurements
lone pair
4.4: Lewis Symbols and Structures

M

macroscopic domain
1.1.1: Chemistry in Context
mass
1.1.2: Phases and Classification of Matter
mass number
1.2.4: Atomic Structure and Symbolism
metal
1.2.6: The Periodic Table
3.1: The Periodic Table
metalloid
1.2.6: The Periodic Table
3.1: The Periodic Table
meter
1.1.4: Measurements
microscopic domain
1.1.1: Chemistry in Context
milliliter
1.1.4: Measurements
mixture
1.1.2: Phases and Classification of Matter
molecular compound
1.2.7: Molecular and Ionic Compounds
molecular formula
1.2.5: Chemical Formulas
molecular orbital theory
5.5: Molecular Orbital Theory
7.1.9: Describing Chemical Bonds- Molecular Orbital Theory
molecular structure
4.5: Formal Charges and Resonance
5.1: Molecular Structure and Polarity
molecule
1.1.2: Phases and Classification of Matter
monatomic ion
1.2.7: Molecular and Ionic Compounds

N

neutron
1.2.3: Evolution of Atomic Theory
noble gas
1.2.6: The Periodic Table
3.1: The Periodic Table
node
2.1: Electromagnetic Energy
5.2: Valence Bond Theory
nomenclature
1.2.8: Chemical Nomenclature
nonmetal
1.2.6: The Periodic Table
3.1: The Periodic Table
nonpolar covalent bond
4.3: Covalent Bonding
nucleus
1.2.3: Evolution of Atomic Theory

O

octahedral
5.1: Molecular Structure and Polarity
octet rule
4.4: Lewis Symbols and Structures
orbital diagram
2.6: Electronic Structure of Atoms (Electron Configurations)
overlap
5.2: Valence Bond Theory
oxyacid
1.2.8: Chemical Nomenclature
oxyanion
1.2.7: Molecular and Ionic Compounds

P

period
1.2.6: The Periodic Table
3.1: The Periodic Table
periodic law
1.2.6: The Periodic Table
3.1: The Periodic Table
periodic table
1.2.6: The Periodic Table
3.1: The Periodic Table
photon
2.1: Electromagnetic Energy
physical change
1.1.3: Physical and Chemical Properties
physical property
1.1.3: Physical and Chemical Properties
pi bond
5.2: Valence Bond Theory
plasma
1.1.2: Phases and Classification of Matter
pnictogen
1.2.6: The Periodic Table
3.1: The Periodic Table
polar covalent bond
4.3: Covalent Bonding
polar molecule
5.1: Molecular Structure and Polarity
polarizability
6.1: Intermolecular Forces
polyatomic ion
1.2.7: Molecular and Ionic Compounds
polycyclic compounds
7.5.2: Naming Cycloalkanes

precision
1.1.5: Measurement Uncertainty, Accuracy, and Precision
proton
1.2.3: Evolution of Atomic Theory
pure covalent bond
4.3: Covalent Bonding
pure substance
1.1.2: Phases and Classification of Matter

Q

quantization
2.1: Electromagnetic Energy

R

representative element
1.2.6: The Periodic Table
3.1: The Periodic Table
resonance
4.5: Formal Charges and Resonance
5.4: Multiple Bonds
resonance forms
4.5: Formal Charges and Resonance
resonance hybrid
4.5: Formal Charges and Resonance
rounding
1.1.5: Measurement Uncertainty, Accuracy, and Precision

S

scientific method
1.1.1: Chemistry in Context
second
1.1.4: Measurements
sequence rules
8.5.2: Sequence Rules - The E,Z Designation
series
1.2.6: The Periodic Table
3.1: The Periodic Table
SI units
1.1.4: Measurements
sigma bond
5.2: Valence Bond Theory
significant figures
1.1.5: Measurement Uncertainty, Accuracy, and Precision
single bond
4.4: Lewis Symbols and Structures
solid
1.1.2: Phases and Classification of Matter
sp hybrid orbital
5.3: Hybrid Atomic Orbitals
7.1.7: sp Hybrid Orbitals and the Structure of Acetylene
sp2 hybrid orbital
5.3: Hybrid Atomic Orbitals
sp3 hybrid orbital
5.3: Hybrid Atomic Orbitals
sp3d hybrid orbital
5.3: Hybrid Atomic Orbitals
sp3d2 hybrid orbital
5.3: Hybrid Atomic Orbitals
spatial isomers
1.2.5: Chemical Formulas
standing wave
2.1: Electromagnetic Energy
stereoisomers
8.1: Types of Isomers
structural formula
1.2.5: Chemical Formulas
structural isomers
1.2.5: Chemical Formulas
8.1: Types of Isomers
symbolic domain
1.1.1: Chemistry in Context

T

Tetrahedral
5.1: Molecular Structure and Polarity
theory
1.1.1: Chemistry in Context
transition metal
1.2.6: The Periodic Table
3.1: The Periodic Table
trigonal bipyramidal
5.1: Molecular Structure and Polarity
Trigonal Planar
5.1: Molecular Structure and Polarity
triple bond
4.4: Lewis Symbols and Structures

U

uncertainty
1.1.5: Measurement Uncertainty, Accuracy, and Precision
unified atomic mass unit
1.2.4: Atomic Structure and Symbolism
unit
1.1.4: Measurements

V

valence bond theory
5.2: Valence Bond Theory
7.1.3: Describing Chemical Bonds - Valence Bond Theory
valence electrons
2.6: Electronic Structure of Atoms (Electron Configurations)
Valence Shell
2.6: Electronic Structure of Atoms (Electron Configurations)
valence shell electron pair repulsion theory
5.1: Molecular Structure and Polarity
van der Waals force
6.1: Intermolecular Forces
volume
1.1.4: Measurements
VSEPR
5.1: Molecular Structure and Polarity

W

wave
2.1: Electromagnetic Energy
wavelength
2.1: Electromagnetic Energy
weight
1.1.2: Phases and Classification of Matter

Glossary

Sample Word 1 | Sample Definition 1

Accuracy | how closely a measurement aligns with a correct value

Acid anhydride | compound that reacts with water to form an acid or acidic solution

Acid ionization | reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

Acid ionization constant (K_a) | equilibrium constant for the ionization of a weak acid

Acid-base indicator | organic acid or base whose color changes depending on the pH of the solution it is in

Acidic | describes a solution in which [H3O+]>[OH−][H3O+]>[OH−]

Actinide | inner transition metal in the bottom of the bottom two rows of the periodic table

Actinide series | (also, actinoid series) actinium and the elements in the second row or the *f*-block, atomic numbers 89–103

Activated complex | (also, transition state) unstable combination of reactant species representing the highest energy state of a reaction system

Activation energy (E_a) | energy necessary in order for a reaction to take place

Active electrode | electrode that participates in the oxidation-reduction reaction of an electrochemical cell; the mass of an active electrode changes during the oxidation-reduction reaction

Actual yield | amount of product formed in a reaction

Addition reaction | reaction in which a double carbon-carbon bond forms a single carbon-carbon bond by the addition of a reactant. Typical reaction for an alkene.

Adhesive force | force of attraction between molecules of different chemical identities

Alcohol | organic compound with a hydroxyl group (–OH) bonded to a carbon atom

Alkali metal | element in group 1

Alkaline earth metal | element in group 2

Alkaline earth metal | any of the metals (beryllium, magnesium, calcium, strontium, barium, and radium) occupying group 2 of the periodic table; they are reactive, divalent metals that form basic oxides

Alkane | molecule consisting of only carbon and hydrogen atoms connected by single (σ) bonds

Alkene | molecule consisting of carbon and hydrogen containing at least one carbon-carbon double bond

Alkyl group | substituent, consisting of an alkane missing one hydrogen atom, attached to a larger structure

Alkyne | molecule consisting of carbon and hydrogen containing at least one carbon-carbon triple bond

Allotropes | two or more forms of the same element, in the same physical state, with different chemical structures

Alloy | solid mixture of a metallic element and one or more additional elements

Alpha (α) decay | loss of an alpha particle during radioactive decay

Alpha particle | (α or He24He24 or α24α24) high-energy helium nucleus; a helium atom that has lost two electrons and contains two protons and two neutrons

Alpha particle (α particle) | positively charged particle consisting of two protons and two neutrons

Amide | organic molecule that features a nitrogen atom connected to the carbon atom in a carbonyl group

Amine | organic molecule in which a nitrogen atom is bonded to one or more alkyl group

Amorphous | solid material such as a glass that does not have a regular repeating component to its three-dimensional structure; a solid but not a crystal

Amorphous solid | (also, noncrystalline solid) solid in which the particles lack an ordered internal structure

Amphiphilic | molecules possessing both hydrophobic (nonpolar) and a hydrophilic (polar) parts

Amphiprotic | species that may either gain or lose a proton in a reaction

Amphoteric | species that can act as either an acid or a base

Amplitude | extent of the displacement caused by a wave (for sinusoidal waves, it is one-half the difference from the peak height to the trough depth, and the intensity is proportional to the square of the amplitude)

Analyte | chemical species of interest

Angular momentum quantum number (*l*) | quantum number distinguishing the different shapes of orbitals; it is also a measure of the orbital angular momentum

Anion | negatively charged atom or molecule (contains more electrons than protons)

Anode | electrode in an electrochemical cell at which oxidation occurs; information about the anode is recorded on the left side of the salt bridge in cell notation

Antimatter | particles with the same mass but opposite properties (such as charge) of ordinary particles

Aqueous solution | solution for which water is the solvent

Aromatic hydrocarbon | cyclic molecule consisting of carbon and hydrogen with delocalized alternating carbon-carbon single and double bonds, resulting in enhanced stability

Arrhenius equation | mathematical relationship between the rate constant and the activation energy of a reaction

Atmosphere (atm) | unit of pressure; 1 atm = 101,325 Pa

Atom | smallest particle of an element that can enter into a chemical combination

Atomic mass | average mass of atoms of an element, expressed in amu

Atomic mass unit (amu) | (also, unified atomic mass unit, u, or Dalton, Da) unit of mass equal to 112112 of the mass of a ^{12}C atom

Atomic number (Z) | number of protons in the nucleus of an atom

Atomic orbital | mathematical function that describes the behavior of an electron in an atom (also called the wavefunction), it can be used to find the probability of locating an electron in a specific region around the nucleus, as well as other dynamical variables

Aufbau principle | procedure in which the electron configuration of the elements is determined by "building" them in order of atomic numbers, adding one proton to the nucleus and one electron to the proper subshell at a time

Autoionization | reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

Average rate | rate of a chemical reaction computed as the ratio of a measured change in amount or concentration of substance to the time interval over which the change occurred

Avogadro's number (N_A) | experimentally determined value of the number of entities comprising 1 mole of substance, equal to $6.022 \times 10^{23}\ mol^{-1}$

Axial position | location in a trigonal bipyramidal geometry in which there is another atom at a 180° angle and the equatorial positions are at a 90° angle

Balanced equation | chemical equation with equal numbers of atoms for each element in the reactant and product

Band of stability | (also, belt of stability, zone of stability, or valley of stability) region of graph of number of protons versus number of neutrons containing stable (nonradioactive) nuclides

Bar | (bar or b) unit of pressure; 1 bar = 100,000 Pa

Barometer | device used to measure atmospheric pressure

Base anhydride | metal oxide that behaves as a base towards acids

Base ionization | reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

Base ionization constant (K_b) | equilibrium constant for the ionization of a weak base

Basic | describes a solution in which $[H_3O^+] < [OH^-]$

Becquerel (Bq) | SI unit for rate of radioactive decay; 1 Bq = 1 disintegration/s

Beta (β) decay | breakdown of a neutron into a proton, which remains in the nucleus, and an electron, which is emitted as a beta particle

Beta particle | (ββ or e−10e−10 or β−10β−10) high-energy electron

Bicarbonate anion | salt of the hydrogen carbonate ion, HCO−3HCO3−

Bidentate ligand | ligand that coordinates to one central metal through coordinate bonds from two different atoms

Binary acid | compound that contains hydrogen and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H^+ ions when dissolved in water)

Binary compound | compound containing two different elements.

Binding energy per nucleon | total binding energy for the nucleus divided by the number of nucleons in the nucleus

Bismuth | heaviest member of group 15; a less reactive metal than other representative metals

Blackbody | idealized perfect absorber of all incident electromagnetic radiation; such bodies emit electromagnetic radiation in characteristic continuous spectra called blackbody radiation

Body-centered cubic (BCC) solid | crystalline structure that has a cubic unit cell with lattice points at the corners and in the center of the cell

Body-centered cubic unit cell | simplest repeating unit of a body-centered cubic crystal; it is a cube containing lattice points at each corner and in the center of the cube

Bohr's model of the hydrogen atom | structural model in which an electron moves around the nucleus only in circular orbits, each with a specific allowed radius; the orbiting electron does not normally emit electromagnetic radiation, but does so when changing from one orbit to another.

Boiling point | temperature at which the vapor pressure of a liquid equals the pressure of the gas above it

Boiling point elevation | elevation of the boiling point of a liquid by addition of a solute

Boiling point elevation constant | the proportionality constant in the equation relating boiling point elevation to solute molality; also known as the ebullioscopic constant

Bomb calorimeter | device designed to measure the energy change for processes occurring under conditions of constant volume; commonly used for reactions involving solid and gaseous reactants or products

Bond angle | angle between any two covalent bonds that share a common atom

Bond dipole moment | separation of charge in a bond that depends on the difference in electronegativity and the bond distance represented by partial charges or a vector

Bond distance | (also, bond length) distance between the nuclei of two bonded atoms

Bond energy | (also, bond dissociation energy) energy required to break a covalent bond in a gaseous substance

Bond length | distance between the nuclei of two bonded atoms at which the lowest potential energy is achieved

Borate | compound containing boron-oxygen bonds, typically with clusters or chains as a part of the chemical structure

Born-Haber cycle | thermochemical cycle relating the various energetic steps involved in the formation of an ionic solid from the relevant elements

Bragg equation | equation that relates the angles at which X-rays are diffracted by the atoms within a crystal

Brønsted-Lowry acid | proton donor

Brønsted-Lowry base | proton acceptor

Buffer | mixture of a weak acid or a weak base and the salt of its conjugate; the pH of a buffer resists change when small amounts of acid or base are added

Buffer capacity | amount of an acid or base that can be added to a volume of a buffer solution before its pH changes significantly (usually by one pH unit)

Buret | device used for the precise delivery of variable liquid volumes, such as in a titration analysis

Calorie (cal) | unit of heat or other energy; the amount of energy required to raise 1 gram of water by 1 degree Celsius; 1 cal is defined as 4.184 J

Calorimeter | device used to measure the amount of heat absorbed or released in a chemical or physical process

Calorimetry | process of measuring the amount of heat involved in a chemical or physical process

Capillary action | flow of liquid within a porous material due to the attraction of the liquid molecules to the surface of the material and to other liquid molecules

Carbonate | salt of the anion $CO2−3CO32−$; often formed by the reaction of carbon dioxide with bases

Catalyst | substance that increases the rate of a reaction without itself being consumed by the reaction

Cathode | electrode in an electrochemical cell at which reduction occurs; information about the cathode is recorded on the right side of the salt bridge in cell notation

Cathodic protection | method of protecting metal by using a sacrificial anode and effectively making the metal that needs protecting the cathode, thus preventing its oxidation

Cation | positively charged atom or molecule (contains fewer electrons than protons)

Cell notation | shorthand way to represent the reactions in an electrochemical cell

Cell potential | difference in electrical potential that arises when dissimilar metals are connected; the driving force for the flow of charge (current) in oxidation-reduction reactions

Celsius (°C) | unit of temperature; water freezes at 0 °C and boils at 100 °C on this scale

Central metal | ion or atom to which one or more ligands is attached through coordinate covalent bonds

Chain reaction | repeated fission caused when the neutrons released in fission bombard other atoms

Chalcogen | element in group 16

Chelate | complex formed from a polydentate ligand attached to a central metal

Chelating ligand | ligand that attaches to a central metal ion by bonds from two or more donor atoms

Chemical change | change producing a different kind of matter from the original kind of matter

Chemical equation | symbolic representation of a chemical reaction

Chemical property | behavior that is related to the change of one kind of matter into another kind of matter

Chemical reduction | method of preparing a representative metal using a reducing agent

Chemical symbol | one-, two-, or three-letter abbreviation used to represent an element or its atoms

Chemical thermodynamics | area of science that deals with the relationships between heat, work, and all forms of energy associated with chemical and physical processes

Chemistry | study of the composition, properties, and interactions of matter

Chemotherapy | similar to internal radiation therapy, but chemical rather than radioactive substances are introduced into the body to kill cancer cells

Chlor-alkali process | electrolysis process for the synthesis of chlorine and sodium hydroxide

Circuit | path taken by a current as it flows because of an electrical potential difference

***cis* configuration** | configuration of a geometrical isomer in which two similar groups are on the same side of an imaginary reference line on the molecule

Clausius-Clapeyron equation | mathematical relationship between the temperature, vapor pressure, and enthalpy of vaporization for a substance

Coefficient | number placed in front of symbols or formulas in a chemical equation to indicate their relative amount

Cohesive force | force of attraction between identical molecules

Colligative property | property of a solution that depends only on the concentration of a solute species

Collision theory | model that emphasizes the energy and orientation of molecular collisions to explain and predict reaction kinetics

Colloid | (also, colloidal dispersion) mixture in which relatively large solid or liquid particles are dispersed uniformly throughout a gas, liquid, or solid

Color-change interval | range in pH over which the color change of an indicator takes place

Combustion analysis | gravimetric technique used to determine the elemental composition of a compound via the collection and weighing of its gaseous combustion products

Common ion effect | effect on equilibrium when a substance with an ion in common with the dissolved species is added to the solution; causes a decrease in the solubility of an ionic species, or a decrease in the ionization of a weak acid or base

Complete ionic equation | chemical equation in which all dissolved ionic reactants and products, including spectator ions, are explicitly represented by formulas for their dissociated ions

Compound | pure substance that can be decomposed into two or more elements

Compressibility factor (Z) | ratio of the experimentally measured molar volume for a gas to its molar volume as computed from the ideal gas equation

Concentrated | qualitative term for a solution containing solute at a relatively high concentration

Concentration | quantitative measure of the relative amounts of solute and solvent present in a solution

Concentration cell | galvanic cell in which the two half-cells are the same except for the concentration of the solutes; spontaneous when the overall reaction is the dilution of the solute

Condensation | change from a gaseous to a liquid state

Conjugate acid | substance formed when a base gains a proton

Conjugate base | substance formed when an acid loses a proton

Containment system | (also, shield) a three-part structure of materials that protects the exterior of a nuclear fission reactor and operating personnel from the high temperatures, pressures, and radiation levels inside the reactor

Continuous spectrum | electromagnetic radiation given off in an unbroken series of wavelengths (e.g., white light from the sun)

Control rod | material inserted into the fuel assembly that absorbs neutrons and can be raised or lowered to adjust the rate of a fission reaction

Coordination compound | stable compound in which the central metal atom or ion acts as a Lewis acid and accepts one or more pairs of electrons

Coordination compound | substance consisting of atoms, molecules, or ions attached to a central atom through Lewis acid-base interactions

Coordination number | number of atoms closest to any given atom in a crystal or to the central metal atom in a complex

Coordination number | number of coordinate covalent bonds to the central metal atom in a complex or the number of closest contacts to an atom in a crystalline form

Coordination sphere | central metal atom or ion plus the attached ligands of a complex

Core electron | electron in an atom that occupies the orbitals of the inner shells

Corrosion | degradation of metal through an electrochemical process

Covalent bond | attractive force between the nuclei of a molecule's atoms and pairs of electrons between the atoms

Covalent bond | bond formed when electrons are shared between atoms

Covalent compound | (also, molecular compound) composed of molecules formed by atoms of two or more different elements

Covalent network solid | solid whose particles are held together by covalent bonds

Covalent radius | one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond

Crenation | process whereby biological cells become shriveled due to loss of water by osmosis

Critical mass | amount of fissionable material that will support a self-sustaining (nuclear fission) chain reaction

Critical point | temperature and pressure above which a gas cannot be condensed into a liquid

Crystal field splitting (Δ_{oct}) | difference in energy between the t_{2g} and e_g sets or t and e sets of orbitals

Crystal field theory | model that explains the energies of the orbitals in transition metals in terms of electrostatic interactions with the ligands but does not include metal ligand bonding

Crystalline solid | solid in which the particles are arranged in a definite repeating pattern

Cubic centimeter (cm^3 or cc) | volume of a cube with an edge length of exactly 1 cm

Cubic closest packing (CCP) | crystalline structure in which planes of closely packed atoms or ions are stacked as a series of three alternating layers of different relative orientations (ABC)

Cubic meter (m^3) | SI unit of volume

Curie (Ci) | larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7×10^{10} disintegrations/s

Current | flow of electrical charge; the SI unit of charge is the coulomb (C) and current is measured in amperes (1A=1Cs) (1A=1Cs)

***d* orbital** | region of space with high electron density that is either four lobed or contains a dumbbell and torus shape; describes orbitals with $l = 2$. An electron in this orbital is called a *d* electron

***d*-block element** | one of the elements in groups 3–11 with valence electrons in *d* orbitals

Dalton (Da) | alternative unit equivalent to the atomic mass unit

Dalton's atomic theory | set of postulates that established the fundamental properties of atoms

Daughter nuclide | nuclide produced by the radioactive decay of another nuclide; may be stable or may decay further

Density | ratio of mass to volume for a substance or object

Deposition | change from a gaseous state directly to a solid state

Diffraction | redirection of electromagnetic radiation that occurs

when it encounters a physical barrier of appropriate dimensions

Dilute | qualitative term for a solution containing solute at a relatively low concentration

Dilution | process of adding solvent to a solution in order to lower the concentration of solutes

Dimensional analysis | (also, factor-label method) versatile mathematical approach that can be applied to computations ranging from simple unit conversions to more complex, multi-step calculations involving several different quantities

Dipole moment | property of a molecule that describes the separation of charge determined by the sum of the individual bond moments based on the molecular structure

Dipole-dipole attraction | intermolecular attraction between two permanent dipoles

Diprotic acid | acid containing two ionizable hydrogen atoms per molecule. A diprotic acid ionizes in two steps

Diprotic base | base capable of accepting two protons. The protons are accepted in two steps

Dispersed phase | substance present as relatively large solid or liquid particles in a colloid

Dispersion force | (also, London dispersion force) attraction between two rapidly fluctuating, temporary dipoles; significant only when particles are very close together

Dispersion medium | solid, liquid, or gas in which colloidal particles are dispersed

Disproportionation reaction | chemical reaction where a single reactant is simultaneously reduced and oxidized; it is both the reducing agent and the oxidizing agent

Dissociation | physical process accompanying the dissolution of an ionic compound in which the compound's constituent ions are solvated and dispersed throughout the solution

Dissolved | describes the process by which solute components are dispersed in a solvent

Donor atom | atom in a ligand with a lone pair of electrons that forms a coordinate covalent bond to a central metal

Double bond | covalent bond in which two pairs of electrons are shared between two atoms

Downs cell | electrochemical cell used for the commercial preparation of metallic sodium (and chlorine) from molten sodium chloride

Dynamic equilibrium | state of a system in which reciprocal processes are occurring at equal rates

Effective nuclear charge | charge that leads to the Coulomb force exerted by the nucleus on an electron, calculated as the nuclear charge minus shielding

e_g orbitals | set of two *d* orbitals that are oriented on the Cartesian axes for coordination complexes; in octahedral complexes, they are higher in energy than the t_{2g} orbitals

Electrical potential | energy per charge; in electrochemical systems, it depends on the way the charges are distributed within the system; the SI unit of electrical potential is the volt (1V=1JC)(1V=1JC)

Electrical work (w_{ele}) | negative of total charge times the cell potential; equal to w_{max} for the system, and so equals the free energy change (ΔG)

Electrolyte | substance that produces ions when dissolved in water

Electromagnetic radiation | energy transmitted by waves that have an electric-field component and a magnetic-field component

Electromagnetic spectrum | range of energies that electromagnetic radiation can comprise, including radio, microwaves, infrared, visible, ultraviolet, X-rays, and gamma rays; since electromagnetic radiation energy is proportional to the frequency and inversely proportional to the wavelength, the spectrum can also be specified by ranges of frequencies or wavelengths

Electron | negatively charged, subatomic particle of relatively low mass located outside the nucleus

Electron affinity | energy required to add an electron to a gaseous atom to form an anion

Electron capture | combination of a core electron with a proton to yield a neutron within the nucleus

Electron configuration | electronic structure of an atom in its ground state given as a listing of the orbitals occupied by the electrons

Electron density | a measure of the probability of locating an electron in a particular region of space, it is equal to the squared absolute value of the wave function ψ

Electron volt (eV) | measurement unit of nuclear binding energies, with 1 eV equaling the amount energy due to the moving an electron across an electric potential difference of 1 volt

Electron-pair geometry | arrangement around a central atom of all regions of electron density (bonds, lone pairs, or unpaired electrons)

Electronegativity | tendency of an atom to attract electrons in a bond to itself

Element | substance that is composed of a single type of atom; a substance that cannot be decomposed by a chemical change

Empirical formula | formula showing the composition of a compound given as the simplest whole-number ratio of atoms

Empirical formula mass | sum of average atomic masses for all atoms represented in an empirical formula

Emulsifying agent | amphiphilic substance used to stabilize the particles of some emulsions

Emulsion | colloid formed from immiscible liquids

End point | measured volume of titrant solution that yields the change in sample solution appearance or other property expected for stoichiometric equivalence (see *equivalence point*)

Endothermic process | chemical reaction or physical change that absorbs heat

Energy | capacity to supply heat or do work

Enthalpy (*H*) | sum of a system's internal energy and the mathematical product of its pressure and volume

Enthalpy change (Δ*H*) | heat released or absorbed by a system under constant pressure during a chemical or physical process

Entropy (*S*) | state function that is a measure of the matter and/or energy dispersal within a system, determined by the number of system microstates often described as a measure of the disorder of the system

Equatorial position | one of the three positions in a trigonal bipyramidal geometry with 120° angles between them; the axial positions are located at a 90° angle

Equilibrium | in chemical reactions, the state in which the conversion of reactants into products and the conversion of products back into reactants occur simultaneously at the same rate; state of balance

Equilibrium constant (*K*) | value of the reaction quotient for a system at equilibrium

Equivalence point | volume of titrant solution required to react completely with the analyte in a titration analysis; provides a stoichiometric amount of titrant for the sample's analyte according to the titration reaction

Ether | organic compound with an oxygen atom that is bonded to two carbon atoms

Exact number | number derived by counting or by definition

Excess reactant | reactant present in an amount greater than required by the reaction stoichiometry

Excited state | state having an energy greater than the ground-state energy

Exothermic process | chemical reaction or physical change that releases heat

Expansion work (pressure-volume work) | work done as a system expands or contracts against external pressure

Extensive property | property of a substance that depends on the amount of the substance

External beam radiation therapy | radiation delivered by a machine outside the body

***f* orbital** | multilobed region of space with high electron density, describes orbitals with $l = 3$. An electron in this orbital is called an *f* electron

***f*-block element** | (also, inner transition element) one of the elements with atomic numbers 58–71 or 90–103 that have valence electrons in *f* orbitals; they are frequently shown offset below the periodic table

Face-centered cubic (FCC) solid | crystalline structure consisting of a cubic unit cell with lattice points on the corners and in the center of each face

Face-centered cubic unit cell | simplest repeating unit of a face-centered cubic crystal; it is a cube containing lattice points at each corner and in the center of each face

Fahrenheit | unit of temperature; water freezes at 32 °F and boils at 212 °F on this scale

Faraday's constant (F) | charge on 1 mol of electrons; $F = 96{,}485$ C/mol e^-

First law of thermodynamics | internal energy of a system changes due to heat flow in or out of the system or work done on or by the system

First transition series | transition elements in the fourth period of the periodic table (first row of the *d*-block), atomic numbers 21–29

Fissile (or fissionable) | when a material is capable of sustaining a nuclear fission reaction

Fission | splitting of a heavier nucleus into two or more lighter nuclei, usually accompanied by the conversion of mass into large amounts of energy

Formal charge | charge that would result on an atom by taking the number of valence electrons on the neutral atom and subtracting the nonbonding electrons and the number of bonds (one-half of the bonding electrons)

Formula mass | sum of the average masses for all atoms represented in a chemical formula; for covalent compounds, this is also the molecular mass

Fourth transition series | transition elements in the seventh period of the periodic table (fourth row of the *d*-block), atomic numbers 89 and 104–111

Frasch process | important in the mining of free sulfur from enormous underground deposits

Free radical | molecule that contains an odd number of electrons

Freezing | change from a liquid state to a solid state

Freezing point | temperature at which the solid and liquid phases of a substance are in equilibrium; see also *melting point*

Freezing point depression | lowering of the freezing point of a liquid by addition of a solute

Freezing point depression constant | (also, cryoscopic constant) proportionality constant in the equation relating freezing point depression to solute molality

Frequency (νν) | number of wave cycles (peaks or troughs) that pass a specified point in space per unit time

Frequency factor (*A*) | proportionality constant in the Arrhenius equation, related to the relative number of collisions having an orientation capable of leading to product formation

Functional group | part of an organic molecule that imparts a specific chemical reactivity to the molecule

Fundamental unit of charge | (also called the elementary charge) equals the magnitude of the charge of an electron (e) with $e = 1.602 \times\times 10^{-19}$ C

Fusion | combination of very light nuclei into heavier nuclei, accompanied by the conversion of mass into large amounts of energy

Fusion reactor | nuclear reactor in which fusion reactions of light nuclei are controlled

Galvanic cell | electrochemical cell that involves a spontaneous oxidation-reduction reaction; electrochemical cells with positive cell potentials; also called a voltaic cell

Galvanized iron | method for protecting iron by covering it with zinc, which will oxidize before the iron; zinc-plated iron

Gamma (γ) emission | decay of an excited-state nuclide accompanied by emission of a gamma ray

Gamma ray | (γ or γ00γ00) short wavelength, high-energy electromagnetic radiation that exhibits wave-particle duality

Gas | state in which matter has neither definite volume nor shape

Geiger counter | instrument that detects and measures radiation via the ionization produced in a Geiger-Müller tube

Gel | colloidal dispersion of a liquid in a solid

Geometric isomers | isomers that differ in the way in which atoms are oriented in space relative to each other, leading to different physical and chemical properties

Gibbs free energy change (*G*) | thermodynamic property defined in terms of system enthalpy and entropy; all spontaneous processes involve a decrease in *G*

Gravimetric analysis | quantitative chemical analysis method involving the separation of an analyte from a sample by a physical or chemical process and subsequent mass measurements of the analyte, reaction product, and/or sample

Gray (Gy) | SI unit for measuring radiation dose; 1 Gy = 1 J absorbed/kg tissue

Ground state | state in which the electrons in an atom, ion, or molecule have the lowest energy possible

Group | vertical column of the periodic table

Haber process | main industrial process used to produce ammonia from nitrogen and hydrogen; involves the use of an iron catalyst and elevated temperatures and pressures

Half-life ($t_{1/2}$) | time required for half of the atoms in a radioactive sample to decay

Half-life of a reaction ($t_{1/2}$) | time required for half of a given amount of reactant to be consumed

Half-reaction method | method that produces a balanced overall oxidation-reduction reaction by splitting the reaction into an oxidation "half" and reduction "half," balancing the two half-reactions, and then combining the oxidation half-reaction and reduction half-reaction in such a way that the number of electrons generated by the oxidation is exactly canceled by the number of electrons required by the reduction

Halide | compound containing an anion of a group 17 element in the 1− oxidation state (fluoride, F^-; chloride, Cl^-; bromide, Br^-; and iodide, I^-)

Hall–Héroult cell | electrolysis apparatus used to isolate pure aluminum metal from a solution of alumina in molten cryolite

Halogen | element in group 17

Heat (*q*) | transfer of thermal energy between two bodies

Heat capacity (*C*) | extensive property of a body of matter that represents the quantity of heat required to increase its temperature by 1 degree Celsius (or 1 kelvin)

Heisenberg uncertainty principle | rule stating that it is impossible to exactly determine both certain conjugate dynamical properties such as the momentum and the position of a particle at the same time. The uncertainty principle is a consequence of quantum particles exhibiting wave–particle duality

Hemolysis | rupture of red blood cells due to the accumulation of excess water by osmosis

Henderson-Hasselbalch equation | equation used to calculate the pH of buffer solutions

Henry's law | law stating the proportional relationship between the concentration of dissolved gas in a solution and the partial pressure of the gas in contact with the solution

Hertz (Hz) | the unit of frequency, which is the number of cycles per second, s^{-1}

Hess's law | if a process can be represented as the sum of several steps, the enthalpy change of the process equals the sum of the enthalpy changes of the steps

Heterogeneous catalyst | catalyst present in a different phase from the reactants, furnishing a surface at which a reaction can occur

Heterogeneous equilibria | equilibria between reactants and products in different phases

Heterogeneous mixture | combination of substances with a composition that varies from point to point

Hexagonal closest packing (HCP) | crystalline structure in which close packed layers of atoms or ions are stacked as a series of two alternating layers of different relative orientations (AB)

High-spin complex | complex in which the electrons maximize the total electron spin by singly populating all of the orbitals before pairing two electrons into the lower-energy orbitals

Hole | (also, interstice) space between atoms within a crystal

Homogeneous catalyst | catalyst present in the same phase as the reactants

Homogeneous equilibria | equilibria within a single phase

Homogeneous mixture | (also, solution) combination of substances with a composition that is uniform throughout

Hund's rule | every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin

Hydrocarbon | compound composed only of hydrogen and carbon; the major component of fossil fuels

Hydrogen bonding | occurs when exceptionally strong dipoles attract; bonding that exists when hydrogen is bonded to one of the three most electronegative elements: F, O, or N

Hydrogen carbonate | salt of carbonic acid, H_2CO_3 (containing the anion HCO−3HCO3−) in which one hydrogen atom has been replaced; an acid carbonate; also known as *bicarbonate ion*

Hydrogen halide | binary compound formed between hydrogen and the halogens: HF, HCl, HBr, and HI

Hydrogen sulfate | HSO−4HSO4− ion

Hydrogen sulfite | HSO−3HSO3− ion

Hydrogenation | addition of hydrogen (H_2) to reduce a compound

Hydrometallurgy | process in which a metal is separated from a mixture by first converting it into soluble ions, extracting the ions, and then reducing the ions to precipitate the pure metal

Hydrostatic pressure | pressure exerted by a fluid due to gravity

Hydroxide | compound of a metal with the hydroxide ion OH^- or the group −OH

Hypertonic | of greater osmotic pressure

Hypervalent molecule | molecule containing at least one main group element that has more than eight electrons in its valence shell

Hypothesis | tentative explanation of observations that acts as a guide for gathering and checking information

Hypotonic | of less osmotic pressure

Ideal solution | solution that forms with no accompanying energy change

Immiscible | of negligible mutual solubility; typically refers to liquid substances

Indicator | substance added to the sample in a titration analysis to permit visual detection of the end point

Induced dipole | temporary dipole formed when the electrons of an atom or molecule are distorted by the instantaneous dipole of a neighboring atom or molecule

Inert electrode | electrode that allows current to flow, but that does not otherwise participate in the oxidation-reduction reaction in an electrochemical cell; the mass of an inert electrode does not change during the oxidation-reduction reaction; inert electrodes are often made of platinum or gold because these metals are chemically unreactive.

Inert gas | (also, noble gas) element in group 18

Inert pair effect | tendency of heavy atoms to form ions in which their valence *s* electrons are not lost

Initial rate | instantaneous rate of a chemical reaction at $t = 0$ s (immediately after the reaction has begun)

Inner transition metal | (also, lanthanide or actinide) element in the bottom two rows; if in the first row, also called lanthanide, or if in the second row, also called actinide

Instantaneous dipole | temporary dipole that occurs for a brief moment in time when the electrons of an atom or molecule are distributed asymmetrically

Instantaneous rate | rate of a chemical reaction at any instant in time, determined by the slope of the line tangential to a graph of concentration as a function of time

Integrated rate law | equation that relates the concentration of a reactant to elapsed time of reaction

Intensity | property of wave-propagated energy related to the amplitude of the wave, such as brightness of light or loudness of sound

Intensive property | property of a substance that is independent of the amount of the substance

Interference pattern | pattern typically consisting of alternating bright and dark fringes; it results from constructive and destructive interference of waves

Interhalogen | compound formed from two or more different halogens

Intermolecular force | noncovalent attractive force between atoms, molecules, and/or ions

Internal energy (U) | total of all possible kinds of energy present in a substance or substances

Internal radiation therapy | (also, brachytherapy) radiation from a radioactive substance introduced into the body to kill cancer cells

Interstitial sites | spaces between the regular particle positions in any array of atoms or ions

Ion | electrically charged atom or molecule (contains unequal numbers of protons and electrons)

Ion pair | solvated anion/cation pair held together by moderate electrostatic attraction

Ion-dipole attraction | electrostatic attraction between an ion and a polar molecule

Ion-product constant for water (K_w) | equilibrium constant for the autoionization of water

Ionic bond | electrostatic forces of attraction between the oppositely charged ions of an ionic compound

Ionic bond | strong electrostatic force of attraction between cations and anions in an ionic compound

Ionic compound | compound composed of cations and anions combined in ratios, yielding an electrically neutral substance

Ionic solid | solid composed of positive and negative ions held together by strong electrostatic attractions

Ionization energy | energy required to remove an electron from a gaseous atom or ion. The associated number (e.g., second ionization energy) corresponds to the charge of the ion produced (X^{2+})

Ionization isomer | (or coordination isomer) isomer in which an anionic ligand is replaced by the counter ion in the inner coordination sphere

Ionizing radiation | radiation that can cause a molecule to lose an electron and form an ion

Isoelectronic | group of ions or atoms that have identical electron configurations

Isomers | compounds with the same chemical formula but different structures

Isomorphous | possessing the same crystalline structure

Isotonic | of equal osmotic pressure

Isotopes | atoms that contain the same number of protons but different numbers of neutrons

Joule (J) | SI unit of energy; 1 joule is the kinetic energy of an object with a mass of 2 kilograms moving with a velocity of 1 meter per second, 1 J = 1 kg m^2/s and 4.184 J = 1 cal

K_c | equilibrium constant for reactions based on concentrations of reactants and products

Kelvin (K) | SI unit of temperature; 273.15 K = 0 ºC

Kilogram (kg) | standard SI unit of mass; 1 kg = approximately 2.2 pounds

Kinetic energy | energy of a moving body, in joules, equal to 12mv212mv2 (where m = mass and v = velocity)

K_P | equilibrium constant for gas-phase reactions based on partial pressures of reactants and products

Lanthanide | inner transition metal in the top of the bottom two rows of the periodic table

Lanthanide series | (also, lanthanoid series) lanthanum and the elements in the first row or the *f*-block, atomic numbers 57–71

Lattice energy ($\Delta H_{lattice}$) | energy required to separate one mole of an ionic solid into its component gaseous ions

Law | statement that summarizes a vast number of experimental observations, and describes or predicts some aspect of the natural world

Law of conservation of matter | when matter converts from one type to another or changes form, there is no detectable change in the total amount of matter present

Law of constant composition | (also, law of definite proportions) all samples of a pure compound contain the same elements in the same proportions by mass

Law of definite proportions | (also, law of constant composition) all samples of a pure compound contain the same elements in the same proportions by mass

Law of mass action | when a reversible reaction has attained equilibrium at a given temperature, the reaction quotient remains constant

Law of multiple proportions | when two elements react to form more than one compound, a fixed mass of one element will react with masses of the other element in a ratio of small whole numbers

Le Chatelier's principle | when a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance

Length | measure of one dimension of an object

Leveling effect of water | any acid stronger than H3O+H3O+, or any base stronger than OH^- will react with water to form H3O+H3O+, or OH^-, respectively; water acts as a base to make all strong acids appear equally strong, and it acts as an acid to make all strong bases appear equally strong

Lewis structure | diagram showing lone pairs and bonding pairs of electrons in a molecule or an ion

Lewis symbol | symbol for an element or monatomic ion that uses a dot to represent each valence electron in the element or ion

Ligand | ion or neutral molecule attached to the central metal ion in a coordination compound

Limiting reactant | reactant present in an amount lower than required by the reaction stoichiometry, thus limiting the amount of product generated

Line spectrum | electromagnetic radiation emitted at discrete wavelengths by a specific atom (or atoms) in an excited state

Linear | shape in which two outside groups are placed on opposite sides of a central atom

Linkage isomer | coordination compound that possesses a ligand that can bind to the transition metal in two different ways (CN^- vs. NC^-)

Liquid | state of matter that has a definite volume but indefinite shape

Liter (L) | (also, cubic decimeter) unit of volume; 1 L = 1,000 cm^3

Lone pair | two (a pair of) valence electrons that are not used to form a covalent bond

Low-spin complex | complex in which the electrons minimize the total electron spin by pairing in the lower-energy orbitals before populating the higher-energy orbitals

Macroscopic domain | realm of everyday things that are large enough to sense directly by human sight and touch

Magic number | nuclei with specific numbers of nucleons that are within the band of stability

Magnetic quantum number (m_l) | quantum number signifying the orientation of an atomic orbital around the nucleus; orbitals having different values of m_l but the same subshell value of l have the same energy (are degenerate), but this degeneracy can be removed by application of an external magnetic field

Main-group element | (also, representative element) element in columns 1, 2, and 12–18

Manometer | device used to measure the pressure of a gas trapped in a container

Mass | fundamental property indicating amount of matter

Mass defect | difference between the mass of an atom and the summed mass of its constituent subatomic particles (or the mass “lost” when nucleons are brought together to form a nucleus)

Mass number (A) | sum of the numbers of neutrons and protons in the nucleus of an atom

Mass percentage | ratio of solute-to-solution mass expressed as a percentage

Mass-energy equivalence equation | Albert Einstein's relationship showing that mass and energy are equivalent

Mass-volume percent | ratio of solute mass to solution volume, expressed as a percentage

Matter | anything that occupies space and has mass

Melting | change from a solid state to a liquid state

Melting point | temperature at which the solid and liquid phases of a substance are in equilibrium; see also *freezing point*

Metal | element that is shiny, malleable, good conductor of heat and electricity

Metal (representative) | atoms of the metallic elements of groups 1, 2, 12, 13, 14, 15, and 16, which form ionic compounds by losing electrons from their outer *s* or *p* orbitals

Metallic solid | solid composed of metal atoms

Metalloid | element that conducts heat and electricity moderately well, and possesses some properties of metals and some properties of nonmetals

Metalloid | element that has properties that are between those of metals and nonmetals; these elements are typically semiconductors

Meter (m) | standard metric and SI unit of length; 1 m = approximately 1.094 yards

Method of initial rates | use of a more explicit algebraic method to determine the orders in a rate law

Microscopic domain | realm of things that are much too small to be sensed directly

Microstate (*W*) | possible configuration or arrangement of matter and energy within a system

Millicurie (mCi) | larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7×10^{10} disintegrations/s

Milliliter (mL) | 1/1,000 of a liter; equal to 1 cm^3

Miscible | mutually soluble in all proportions; typically refers to liquid substances

Mixture | matter that can be separated into its components by physical means

Molality (*m*) | a concentration unit defined as the ratio of the numbers of moles of solute to the mass of the solvent in kilograms

Molar mass | mass in grams of 1 mole of a substance

Molar solubility | solubility of a compound expressed in units of moles per liter (mol/L)

Molarity (*M*) | unit of concentration, defined as the number of moles of solute dissolved in 1 liter of solution

Mole | amount of substance containing the same number of atoms, molecules, ions, or other entities as the number of atoms in exactly 12 grams of ^{12}C

Molecular compound | (also, covalent compound) composed of molecules formed by atoms of two or more different elements

Molecular equation | chemical equation in which all reactants and products are represented as neutral substances

Molecular formula | formula indicating the composition of a molecule of a compound and giving the actual number of atoms of each element in a molecule of the compound.

Molecular solid | solid composed of neutral molecules held together by intermolecular forces of attraction

Molecular structure | arrangement of atoms in a molecule or ion

Molecular structure | structure that includes only the placement of the atoms in the molecule

Molecule | bonded collection of two or more atoms of the same or different elements

Monatomic ion | ion composed of a single atom

Monodentate | ligand that attaches to a central metal through just one coordinate covalent bond

Monoprotic acid | acid containing one ionizable hydrogen atom per molecule

Multiple equilibrium | system characterized by more than one state of balance between a slightly soluble ionic solid and an aqueous solution of ions working simultaneously

Nernst equation | equation that relates the logarithm of the reaction quotient (Q) to nonstandard cell potentials; can be used to relate equilibrium constants to standard cell potentials

Net ionic equation | chemical equation in which only those dissolved ionic reactants and products that undergo a chemical or physical change are represented (excludes spectator ions)

Neutral | describes a solution in which $[H_3O^+] = [OH^-]$

Neutron | uncharged, subatomic particle located in the nucleus

Nitrate | NO−3NO3− ion; salt of nitric acid

Nitrogen fixation | formation of nitrogen compounds from molecular nitrogen

Noble gas | (also, inert gas) element in group 18

Node | any point of a standing wave with zero amplitude

Node | plane separating different lobes of orbitals, where the probability of finding an electron is zero

Nomenclature | system of rules for naming objects of interest

Nonelectrolyte | substance that does not produce ions when dissolved in water

Nonionizing radiation | radiation that speeds up the movement of atoms and molecules; it is equivalent to heating a sample, but is not energetic enough to cause the ionization of molecules

Nonmetal | element that appears dull, poor conductor of heat and electricity

Nonspontaneous process | process that requires continual input of energy from an

external source

Normal boiling point | temperature at which a liquid's vapor pressure equals 1 atm (760 torr)

Nuclear binding energy | energy lost when an atom's nucleons are bound together (or the energy needed to break a nucleus into its constituent protons and neutrons)

Nuclear chemistry | study of the structure of atomic nuclei and processes that change nuclear structure

Nuclear fuel | fissionable isotope present in sufficient quantities to provide a self-sustaining chain reaction in a nuclear reactor

Nuclear moderator | substance that slows neutrons to a speed low enough to cause fission

Nuclear reaction | change to a nucleus resulting in changes in the atomic number, mass number, or energy state

Nuclear reactor | environment that produces energy via nuclear fission in which the chain reaction is controlled and sustained without explosion

Nuclear transmutation | conversion of one nuclide into another nuclide

Nucleon | collective term for protons and neutrons in a nucleus

Nucleus | massive, positively charged center of an atom made up of protons and neutrons

Nuclide | nucleus of a particular isotope

Nutritional calorie (Calorie) | unit used for quantifying energy provided by digestion of foods, defined as 1000 cal or 1 kcal

Octahedral | shape in which six outside groups are placed around a central atom such that a three-dimensional shape is generated with four groups forming a square and the other two forming the apex of two pyramids, one above and one below the square plane

Octahedral hole | open space in a crystal at the center of six particles located at the corners of an octahedron

Octet rule | guideline that states main group atoms will form structures in which eight valence electrons interact with each nucleus, counting bonding electrons as interacting with both atoms connected by the bond

Optical isomer | (also, enantiomer) molecule that is a nonsuperimposable mirror image with identical chemical and physical properties, except when it reacts with other optical isomers

Orbital diagram | pictorial representation of the electron configuration showing each orbital as a box and each electron as an arrow

Organic compound | natural or synthetic compound that contains carbon

Osmosis | diffusion of solvent molecules through a semipermeable membrane

Osmotic pressure (Π) | opposing pressure required to prevent bulk transfer of solvent molecules through a semipermeable membrane

Ostwald process | industrial process used to convert ammonia into nitric acid

Overall reaction order | sum of the reaction orders for each substance represented in the rate law

Overlap | coexistence of orbitals from two different atoms sharing the same region of space, leading to the formation of a covalent bond

Oxidation half-reaction | the "half" of an oxidation-reduction reaction involving oxidation; the half-reaction in which electrons appear as products; balanced when each atom type, as well as the charge, is balanced

Oxide | binary compound of oxygen with another element or group, typically containing O^{2-} ions or the group –O– or =O

Oxyacid | compound that contains hydrogen, oxygen, and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H^+ ions when dissolved in water)

Oxyacid | compound containing a nonmetal and one or more hydroxyl groups

Oxyanion | polyatomic anion composed of a central atom bonded to oxygen atoms

Ozone | allotrope of oxygen; O_3

***p* orbital** | dumbbell-shaped region of space with high electron density, describes orbitals with $l = 1$. An electron in this orbital is called a *p* electron

Pairing energy (P) | energy required to place two electrons with opposite spins into a single orbital

Parent nuclide | unstable nuclide that changes spontaneously into another (daughter) nuclide

Partially miscible | of moderate mutual solubility; typically refers to liquid substances

Particle accelerator | device that uses electric and magnetic fields to increase the kinetic energy of nuclei used in transmutation reactions

Parts per billion (ppb) | ratio of solute-to-solution mass multiplied by 10^9

Parts per million (ppm) | ratio of solute-to-solution mass multiplied by 10^6

Pascal (Pa) | SI unit of pressure; 1 Pa = 1 N/m^2

Passivation | metals with a protective nonreactive film of oxide or other compound that creates a barrier for chemical reactions; physical or chemical removal of the passivating film allows the metals to demonstrate their expected chemical reactivity

Pauli exclusion principle | specifies that no two electrons in an atom can have the same value for all four quantum numbers

Percent composition | percentage by mass of the various elements in a compound

Percent ionization | ratio of the concentration of the ionized acid to the initial acid concentration, times 100

Percent yield | measure of the efficiency of a reaction, expressed as a percentage of the theoretical yield

Period | (also, series) horizontal row of the periodic table

Periodic law | properties of the elements are periodic function of their atomic numbers.

Periodic table | table of the elements that places elements with similar chemical properties close together

Peroxide | molecule containing two oxygen atoms bonded together or as the anion, $O2−2O22−$

PH | logarithmic measure of the concentration of hydronium ions in a solution

Phase diagram | pressure-temperature graph summarizing conditions under which the phases of a substance can exist

Photon | smallest possible packet of electromagnetic radiation, a particle of light

Photosynthesis | process whereby light energy promotes the reaction of water and carbon dioxide to form carbohydrates and oxygen; this allows photosynthetic organisms to store energy

Physical change | change in the state or properties of matter that does not involve a change in its chemical composition

Physical property | characteristic of matter that is not associated with any change in its chemical composition

Pi bond (π bond) | covalent bond formed by side-by-side overlap of atomic orbitals; the electron density is found on opposite sides of the internuclear axis

Pidgeon process | chemical reduction process used to produce magnesium through the thermal reaction of magnesium oxide with silicon

Plasma | gaseous state of matter containing a large number of electrically charged atoms and/or molecules

Platinum metals | group of six transition metals consisting of ruthenium, osmium, rhodium, iridium, palladium, and platinum that tend to occur in the same minerals and demonstrate similar chemical properties

Pnictogen | element in group 15

POH | logarithmic measure of the concentration of hydroxide ions in a solution

Polar covalent bond | covalent bond between atoms of different electronegativities; a covalent bond with a positive end and a negative end

Polar molecule | (also, dipole) molecule with an overall dipole moment

Polarizability | measure of the ability of a charge to distort a molecule's charge distribution (electron cloud)

Polyatomic ion | ion composed of more than one atom

Polydentate ligand | ligand that is attached to a central metal ion by bonds from two or more donor atoms, named with prefixes specifying how many donors are present (e.g., hexadentate = six coordinate bonds formed)

Polymorph | variation in crystalline structure that results in different physical properties for the resulting compound

Position of equilibrium | concentrations or partial pressures of components of a reaction at equilibrium (commonly used to describe conditions before a disturbance)

Positron (β+10β+10 or e+10e+10) | antiparticle to the electron; it has identical properties to an electron, except for having the opposite (positive) charge

Positron emission | (also, β^+ decay) conversion of a proton into a neutron, which remains in the nucleus, and a positron, which is emitted

Potential energy | energy of a particle or system of particles derived from relative position, composition, or condition

Pounds per square inch (psi) | unit of pressure common in the US

Precision | how closely a measurement matches the same measurement when repeated

Pressure | force exerted per unit area

Principal quantum number (*n*) | quantum number specifying the shell an electron occupies in an atom

Product | substance formed by a chemical or physical change; shown on the right side of the arrow in a chemical equation

Proton | positively charged, subatomic particle located in the nucleus

Pure covalent bond | (also, nonpolar covalent bond) covalent bond between atoms of identical electronegativities

Pure substance | homogeneous substance that has a constant composition

Quantitative analysis | the determination of the amount or concentration of a substance in a sample

Quantization | occurring only in specific discrete values, not continuous

Quantum mechanics | field of study that includes quantization of energy, wave-particle duality, and the Heisenberg uncertainty principle to describe matter

Quantum number | integer number having only specific allowed values and used to characterize the arrangement of electrons in an atom

Radiation absorbed dose (rad) | SI unit for measuring radiation dose, frequently used in medical applications; 1 rad = 0.01 Gy

Radiation dosimeter | device that measures ionizing radiation and is used to determine personal radiation exposure

Radiation therapy | use of high-energy radiation to damage the DNA of cancer cells, which kills them or keeps them from dividing

Radioactive decay | spontaneous decay of an unstable nuclide into another nuclide

Radioactive decay series | chains of successive disintegrations (radioactive decays) that ultimately lead to a stable end-product

Radioactive tracer | (also, radioactive label) radioisotope used to track or follow a substance by monitoring its radioactive emissions

Radioactivity | phenomenon exhibited by an unstable nucleon that spontaneously undergoes change into a nucleon that is more stable; an unstable nucleon is said to be radioactive

Radiocarbon dating | highly accurate means of dating objects 30,000–50,000 years old that were derived from once-living matter; achieved by calculating the ratio of C614:C612C614:C612 in the object vs. the ratio of C614:C612C614:C612 in the present-day atmosphere

Radioisotope | isotope that is unstable and undergoes conversion into a different, more stable isotope

Radiometric dating | use of radioisotopes and their properties to date the formation of objects such as archeological artifacts, formerly living organisms, or geological formations

Raoult's law | the partial pressure exerted by a solution component is equal to the product of the component's mole fraction in the solution and its equilibrium vapor pressure in the pure state

Rare earth element | collection of 17 elements including the lanthanides, scandium, and yttrium that often occur together and have similar chemical properties, making separation difficult

Rate constant (*k*) | proportionality constant in the relationship between reaction rate and concentrations of reactants

Rate expression | mathematical representation relating reaction rate to changes in amount, concentration, or pressure of reactant or product species per unit time

Rate law | (also, rate equation) mathematical equation showing the dependence of reaction rate on the rate constant and the concentration of one or more reactants

Rate of reaction | measure of the speed at which a chemical reaction takes place

Reactant | substance undergoing a chemical or physical change; shown on the left side of the arrow in a chemical equation

Reaction order | value of an exponent in a rate law, expressed as an ordinal number (for example, zero order for 0, first order for 1, second order for 2, and so on)

Reaction quotient (*Q*) | ratio of the product of molar concentrations (or pressures) of the products to that of the reactants, each concentration (or pressure) being raised to the power equal to the coefficient in the equation

Reactor coolant | assembly used to carry the heat produced by fission in a reactor to an external boiler and turbine where it is transformed into electricity

Reduction half-reaction | the "half" of an oxidation-reduction reaction involving reduction; the half-reaction in which electrons appear as reactants; balanced when each atom type, as well as the charge, is balanced

Relative biological effectiveness (RBE) | measure of the relative damage done by radiation

Representative element | (also, main-group element) element in columns 1, 2, and 12–18

Representative element | element where the *s* and *p* orbitals are filling

Representative metal | metal among the representative elements

Resonance | situation in which one Lewis structure is insufficient to describe the bonding in a molecule and the average of multiple structures is observed

Resonance forms | two or more Lewis structures that have the same arrangement of atoms but different arrangements of electrons

Resonance hybrid | average of the resonance forms shown by the individual Lewis structures

Reversible process | process that takes place so slowly as to be capable of reversing direction in response to an infinitesimally small change in conditions; hypothetical construct that can only be approximated by real processes removed

Reversible reaction | chemical reaction that can proceed in both the forward and reverse directions under given conditions

Roentgen equivalent man (rem) | unit for radiation damage, frequently used in medicine; 1 rem = 1 Sv

Rounding | procedure used to ensure that calculated results properly reflect the uncertainty in the measurements used in the calculation

***s* orbital** | spherical region of space with high electron density, describes orbitals with $l = 0$. An electron in this orbital is called an *s* electron

Sacrificial anode | more active, inexpensive metal used as the anode in cathodic protection; frequently made from magnesium or zinc

Saturated | of concentration equal to solubility; containing the maximum concentration of solute possible for a given temperature and pressure

Saturated hydrocarbon | molecule containing carbon and hydrogen that has only single bonds between carbon atoms

Scientific method | path of discovery that leads from question and observation to law or hypothesis to theory, combined with experimental verification of the hypothesis and any necessary modification of the theory

Scintillation counter | instrument that uses a scintillator—a material that emits light when excited by ionizing radiation—to detect and measure radiation

Second (s) | SI unit of time

Second law of thermodynamics | entropy of the universe increases for a spontaneous process

Second transition series | transition elements in the fifth period of the periodic table (second row of the *d*-block), atomic numbers 39–47

Selective precipitation | process in which ions are separated using differences in their solubility with a given precipitating reagent

Semipermeable membrane | a membrane that selectively permits passage of certain ions or molecules

Series | (also, period) horizontal row of the period table

Shell | set of orbitals with the same principal quantum number, *n*

SI units (International System of Units) | standards fixed by international agreement in the International System of Units (*Le Système International d'Unités*)

Sievert (Sv) | SI unit measuring tissue damage caused by radiation; takes into account energy and biological effects of radiation

Sigma bond (σ bond) | covalent bond formed by overlap of atomic orbitals along the internuclear axis

Significant figures | (also, significant digits) all of the measured digits in a determination, including the uncertain last digit

Silicate | compound containing silicon-oxygen bonds, with silicate tetrahedra connected in rings, sheets, or three-dimensional networks, depending on the other elements involved in the formation of the compounds

Simple cubic structure | crystalline structure with a cubic unit cell with lattice points only at the corners

Simple cubic unit cell | (also, primitive cubic unit cell) unit cell in the simple cubic structure

Single bond | bond in which a single pair of electrons is shared between two atoms

Skeletal structure | shorthand method of drawing organic molecules in which carbon atoms are represented by the ends of lines and bends in between lines, and hydrogen atoms attached to the carbon atoms are not shown (but are understood to be present by the context of the structure)

Smelting | process of extracting a pure metal from a molten ore

Solid | state of matter that is rigid, has a definite shape, and has a fairly constant volume

Solubility | extent to which a solute may be dissolved in water, or any solvent

Solubility product (K_{sp}) | equilibrium constant for the dissolution of a slightly soluble electrolyte

Solute | solution component present in a concentration less than that of the solvent

Solvation | exothermic process in which intermolecular attractive forces between the solute and solvent in a solution are established

Solvent | solution component present in a concentration that is higher relative to other components

Space lattice | all points within a crystal that have identical environments

Spatial isomers | compounds in which the relative orientations of the atoms in space differ

Specific heat capacity (c) | intensive property of a substance that represents the quantity of heat required to raise the temperature of 1 gram of the substance by 1 degree Celsius (or 1 kelvin)

Spectator ion | ion that does not undergo a chemical or physical change during a reaction, but its presence is required to maintain charge neutrality

Spectrochemical series | ranking of ligands according to the magnitude of the crystal field splitting they induce

Spin quantum number (m_s) | number specifying the electron spin direction, either +12+12 or −12−12

Spontaneous change | process that takes place without a continuous input of energy from an external source

Spontaneous process | physical or chemical change that occurs without the addition of energy from an external source

Standard cell potential (E∘cell)(Ecell∘) | the cell potential when all reactants and products are in their standard states (1 bar or 1 atm or gases; 1 M for solutes), usually at 298.15 K; can be calculated by subtracting the standard reduction potential for the half-reaction at the anode from the standard reduction potential for the half-reaction occurring at the cathode

Standard enthalpy of combustion (ΔH∘cΔHc∘) | heat released when one mole of a compound undergoes complete combustion under standard conditions

Standard enthalpy of formation (ΔH∘fΔHf∘) | enthalpy change of a chemical reaction in which 1 mole of a pure substance is formed from its elements in their most stable states under standard state conditions

Standard entropy ($S°$) | entropy for a substance at 1 bar pressure; tabulated values are usually determined at 298.15 K and denoted S∘298S298∘

Standard entropy change ($\Delta S°$) | change in entropy for a reaction calculated using the standard entropies, usually at room temperature and denoted ΔS∘298ΔS298∘

Standard free energy change ($\Delta G°$) | change in free energy for a process occurring under standard conditions (1 bar pressure for gases, 1 M concentration for solutions)

Standard free energy of formation (ΔG∘f)(ΔGf∘) | change in free energy accompanying the formation of one mole of substance from its elements in their standard states

Standard hydrogen electrode (SHE) | the electrode consists of hydrogen gas bubbling through hydrochloric acid over an inert platinum electrode whose reduction at standard conditions is assigned a value of 0 V; the reference point for standard reduction potentials

Standard reduction potential ($E°$) | the value of the reduction under standard conditions (1 bar or 1 atm for gases; 1 M for solutes) usually at 298.15 K; tabulated values used to calculate standard cell potentials

Standard state | set of physical conditions as accepted as common reference conditions for reporting thermodynamic properties; 1 bar of pressure, and solutions at 1 molar concentrations, usually at a temperature of 298.15 K

Standing wave | (also, stationary wave) localized wave phenomenon characterized by discrete wavelengths determined by the boundary conditions used to generate the waves; standing waves are inherently quantized

State function | property depending only on the state of a system, and not the path taken to reach that state

Steel | material made from iron by removing impurities in the iron and adding substances that produce alloys with properties suitable for specific uses

Stepwise ionization | process in which an acid is ionized by losing protons sequentially

Stress | change to a reaction's conditions that may cause a shift in the equilibrium

Strong electrolyte | substance that dissociates or ionizes completely when dissolved in water

Strong nuclear force | force of attraction between nucleons that holds a nucleus together

Strong-field ligand | ligand that causes larger crystal field splittings

Structural formula | shows the atoms in a molecule and how they are connected

Structural isomer | one of two substances that have the same molecular formula but different physical and chemical properties because their atoms are bonded differently

Subcritical mass | amount of fissionable material that cannot sustain a chain reaction; less than a critical mass

Sublimation | change from solid state directly to gaseous state

Subshell | set of orbitals in an atom with the same values of n and l

Substituent | branch or functional group that replaces hydrogen atoms in a larger hydrocarbon chain

Substitution reaction | reaction in which one atom replaces another in a molecule

Sulfate | $SO2−4SO42−$ ion

Sulfite | $SO2−3SO32−$ ion

Superconductor | material that conducts electricity with no resistance

Supercritical fluid | substance at a temperature and pressure higher than its critical point; exhibits properties intermediate between those of gaseous and liquid states

Supercritical mass | amount of material in which there is an increasing rate of fission

Superoxide | oxide containing the anion $O−2O2−$

Supersaturated | of concentration that exceeds solubility; a nonequilibrium state

Surface tension | energy required to increase the area, or length, of a liquid surface by a given amount

Surroundings | all matter other than the system being studied

Symbolic domain | specialized language used to represent components of the macroscopic and microscopic domains, such as chemical symbols, chemical formulas, chemical equations, graphs, drawings, and calculations

System | portion of matter undergoing a chemical or physical change being studied

t_{2g} **orbitals** | set of three d orbitals aligned between the Cartesian axes for coordination complexes; in octahedral complexes, they are lowered in energy compared to the e_g orbitals according to CFT

Temperature | intensive property of matter that is a quantitative measure of “hotness” and “coldness”

Tetrahedral | shape in which four outside groups are placed around a central atom such that a three-dimensional shape is generated with four corners and 109.5° angles between each pair and the central atom

Tetrahedral hole | tetrahedral space formed by four atoms or ions in a crystal

Theoretical yield | amount of product that may be produced from a given amount of reactant(s) according to the reaction stoichiometry

Theory | well-substantiated, comprehensive, testable explanation of a particular aspect of nature

Thermal energy | kinetic energy associated with the random motion of atoms and molecules

Thermochemistry | study of measuring the amount of heat absorbed or released during a chemical reaction or a physical change

Third law of thermodynamics | entropy of a perfect crystal at absolute zero (0 K) is zero

Third transition series | transition elements in the sixth period of the periodic table (third row of the d-block), atomic numbers 57 and 72–79

Titrant | solution containing a known concentration of substance that will react with the analyte in a titration analysis

Titration analysis | quantitative chemical analysis method that involves measuring the volume of a reactant solution required to completely react with the analyte in a sample

Titration curve | plot of the pH of a solution of acid or base versus the volume of base or acid added during a titration

Torr | unit of pressure; $1torr=1760atm1torr=1760atm$

***trans* configuration** | configuration of a geometrical isomer in which two similar groups are on opposite sides of an imaginary reference line on the molecule

Transition metal | element in columns 3–11

Transmutation reaction | bombardment of one type of nuclei with other nuclei or neutrons

Transuranium element | element with an atomic number greater than 92; these elements do not occur in nature

Trigonal bipyramidal | shape in which five outside groups are placed around a central atom such that three form a flat triangle with 120° angles between each pair and the central atom, and the other two form the apex of two pyramids, one above and one below the triangular plane

Trigonal planar | shape in which three outside groups are placed in a flat triangle around a central atom with 120° angles between each pair and the central atom

Triple bond | bond in which three pairs of electrons are shared between two atoms

Triple point | temperature and pressure at which the vapor, liquid, and solid phases of a substance are in equilibrium

Triprotic acid | acid that contains three ionizable hydrogen atoms per molecule; ionization of triprotic acids occurs in three steps

Tyndall effect | scattering of visible light by a colloidal dispersion

Uncertainty | estimate of amount by which measurement differs from true value

Unified atomic mass unit (u) | alternative unit equivalent to the atomic mass unit

Unit | standard of comparison for measurements

Unit cell | smallest portion of a space lattice that is repeated in three dimensions to form the entire lattice

Unit conversion factor | ratio of equivalent quantities expressed with different units; used to convert from one unit to a different unit

Unsaturated | of concentration less than solubility

Vacancy | defect that occurs when a position that should contain an atom or ion is vacant

Valence bond theory | description of bonding that involves atomic orbitals overlapping to form σ or π bonds, within which pairs of electrons are shared

Valence electrons | electrons in the outermost or valence shell (highest value of n) of a ground-state atom; determine how an element reacts

Valence shell | outermost shell of electrons in a ground-state atom; for main group elements, the orbitals with the highest n level (s and p subshells) are in the valence shell, while for transition metals, the highest energy s and d subshells make up the valence shell and for inner transition elements, the highest s, d, and f subshells are included

Valence shell electron-pair repulsion theory (VSEPR) | theory used to predict the bond angles in a molecule based on positioning regions of high electron density as far apart as possible to minimize electrostatic repulsion

Van der Waals equation | modified version of the ideal gas equation containing additional terms to account for non-ideal gas behavior

Van der Waals force | attractive or repulsive force between molecules, including dipole-dipole, dipole-induced dipole, and London dispersion forces; does not include forces due to covalent or ionic bonding, or the attraction between ions and molecules

Van't Hoff factor (i) | the ratio of the number of moles of particles in a solution to the number of moles of formula units dissolved in the solution

Vapor pressure | (also, equilibrium vapor pressure) pressure exerted by a vapor in equilibrium with a solid or a liquid at a given temperature

Vaporization | change from liquid state to gaseous state

Vector | quantity having magnitude and direction

Viscosity | measure of a liquid's resistance to flow

Voltaic cell | another name for a galvanic cell

Volume | amount of space occupied by an object

Volume percentage | ratio of solute-to-solution volume expressed as a percentage

Wave | oscillation that can transport energy from one point to another in space

Wave-particle duality | term used to describe the fact that elementary particles including matter exhibit properties of both particles (including localized position, momentum) and waves (including nonlocalization, wavelength, frequency)

Wavefunction (ψ) | mathematical description of an atomic orbital that describes the shape of the orbital; it can be used to calculate the probability of finding the electron at any given location in the orbital, as well as dynamical variables such as the energy and the angular momentum

Wavelength (λ) | distance between two consecutive peaks or troughs in a wave

Weak electrolyte | substance that ionizes only partially when dissolved in water

Weak-field ligand | ligand that causes small crystal field splittings

Weight | force that gravity exerts on an object

Work (w) | energy transfer due to changes in external, macroscopic variables such as pressure and volume; or causing matter to move against an opposing force

X-ray crystallography | experimental technique for determining distances between atoms in a crystal by measuring the angles at which X-rays are diffracted when passing through the crystal

Detailed Licensing

Overview

Title: CHEM 1500: Chemical Bonding and Organic Chemistry

Webpages: 98

Applicable Restrictions: Noncommercial

All licenses found:

- Undeclared: 42.9% (42 pages)
- CC BY 4.0: 38.8% (38 pages)
- CC BY-SA 4.0: 17.3% (17 pages)
- CC BY-NC 4.0: 1% (1 page)

By Page

- CHEM 1500: Chemical Bonding and Organic Chemistry - *Undeclared*
  - Front Matter - *Undeclared*
    - TitlePage - *Undeclared*
    - InfoPage - *Undeclared*
    - Table of Contents - *Undeclared*
    - Licensing - *Undeclared*
  - 1: Background Material - *Undeclared*
    - 1.1: Essential Ideas of Chemistry - *CC BY 4.0*
      - 1.1.1: Chemistry in Context - *CC BY 4.0*
      - 1.1.2: Phases and Classification of Matter - *CC BY 4.0*
      - 1.1.3: Physical and Chemical Properties - *CC BY 4.0*
      - 1.1.4: Measurements - *CC BY 4.0*
      - 1.1.5: Measurement Uncertainty, Accuracy, and Precision - *CC BY 4.0*
      - 1.1.6: Mathematical Treatment of Measurement Results - *CC BY 4.0*
      - 1.1.E: Essential Ideas of Chemistry (Exercises) - *CC BY 4.0*
    - 1.2: Atoms, Molecules, and Ions - *CC BY 4.0*
      - 1.2.1: Prelude to Atoms - *CC BY 4.0*
      - 1.2.2: Early Ideas in Atomic Theory - *CC BY 4.0*
      - 1.2.3: Evolution of Atomic Theory - *CC BY 4.0*
      - 1.2.4: Atomic Structure and Symbolism - *CC BY 4.0*
      - 1.2.5: Chemical Formulas - *CC BY 4.0*
      - 1.2.6: The Periodic Table - *CC BY 4.0*
      - 1.2.7: Molecular and Ionic Compounds - *CC BY 4.0*
      - 1.2.8: Chemical Nomenclature - *CC BY 4.0*
      - 1.2.E: Atoms, Molecules, and Ions (Exercises) - *CC BY 4.0*
  - 2: Quantum Theory and Electronic Structure of Atoms - *Undeclared*
    - 2.1: Electromagnetic Energy - *CC BY 4.0*
    - 2.2: Atomic Spectroscopy and The Bohr Model - *Undeclared*
    - 2.3: The Wavelength Nature of Matter - *Undeclared*
    - 2.4: Quantum Mechanics and The Atom - *Undeclared*
    - 2.5: The Shape of Atomic Orbitals - *Undeclared*
    - 2.6: Electronic Structure of Atoms (Electron Configurations) - *CC BY 4.0*
    - 2.E: Quantum Theory and Electronic Structure (Exercises) - *CC BY 4.0*
    - 2.S: Study Guide - *Undeclared*
  - 3: Periodic Relationships Among the Elements - *Undeclared*
    - 3.1: The Periodic Table - *CC BY 4.0*
    - 3.2: Periodic Variations in Element Properties - *CC BY 4.0*
    - 3.E: Periodic Properties (Exercises) - *CC BY 4.0*
    - 3.S: Study Guide - *Undeclared*
  - 4: Chemical Bonding I- Basic Concepts - *Undeclared*
    - 4.1: Ionic Bonding - *CC BY 4.0*
    - 4.2: Lattice Enthalpies and Born Haber Cycles - *CC BY-NC 4.0*
    - 4.3: Covalent Bonding - *CC BY 4.0*
    - 4.4: Lewis Symbols and Structures - *CC BY 4.0*
    - 4.5: Formal Charges and Resonance - *CC BY 4.0*
    - 4.6: Strengths of Ionic and Covalent Bonds - *CC BY 4.0*
    - 4.E: Chemical Bonding and Molecular Geometry (Exercises) - *CC BY 4.0*
    - 4.S: Study Guide - *Undeclared*
  - 5: Chemical Bonding II- Molecular Geometry and Hybridization of Atomic Orbitals - *Undeclared*
    - 5.1: Molecular Structure and Polarity - *CC BY 4.0*

- 5.2: Valence Bond Theory - *CC BY 4.0*
- 5.3: Hybrid Atomic Orbitals - *CC BY 4.0*
- 5.4: Multiple Bonds - *CC BY 4.0*
- 5.5: Molecular Orbital Theory - *CC BY 4.0*
- 5.E: Advanced Theories of Covalent Bonding (Exercises) - *CC BY 4.0*
- 5.S: Study Guide - *Undeclared*

6: Intermolecular Forces and Liquids and Solids - *Undeclared*

- 6.1: Intermolecular Forces - *CC BY 4.0*
- 6.E: Intermolecular Forces and Liquids and Solids (Exercises) - *CC BY 4.0*
- 6.S: Study Guide - *Undeclared*

7: Organic Chemistry I - Bonding and Structure - *Undeclared*

- 7.1: Bonding and Structure I- Review of Bonding - *Undeclared*
  - 7.1.1: Introduction to Organic Chemistry - *CC BY-SA 4.0*
  - 7.1.2: Development of Chemical Bonding Theory - *CC BY-SA 4.0*
  - 7.1.3: Describing Chemical Bonds - Valence Bond Theory - *CC BY-SA 4.0*
  - 7.1.4: sp^3 Hybrid Orbitals and the Structure of Methane - *CC BY-SA 4.0*
  - 7.1.5: sp^3 Hybrid Orbitals and the Structure of Ethane - *CC BY-SA 4.0*
  - 7.1.6: sp^2 Hybrid Orbitals and the Structure of Ethylene - *CC BY-SA 4.0*
  - 7.1.7: sp Hybrid Orbitals and the Structure of Acetylene - *CC BY-SA 4.0*
  - 7.1.8: Hybridization of Nitrogen, Oxygen, Phosphorus and Sulfur - *CC BY-SA 4.0*
  - 7.1.9: Describing Chemical Bonds- Molecular Orbital Theory - *CC BY-SA 4.0*
- 7.2: Drawing Chemical Structures - *CC BY-SA 4.0*
- 7.3: Functional Groups - *CC BY-SA 4.0*
- 7.4: Alkanes and Alkane Isomers - *CC BY-SA 4.0*
- 7.5: Naming of Alkanes and Cycloalkanes - *Undeclared*
  - 7.5.1: Naming Alkanes - *CC BY-SA 4.0*
  - 7.5.2: Naming Cycloalkanes - *CC BY-SA 4.0*
- 7.6: Study Guide - *Undeclared*

8: Organic Chemistry II - Stereochemistry - *Undeclared*

- 8.1: Types of Isomers - *CC BY-SA 4.0*
- 8.2: Chiral Molecules - *Undeclared*
- 8.3: Optical Activity - *Undeclared*
- 8.4: Absolute Configuration- R-S Sequence Rules - *Undeclared*
- 8.5: Stereochemistry of the Alkenes - *Undeclared*
  - 8.5.1: Cis-Trans Isomerism in Alkenes - *CC BY-SA 4.0*
  - 8.5.2: Sequence Rules - The E,Z Designation - *CC BY-SA 4.0*
- 8.6: Study Guide - *Undeclared*

9: Organic Chemistry III - Conformational Analysis - *Undeclared*

- 9.1: Rotation about Single Bonds- Conformations - *Undeclared*
- 9.2: Rotation in Substituted Ethanes - *Undeclared*
- 9.3: Ring Strain and the Structure of Cycloalkanes - *Undeclared*
- 9.4: Cyclohexane- A Strain-Free Cycloalkane - *Undeclared*
- 9.5: Substituted Cyclohexanes - *Undeclared*
- 9.S: Study Guide - *Undeclared*

Back Matter - *Undeclared*

- Index - *Undeclared*
- Glossary - *Undeclared*
- Detailed Licensing - *Undeclared*