CHEM 175 - GENERAL CHEMISTRY I



Scott Van Bramer
Widener University

LibreTexts™

Widener University: Chem 175

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: Essential Ideas of Chemistry

- 1.1: Introduction to Chemistry
- 1.2: Measurements
- 1.3: Mathematical Treatment of Measurement Results
- 1.E: Essential Ideas of Chemistry- Homework

2: Atoms, Molecules, and Ions

- 2.1: Atomic Theory
- 2.2: Atomic Structure, Isotopes, and Atomic Mass
- 2.3: Chemical Formulas
- 2.E: Atoms, Molecules, and Ions- Homework

3: Composition of Substances and Solutions

- 3.1: Formula Mass and the Mole Concept
- 3.2: Determining Empirical and Molecular Formulas
- 3.3: Percent Composition and Molecular Formula
- 3.4: Molarity
- 3.E: Composition of Substances and Solutions- Homework

4: Stoichiometry of Chemical Reactions

- 4.1: Writing and Balancing Chemical Equations
- 4.2: Reaction Stoichiometry
- 4.3: Classifying Chemical Reactions - Precipitation Reactions
- 4.4: Classifying Chemical Reactions - Acid Base Reactions
- 4.5: Classifying Chemical Reactions - Combustion Reactions
- 4.E: Stoichiometry of Chemical Reactions- Homework

5: Electronic Structure and Periodic Properties

- 5.1: Light and Atomic Structure
- 5.2: Development of Quantum Theory
- 5.3: Electronic Structure of Atoms (Electron Configurations)
- 5.4: Periodic Variations in Element Properties
- 5.E: Electronic Structure and Periodic Properties- Homework

6: Chemical Bonding and Molecular Geometry

- 6.1: Ionic and Covalent Bonding
- 6.2: Lewis Symbols and Structures
- 6.3: Formal Charge and Resonance
- 6.4: Molecular Structure and Polarity
- 6.5: Intermolecular Forces
- 6.E: Chemical Bonding and Molecular Geometry- Homework

7: Advanced Theories of Covalent Bonding

- 7.1: Valence Bond Theory and Hybrid Orbitals
- 7.2: Multiple Bonds
- 7.3: Molecular Orbital Theory
- 7.E: Advanced Theories of Covalent Bonding- Homework

8: Kinetics

- 8.1: Introduction to Chemical Reaction Rates
- 8.2: Collision Theory and Reaction Mechanisms
- 8.3: Catalysis
- 8.E: Kinetics - Homework

9: Fundamental Equilibrium Concepts

- 9.1: Chemical Equilibria
- 9.2: Equilibrium Constants
- 9.E: Fundamental Equlibrium Concepts - Homework

10: Acid-Base Equilibria

- 10.1: Introduction to Brønsted-Lowry Acids and Bases
- 10.2: pH, pOH, and Relative Strengths of Acids and Bases
- 10.3: Hydrolysis of Salt Solutions
- 10.4: Buffers
- 10.E: Acid-Base Equilibria - Homework

11: Thermochemistry

- 11.1: Energy Basics
- 11.2: Calorimetry
- 11.3: Enthalpy- Introduction
- 11.4: Enthalpy- Heat of Combustion
- 11.5: Enthalpy- Heat of Formation
- 11.6: Bond Energy
- 11.E: Thermochemistry- Homework

12: Thermodynamics

- 12.1: Introduction to Spontaneity and Entropy
- 12.2: The Second and Third Laws of Thermodynamics
- 12.3: Free Energy
- 12.E: Thermodynamics - Homework

13: Appendices

- 13.1: Dr Martin's Math Minutes
- 13.2: Composition of Commercial Acids and Bases
- 13.3: Essential Mathematics
- 13.4: Fundamental Physical Constants
- 13.5: Standard Thermodynamic Properties for Selected Substances
- 13.6: The Periodic Table
- 13.7: Units and Conversion Factors
- 13.8: Water Properties

Index

Glossary

Detailed Licensing

Detailed Licensing

Detailed Licensing

Licensing

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

CHAPTER OVERVIEW

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: Introduction to Chemistry

1.2: Measurements

1.3: Mathematical Treatment of Measurement Results

1.E: Essential Ideas of Chemistry- Homework

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: Essential Ideas of Chemistry is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

1.1: Introduction to Chemistry

Learning Objectives

- Distinguish beween *chemistry* and *physics*;
- Suggest ways in which the fields of engineering, economics, and geology relate to Chemistry;
- Define the following terms, and classify them as primarily *microscopic* or *macroscopic* concepts: element, atom, compound, molecule, formula, structure.

So just what is chemistry?

Chemistry is a *point of view* that places its major focus on the structure and properties of *substances*— particular kinds of matter— and especially on the changes they undergo. Chemistry is the study of *substances*; their properties, structure, and the changes they undergo.

The real importance of Chemistry is that it serves as the interface to practically all of the other sciences, as well as to many other areas of human endeavor. For this reason, Chemistry is often said (at least by chemists!) to be the "central science". Chemistry can be "central" in a much more personal way: with a solid background in Chemistry, you will find it far easier to migrate into other fields as your interests develop. Figure 1.1.1 shows the this relationship between chemistry and many other disciplines.

> *Chemistry is deeply ingrained into so many areas of business, government, and environmental management and background in the subject is useful. It will give you a career edge with special skills in fields as varied as product development, marketing, management, computer science, technical writing, and even law.*

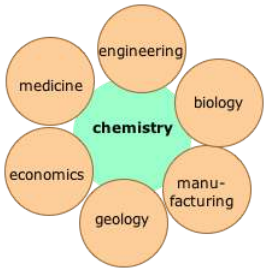


Figure 1.1.1. Chemistry as the central science.

Micro-macro: the forest or the trees

Chemistry, like all natural sciences, begins with the direct observation of nature — in this case, of matter. But when we look at matter in bulk, we see only the "forest", not the "trees" — the atoms and molecules of which matter is composed of — whose properties ultimately determine the nature and behavior of the matter we are looking at. This dichotomy between what we can and cannot directly see constitutes two contrasting views which run through all of chemistry, which we call *macroscopic* and *microscopic*.

In the context of Chemistry, "microscopic" implies the atomic or subatomic levels which cannot be seen directly (even with a microscope!) whereas "macroscopic" implies things that we can know by direct observations of physical properties such as mass, volume, etc. The following table provides a conceptual overview of Chemical science according to the macroscopic/microscopic dichotomy we have discussed above. It is of course only one of the many ways of looking at the subject, but you may find it helpful in organizing the many facts and ideas that you will encounter in your study of Chemistry. We will organize the discussion in this lesson along similar lines.

Table 1.1.1: Realms of Chemistry

realm	macroscopic view	microscopic view
composition	formulas, mixtures	structures of solids, molecules, and atoms
properties	intensive properties of bulk matter	particle sizes, masses and interactions

realm	macroscopic view	microscopic view
change (energetics)	energetics and equilibrium	statistics of energy distribution
change (dynamics)	kinetics (rates of reactions)	mechanisms

Chemical composition

Mixture or "pure substance" ?

In science it is necessary to know what we are talking about, so before we can begin to consider matter from a chemical point of view, we need to know its *composition*; whether it is a *single substance*, or a *mixture*? (We will get into the details of the definitions later, but for the moment you probably have a fair understanding of the distinction; think of a sample of salt (sodium chloride) as opposed to a *solution* of salt in water— a *mixture* of salt and water.)

Elements and compounds

It has been known for at least a thousand years that some substances can be broken down by heating or chemical treatment into "simpler" ones, but there is always a limit; we eventually get substances known as *elements* that cannot be reduced to any simpler forms by ordinary chemical or physical means. What is our criterion for "simpler"? The most observable (and therefore macroscopic) property is the weight.

The idea of a minimal unit of chemical identity that we call an *element* developed from experimental observations of the relative weights of substances involved in chemical reactions. For example, the compound mercuric oxide can be broken down by heating into two other substances:

$$2\,\mathrm{HgO} \rightarrow 2\,\mathrm{Hg} + \mathrm{O_2} \tag{1.1.1}$$

... but the two products, metallic mercury and dioxygen, cannot be decomposed into simpler substances, so they must be elements.

Elements and atoms

The definition of an element given above is an *operational* one; a certain result (or in this case, a non-result!) of a procedure that might lead to the decomposition of a substance into lighter units will tentatively place that substance into one of the categories: element or compound. Because this operation is carried out on bulk matter, the concept of the element is also a *macroscopic* one. The *atom*, by contrast, is a *microscopic* concept which in modern chemistry relates the unique character of every chemical element to an actual physical particle.

The idea of the atom as the smallest particle of matter had its origins in Greek philosophy around 400 BCE but was controversial from the start (both Plato and Aristotle maintained that matter was infinitely divisible.) It was not until 1803 that John Dalton proposed a rational atomic theory to explain the facts of chemical combination as they were then known, thus being the first to employ macroscopic evidence to illuminate the microscopic world. It wasn't until the 1900s that the atomic theory became universally accepted. In the 1920's it became possible to measure the sizes and masses of atoms, and in the 1970's techniques were developed that produced images of individual atoms.



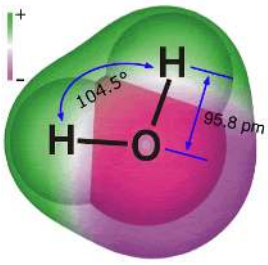
Figure 1.1.1: Joseph Wright's painting from 1776 showing The Alchemist Discovering Phosphorus

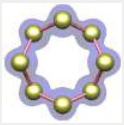
Formula and structure

The formula of a substance expresses the relative number of atoms of each element it contains. Because the formula can be determined by experiments on bulk matter, it is a macroscopic concept even though it is expressed in terms of atoms.

What the ordinary chemical formula does *not* tell us is the order in which the component atoms are connected, whether they are grouped into discrete units (*molecules*) or are two- or three dimensional extended structures, as is the case with solids such as ordinary salt. The microscopic aspect of composition is the *structure*, which gives detailed relative locations (in two or three dimensional space) of each atom within the minimum collection needed to define the structure of the substance.

Table 1.1.2: Differences between macroscopic and microscopic view

Macroscopic		Microscopic
Substances are defined at the macroscopic level by their **formulas** or **compositions**, and at the microscopic level by their **structures**.	The elements hydrogen and oxygen combine to form a compound whose composition is expressed by the formula H_2O.	The molecule of water has the structure  shown here.

	Macroscopic	Microscopic
Chemical substances that cannot be broken down into simpler ones are known as **elements**. The actual physical particles of which elements are composed are **atoms** or **molecules**.	Sulfur – the **element** in its orthorhombic crystalline form. 	**molecule** is an octagonal ring of sulfur **atoms**. The crystal shown at the left is composed of an ordered array of these molecules. (No, they don't actually move around like this, although they are in a constant state of vibrational motion.) 

Compounds and molecules

Compounds

As we indicated above, a *compound* is a substance containing more than one element. Since the concept of an element is macroscopic and the distinction between elements and compounds was recognized long before the existence of physical atoms was accepted, the concept of a compound must also be a macroscopic one that makes no assumptions about the nature of atoms. When carbon burns in the presence of oxygen, the product carbon dioxide can be shown by (macroscopic) weight measurements to follow the law of conservation of mass and contain both of the original elements:

$$\mathrm{C} + \mathrm{O}_2 \longrightarrow \mathrm{CO}\,2 \tag{1.1.2}$$

10.0 g + 26.7 g = 36.7 g

One of the important characteristics of a compound is that the proportions by weight of each element in a given compound are constant. For example, no matter what weight of carbon dioxide we have, the percentage of carbon it contains is (10.0 / 36.7) = 0.27, or 27%.

Molecules

A *molecule* is an assembly of atoms having a fixed composition, structure, and distinctive, measurable properties. A molecule, like the model of nicotine shown in Figure 1.1.2, refers to a kind of particle and is therefore a microscopic concept. Even at the end of the 19th century, when compounds and their formulas had long been in use, some prominent chemists doubted that molecules (or atoms) were any more than a convenient model. refers to a kind of particle, and is therefore a microscopic concept.

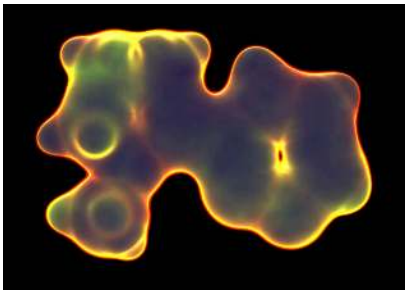


Figure 1.1.2 Computer-model of Nicotine molecule $C_{10}H_{14}N_2$ by Ronald Perry

Molecules suddenly became real in 1905, when Albert Einstein showed that Brownian motion, the irregular microscopic movements of tiny pollen grains floating in water, could be directly attributed to collisions with molecule-sized particles.

In 2009 we finally get to see molecules. Figure 1.1.3 shows how IBM scientists in Switzerland succeeded in imaging a real molecule, using a technique known as atomic force microscopy in which an atoms thin metallic probe is drawn ever-so-slightly above the surface of an immobilized pentacene molecule cooled to nearly absolute zero. In order to improve the image quality, a molecule of carbon monoxide was placed on the end of the probe.

The image produced by the AFM probe is shown at the very bottom. What is actually being imaged is the surface of the electron clouds of the molecule, which consists of six hexagonal rings of carbon atoms with hydrogen on its periphery. The tiny bumps that correspond to these hydrogen atoms attest to the remarkable resolution of this experiment.

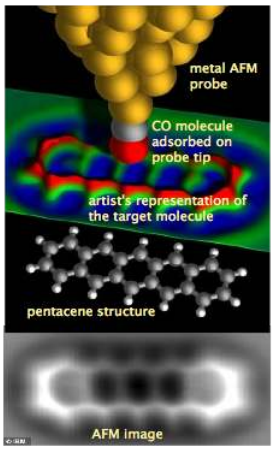


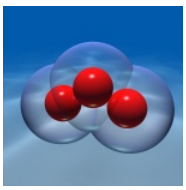
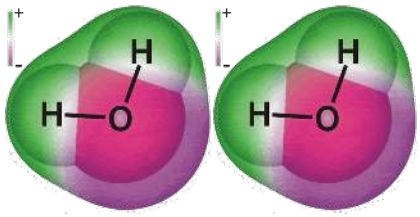
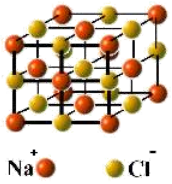
Figure 1.1.3: Molecular level illustration of metal AFM probe with CO molecule on tip scanning pentracene structure

The atomic composition of a molecule is given by its *formula*. Thus the formulas CO, CH_4, and O_2 represent the molecules carbon monoxide, methane, and dioxygen. However, the fact that we can write a formula for a compound does not imply the existence of molecules having that composition. Gases and most liquids consist of molecules, but many solids exist as extended lattices of atoms or ions (electrically charged atoms or molecules.) For example, there is no such thing as a "molecule" of ordinary salt, NaCl (see below.)

Confused about the distinction between molecules and compounds?

Maybe the following will help:

Table 1.1.3: Distinguishing molecules and compounds

		
A molecule but not a compound - Ozone, O_3, is *not* a compound because it contains only a single element.	**This well-known molecule is a compound** because it contains more than one element.	Ordinary solid **salt is a compound but not a molecule**. It is built from interpenetrating lattices of sodium and chloride ions that extend indefinitely.

Physical and Chemical Properties

Composition and structure lie at the core of Chemistry, but they encompass only a very small part of it. It is largely the *properties* of chemical substances that interest us; it is through these that we experience and find uses for substances, and much of chemistry as a science is devoted to understanding the relation between structure and properties. For some purposes it is convenient to distinguish between chemical properties and physical properties, but as with most human-constructed dichotomies, the distinction becomes more fuzzy as one looks more closely.

Physical Properties

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 1.1.4). 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 1.1.4: (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).

Chemical Properties

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, and acidity. Iron, for example, combines with oxygen in the presence of water to form rust; chromium does not oxidize so it is used to prevent rust (Figure 1.1.5). Nitroglycerin is very dangerous because it explodes easily; neon poses almost no hazard because it is very unreactive.



Figure 1.1.5: (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 rust so it is used to coat metal to keep it shiny. (credit a: modification of work by Tony Hisgett; credit b: modification of work by "Atoma"/Wikimedia Commons)

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 1.1.6).

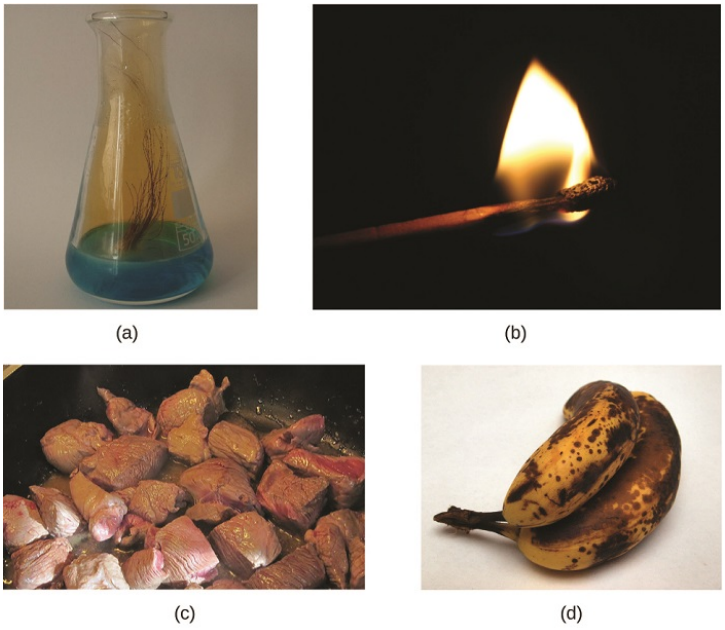


Figure 1.1.6: (a) Copper and nitric acid undergo a chemical change to form copper nitrate and brown, gaseous nitrogen dioxide. (b) During the combustion of a match, cellulose in the match and oxygen from the air undergo a chemical change to form carbon dioxide and water vapor. (c) Cooking red meat causes 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)

Chemical change is defined macroscopically as a process in which new substances are formed. On a microscopic basis it can be thought of as a re-arrangement of atoms. A given chemical change is commonly referred to as a chemical reaction and is described by a chemical equation that has the form

reactants → products

Comparing physical and chemical properties

In elementary courses it is customary to distinguish between "chemical" and "physical" change, the latter usually relating to changes in physical state such as melting and vaporization. As with most human-created dichotomies, this begins to break down when examined closely. This is largely because of some ambiguity in what we regard as a distinct "substance".

✔ Example 1: Chlorine

Elemental chlorine exists as the diatomic molecule $\mathrm{Cl_2}$ in the gas, liquid, and solid states; the major difference between them lies in the degree of organization. In the gas the molecules move about randomly, whereas in the solid they are constrained to locations in a 3-dimensional lattice. In the liquid, this tight organization is relaxed, allowing the molecules to slip and slide around each other.

Since the basic molecular units remain the same in all three states, the processes of melting, freezing, condensation and vaporization are usually regarded as *physical* rather than chemical changes.

✔ Example 2: Sodium Chloride

Solid salt consists of an indefinitely extended 3-dimensional array of $\mathrm{Na^+}$ and $\mathrm{Cl^-}$ *ions* (electrically charged atoms.)

When heated above 801°C, the solid melts to form a liquid consisting of these same ions. This liquid boils at 1430° to form a vapor made up of discrete molecules having the formula $\mathrm{Na_2Cl_2(aq)}$.. Because the ions in the solid, the hydrated ions in the solution, and the molecule $\mathrm{Na_2Cl_2}$ are really different chemical species, so the distinction between physical and chemical change becomes a bit fuzzy.

Extensive and Intensive Properties

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).

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 1.1.7). You will learn more about the periodic table as you continue your study of chemistry.

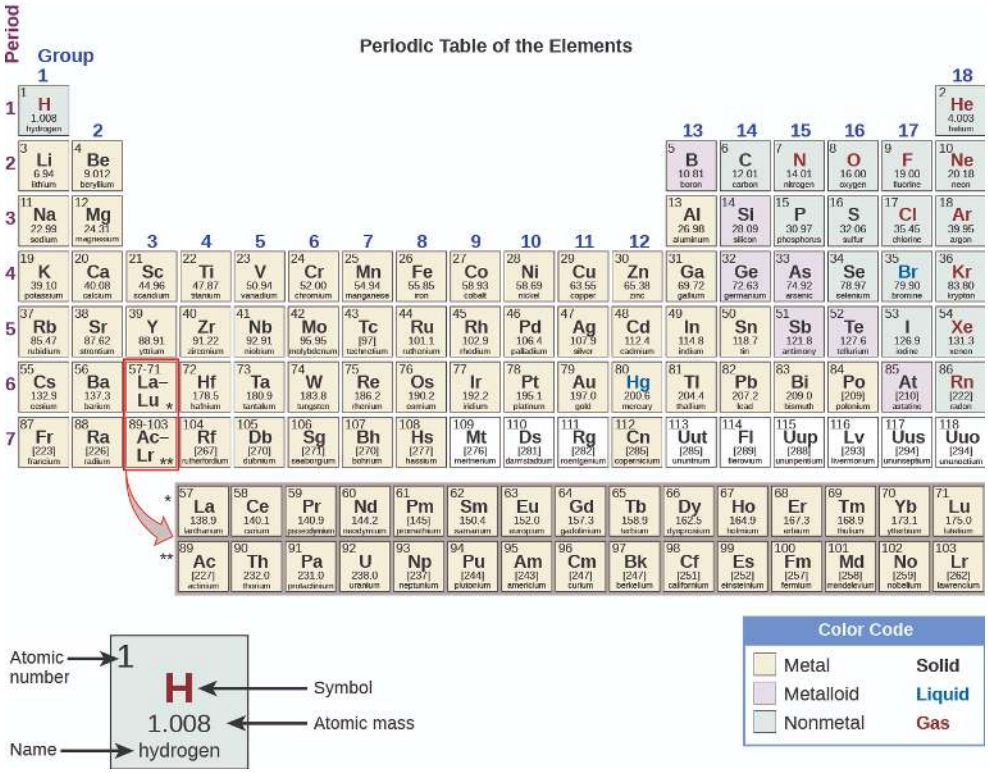


Figure 1.1.7: The periodic table shows how elements may be grouped according to certain similar properties. Note the background color denotes whether an element is a metal, metalloid, or nonmetal, whereas the element symbol color indicates whether it is a solid, liquid, or gas.

Currents of modern Chemistry

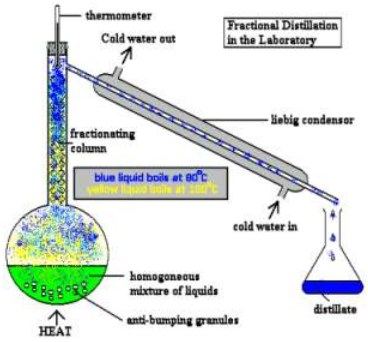
In the preceding section we looked at chemistry from a conceptual standpoint. If this can be considered a "macroscopic" view of chemistry, what is the "microscopic" view? It would likely be what chemists actually do. Because a thorough exploration of this would lead us into far more detail than we can accommodate here, we will mention only a few of the areas that have emerged as being especially important in modern chemistry.

Separation science

A surprisingly large part of chemistry has to do with isolating one component from a mixture. This may occur at any number of stages in a manufacturing process, including the very critical steps involved in removing toxic, odiferous, or otherwise undesirable

by-products from a waste stream. But even in the research lab, a considerable amount of effort is often devoted to separating the desired substance from the many components of a reaction mixture, or in separating a component from a complex mixture (for example, a drug metabolite from a urine sample), prior to measuring the amount present.

Distillation - separation of liquids having different boiling points. This ancient technique (believed to have originated with Arabic alchemists in 3500 BCE), is still one of the most widely employed operations both in the laboratory and in industrial processes such as oil refining.



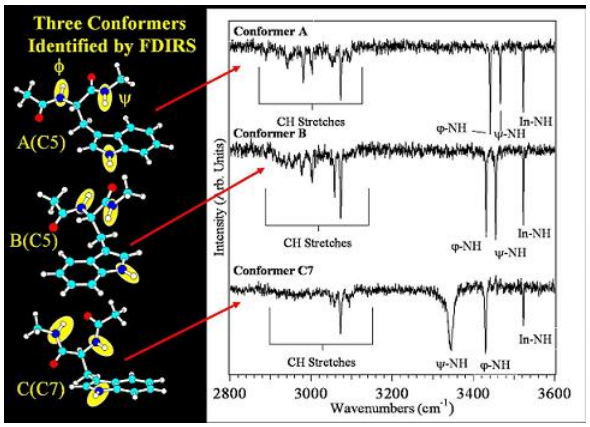
Identification and assay

What do the following people have in common?

- A plant manager deciding on whether to accept a rail tank car of vinyl chloride for manufacture into plastic pipe
- An agricultural chemist who wants to know about the vitamin content of a new vegetable hybrid
- The manager of a city water-treatment plant who needs to make sure that the carbonate content of the water is maintained high enough to prevent corrosion, but low enough to prevent scale build-up

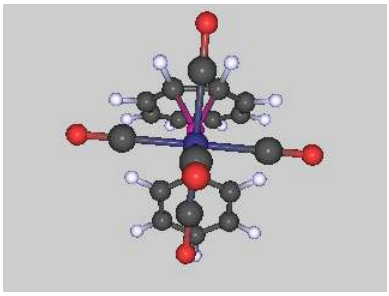
The answer is that all depend on *analytical techniques* — measurements of the nature or quantity ("assays") of some substance of interest, sometimes at very low concentrations. A large amount of research is devoted to finding more accurate and convenient means of making such measurements. Many of these involve sophisticated instruments; among the most widely used are the following:

Spectrophotometers that examine the ways that light of various wavelengths is absorbed, emitted, or altered by atomic and molecular species.



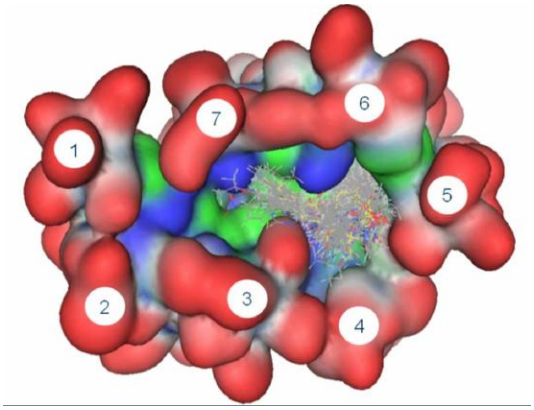
Materials, polymers, and nanotechnology

Materials science attempts to relate the physical properties and performance of engineering materials to their underlying chemical structure with the aim of developing improved materials for various applications.

Nanodevice chemistry — constructing molecular-scale assemblies for specific tasks such as computing, producing motions, etc.	

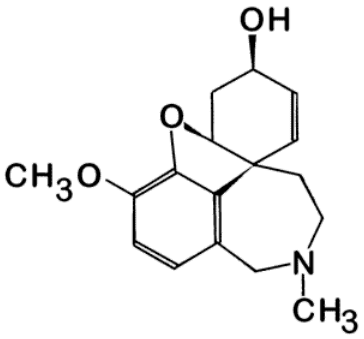
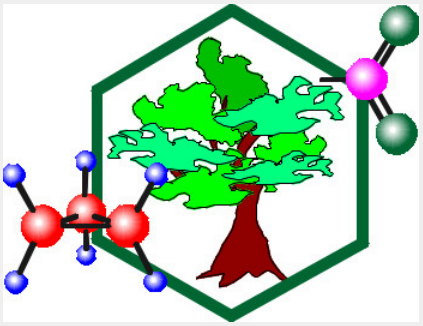
Biochemistry and Molecular biology

This field covers a wide range of studies ranging from fundamental studies on the chemistry of gene expression and enzyme-substrate interactions to drug design. Much of the activity in this area is directed to efforts in ***drug discovery.***

Drug design looks at interactions between enzymes and possible inhibitors. Computer-modeling is an essential tool in this work.	

Synthesis

In its most general sense, this word refers to any reaction that leads to the formation of a particular molecule. It is both one of the oldest areas of chemistry and one of the most actively pursued. Some of the major threads are

New-molecule synthesis - Chemists are always challenged to come up with molecules containing novel features such as new shapes or unusual types of bonds.	
Green chemistry - synthetic methods that focus on reducing or eliminating the use or release of toxic or non-biodegradable chemicals or byproducts.	

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

Contributors and Attributions

- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook
- 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: Introduction to Chemistry is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer via source content that was edited to the style and standards of the LibreTexts platform.

- **1.1: Introduction to Chemistry** by Stephen Lower is licensed CC BY 3.0. Original source: http://www.chem1.com/acad/webtext/virtualtextbook.html.
- **1.3: Physical and Chemical Properties** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

1.2: 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. The number and unit are explicitly represented when a quantity is written. The uncertainty is an important aspect of measurements 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 in scientific notation 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.

1.2.1: SI Base Units

We usually report the results of scientific measurements in SI units, an updated version of the metric system, using the units listed in Table 1.2.1. 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 1.2.1: 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
amount of substance	mole	mol

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. There are five SI base units commonly used in chemistry. Other SI units will be introduced as needed.

1.2.1.1: 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 1.2.1); 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).

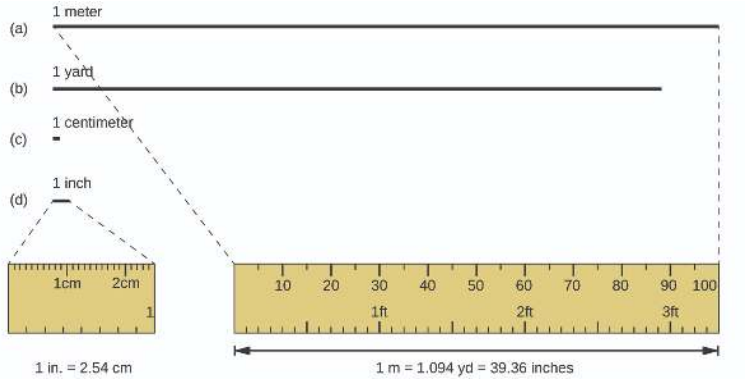


Figure 1.2.1: The relative lengths of 1 m, 1 yd, 1 cm, and 1 in. are shown (not actual size), as well as comparisons of 2.54 cm and 1 in., and of 1 m and 1.094 yd.

1.2.1.2: 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 was changed in 1879 to a certain cylinder of platinum-iridium alloy, which was kept in France with a copy in the United States (Figure 1.4.2). Any object with the same mass as this cylinder was said to have a mass of 1 kilogram. In 2018 the definition of the kilogram was revised to allow it to be determined experimentally using electrical current with a specially designed balance. One kilogram is about 2.2 pounds. The gram (g) is exactly equal to 0.001 kilogram, 10^{-3} kg.



Figure 1.2.2: This replica prototype kilogram is housed at the National Institute of Standards and Technology (NIST) in Maryland. (credit: National Institutes of Standards and Technology).

1.2.1.3: 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.

1.2.1.4: Temperature

Temperature is an intensive property, so it does not matter how much matter is present. 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. Do not use the word “degree” or the degree symbol (°) with temperature in kelvins. The degree Celsius (°C) is also allowed in the SI system but needs to included either the word “degree” or the degree symbol. 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) 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.

1.2.1.5: Amount of Substance

The SI base unit for the amount of substance is the mole (mol). The unit was redefined by IUPAC in 2019 as $6.02214076 \times 10^{23}$ elementary entities. An elementary entity can be an atom, a molecule, an ion, an electron, or any other particle or specified group of particles.

1.2.2: SI Prefixes

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 common prefixes used and the powers to which 10 are raised are listed in Table 1.2.2. For complete details on the SI system see NIST SP 811.

Table 1.2.2: Common Unit Prefixes - For Chem 145

Prefix	Symbol	Factor
pico	p	10^{-12}
nano	n	10^{-9}
micro	μ	10^{-6}
milli	m	10^{-3}
centi	c	10^{-2}
kilo	k	10^{3}
mega	M	10^{6}

1.2.3: 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. Since density is independent of the amount of matter it is an intensive property. The SI unit for density is the kilogram per cubic meter (kg/m^3) but in chemistry this is an inconvenient unit. As a result, chemists 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 1.2.3 shows the densities of some common substances.

Table 1.2.3: Densities of Common Substances

Solids	Liquids	Gases (at 25 °C and 1 atm)
ice (at 0 °C) 0.92 g/cm^3	gasoline 0.70–0.77 g/cm^3	helium 0.16 g/L
silver 10.5 g/cm^3	water (at 4 °C) 1.0 g/cm^3	dry air 1.20 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	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.

$$\text{density} = \frac{\text{mass}}{\text{volume}} \tag{1.2.1}$$

Example 1.2.1

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 1.2.1

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 1.2.2: 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 1.2.2

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

1.2.4: 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.

1.2.5: 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

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 1.2: Measurements is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

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

1.3: 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.

1.3.1: Math Support

If you have any concerns about your math background or just want to make sure you have all the math tools needed to succeed in this course, review the short "Math Minutes" videos from Dr. Martin in the Appendix: 11.1: Dr Martin's Math Minutes. You may also want to review Appendix: 11.3: Essential Mathematics.

1.3.2: Introduction

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:

$$\text{speed} = \frac{\text{distance}}{\text{time}} \tag{1.3.1}$$

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

$$\frac{100\ \text{m}}{10\ \text{s}} = 10\ \text{m/s} \tag{1.3.2}$$

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:

$$\text{time} = \frac{\text{distance}}{\text{speed}} \tag{1.3.3}$$

The time can then be computed as:

$$\frac{25\ \text{m}}{10\ \text{m/s}} = 2.5\ \text{s} \tag{1.3.4}$$

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.

1.3.3: Conversion Factors

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,

$$\frac{2.54\ \text{cm}}{1\ \text{in.}}\ (2.54\ \text{cm} = 1\ \text{in.}\ )\ \text{or}\ 2.54\ \frac{\text{cm}}{\text{in.}} \tag{1.3.5}$$

Several other commonly used conversion factors are given in Table 1.3.1. A more extensive list is in Appendix 11.6: Units and Conversion Factors.

Table 1.3.1: 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:

$$34\ \cancel{\text{in.}} \times \frac{2.54\ \text{cm}}{1\ \cancel{\text{in.}}} = 86\ \text{cm} \tag{1.3.6}$$

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

$$\frac{\text{in.} \times \text{cm}}{\text{in.}}. \tag{1.3.7}$$

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

$$\frac{\text{in.}}{\text{in.}} = 1 \tag{1.3.8}$$

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 1.3.1: 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 1.3.1).

Solution

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

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

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.

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

? Exercise 1.3.1

Convert a volume of 9.345 qt to liters.

Answer

8.844 L

1.3.4: Conversion Factors and SI Prefixes

The same problem solving strategy can be used to convert units within the SI system using SI prefixes. The prefix is a conversion factor that allows conversion between units. For example when we multiply a quantity (such as distance given in cm) by an appropriate unit conversion factor, we convert the quantity to an equivalent value with different units (such as distance in meters). For example, since centi = 10^{-2}, a basketball player's vertical jump of 86 cm can be converted to meters by:

$$86 \text{ cm} \times \frac{1 \text{ cm}}{10^{-2} \text{ m}} = 0.86 \text{ m} \tag{1.3.9}$$

✓ Example 1.3.2: Using SI Prefixes for Unit Conversion

The mass of a competition Frisbee is 125 g. Convert its mass to milligrams using the unit conversion factor derived from the relationship milli = 10^{-3}.

Solution

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

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

We write the unit conversion factor in its two forms:

$$\frac{1 \text{ mg}}{10^{-3} \text{ g}} \text{ and } \frac{10^{-3} \text{ g}}{1 \text{ mg}}$$

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

$$x \text{ g} = 125 \text{ g} \times \frac{1 \text{ mg}}{10^{-3} \text{ g}}$$
$$= \left(\frac{125}{10^{-3}}\right) \text{ mg}$$
$$= 1.25 \times 10^{5} \text{ mg (three significant figures)}$$

? Exercise 1.3.2

Convert a volume of 25.4 milliliters to liters.

Answer

0.0254 L

1.3.5: Conversion Factors and Dimensional Analysis

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 1.3.3: 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 $\text{density} = \dfrac{\text{mass}}{\text{volume}}$, 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:

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

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

1. *Convert quarts to liters.*

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

2. *Convert liters to milliliters.*

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

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:

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

Exercise 1.3.3

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

Answer

2.956×10^{-2} L

Example 1.3.4: 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:

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

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:

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

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

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

? Exercise 1.3.4

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

1.3.6: Unit Conversion Video Example

This project was preformed to supply **Libretext authors** with videos on General Chemistry topics which can be used to enhance their projects. Also, these videos are meant to act as a learning resource for **all General Chemistry students**.

Video Topics

Dimensional analysis: Units can be multiplied, divided, and canceled just like an algebraic quantity. A conversion factor is a fractional quantity used to convert one unit to another.

Link to Video

Converting Between Units: https://youtu.be/wSaOh48k8Wg



1.3.7: Attribution

- Prof. Steven Farmer (Sonoma State University)

1.3.8: Significant Digits in Measurement

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.

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.

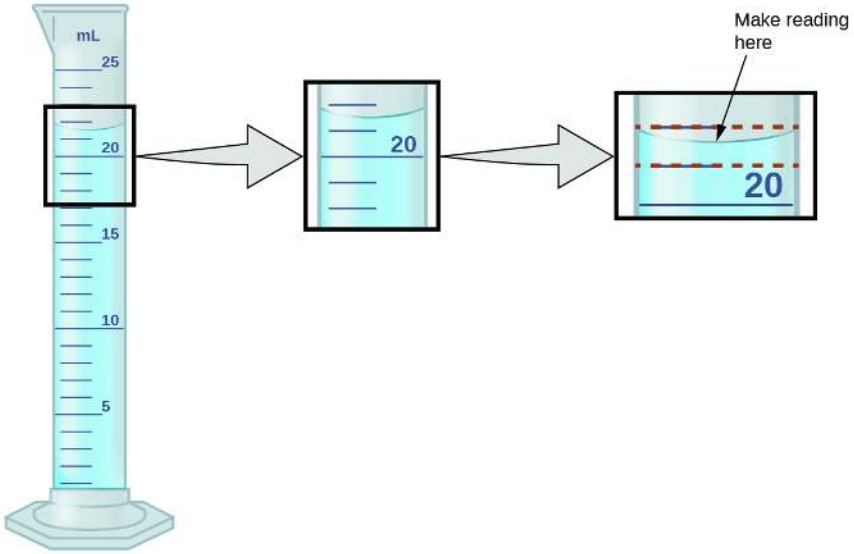
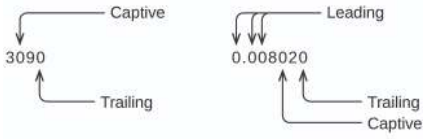


Figure 1.3.1: To measure the volume of liquid in this graduated cylinder, you must mentally subdivide the distance between the 21 and 22 mL marks into tenths of a milliliter, and then make a reading (estimate) at the bottom of the meniscus.

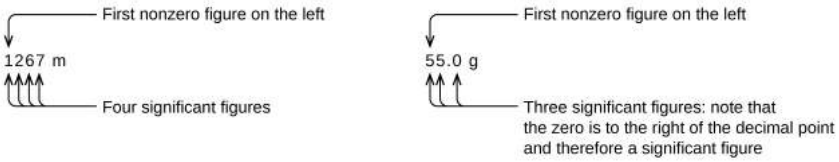
Refer to the illustration in Figure 1.3.1. The bottom of the meniscus in this case clearly lies between the 21 and 22 markings, meaning the liquid volume is *certainly* greater than 21 mL but less than 22 mL. The meniscus appears to be a bit closer to the 22-mL mark than to the 21-mL mark, and so a reasonable 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 precise 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 digits or significant figures. 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.



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 digits in the measurement unless the last digit is a trailing zero lying to the left of the decimal point.

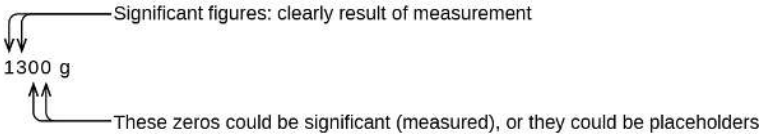


Captive zeros result from measurement and are therefore always significant. Leading zeros, however, are never significant—they merely tell us where the decimal point is located.



The 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 digits, and 10^{-3} locates the decimal point.

The number of significant digits 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 digits), 1.30×10^3 (three significant digits, if the tens place was measured), or 1.300×10^3 (four significant digits, 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.



When determining significant digits, be sure to pay attention to reported values and think about the measurement and significant digits 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 digits, 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.

1.3.9: Significant Digits 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 digits, 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 digits (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 digits:

- 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 1.3.5: Rounding Numbers

Round the following to the indicated number of significant digits:

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

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 1.3.5

Round the following to the indicated number of significant digits:

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

Answer a

0.42

Answer b

0.00387

Answer c

421.2

Answer d

28,684

Example 1.3.6: Addition and Subtraction with Significant Digits 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)

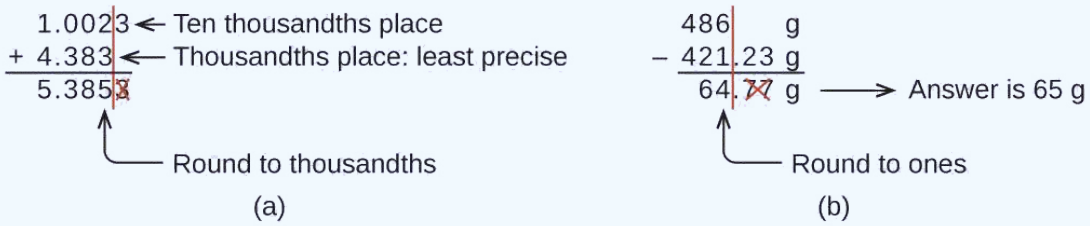
$$\begin{array}{r} 1.0023\ \text{g} \\ +\ 4.383\ \text{g} \\ \hline 5.3853\ \text{g} \end{array}$$

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)



Exercise 1.3.6

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 1.3.7: Multiplication and Division with Significant Digits

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 digits (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)

$$0.6238\ \text{cm} \times 6.6\ \text{cm} = 4.11708\ \text{cm}^2 \rightarrow \text{result is } 4.1\ \text{cm}^2\ (\text{round to two significant digits}) \tag{1.3.10}$$

$$\text{four significant digits} \times \text{two significant digits} \rightarrow \text{two significant digits answer} \tag{1.3.11}$$

(b)

$$\frac{421.23\ \text{g}}{486\ \text{mL}} = 0.86728\ldots\ \text{g/mL} \rightarrow \text{result is } 0.867\ \text{g/mL}\ (\text{round to three significant digits}) \tag{1.3.12}$$

$$\frac{\text{five significant digits}}{\text{three significant digits}} \rightarrow \text{three significant digits answer} \tag{1.3.13}$$

Exercise 1.3.7

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 digits 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 1.3.8: Calculation with Significant Digits

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. Give your answer with the appropriate number of significant digits.

Solution

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

Exercise 1.3.8:

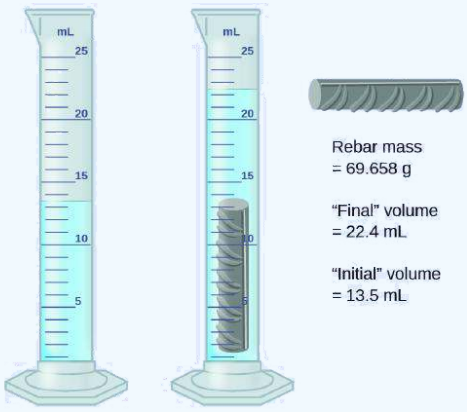
What is the density of a liquid with a mass of 31.1415 g and a volume of 30.13 cm^3? Give your answer with the appropriate number of significant digits.

Answer

1.034 g/mL

Example 1.3.9: Determining Density by Water Displacement

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



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 digits, 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 1.3.9

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



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.

1.3.10: 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 accepted or true value. Precise values agree with each other; accurate values agree with an accepted value. These characterizations can be extended to other contexts, such as the results of an archery competition (Figure 1.3.2).

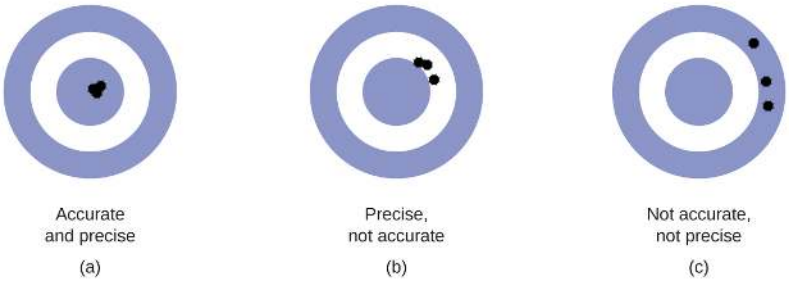


Figure 1.3.2: (a) These arrows are close to both the bull's eye and one another, so they are both accurate and precise. (b) These arrows are close to one another but not on target, so they are precise but not accurate. (c) These arrows are neither on target nor close to one another, so they are neither 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 1.3.2.

Table 1.3.2: Volume (mL) of Cough Medicine Delivered by 10-oz (296 mL) Dispensers

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

1.3.11: 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.

Quantities can be exact or measured. Measured quantities have an associated uncertainty that is represented by the number of significant digits 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 accepted value) and/or precise (showing little variation when measured repeatedly).

1.3.12: Key Equations

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

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

uncertainty
estimate of amount by which measurement differs from accepted value

significant digits

(also, significant figures) 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

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).
- 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 1.3: Mathematical Treatment of Measurement Results is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

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

1.E.1: For Chapter 1 you MUST know the following:

- The names and symbols for elements 1-18
- The SI Base units, the measured property, and the symbol
- The SI Prefixes, their abbreviation, and their meaning (M, k, c, m, *u*, n, p)

1.E.2: Turn in your answers for the following questions - show your work

1. Perform the following unit conversions. Express your answers in scientific notation with the appropriate number of significant figures.
   a. Convert 78.01 inches into: feet, meters, and centimeters.
   b. Convert 15.42 meters into kilometers, centimeters, and millimeters.
   c. Convert 98.6 °F into °C and K.
   d. Convert 75 miles per hour into: km per hour and m s^{-1}.
2. 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.
   a. Determine the density of this piece of jewelry.
   b. Assuming that the jewelry is made from only one substance, what substance is it likely to be? Explain.
3. In the movie *Goldfinger*, James Bond foils a plot to break into Fort Knox. 007 does some quick mental calculations to determine the feasibility of removing the gold. If the price of gold is $14.00 per troy ounce (31.1035 grams) at the time the movie was produced, what is the mass (in kg) of 1 million dollars of gold? What is the volume of 1 million dollars of gold in L. How much would this gold be worth today if the price of gold is $9068.77 per kg?
4. The following experiment is performed with an unknown liquid. The liquid is added to a graduated cylinder with a mass of 54.6789 grams. After 20.00 mL of the liquid is added to the cylinder (at 298 K), the mass is 74.6215 grams. Is the liquid water? How do you know? If it is not water, what could it be?
5. The experiment above is repeated with a second liquid, after 21.3 mL of this liquid (at 20 °C) is added the mass of the cylinder is 72.7364 grams. Is the second liquid ethanol? How do you know? If it is not ethanol, what could it be?

1.E.3: The Following Questions are for your practice - Do Not Turn In. They include answers so you can check your work

1. Perform the following calculations and report each answer with the correct number of significant figures.
   a. 628×342
   b. $(5.63 \times 10^2) \times (7.4 \times 10^3)$
   c. $\dfrac{28.0}{13.483}$
   d. 14.98 + 27,340 + 84.7593
   e. 42.7 + 0.259

Answer (a)

(2.15×10^5)

Answer (b)

4.2×10^6

Answer (c)

2.08

Answer (d)

27,440

Answer (e)

43.0

2. Use scientific (exponential) notation to express the following quantities in terms of the SI base units in
   a. 0.13 g
   b. 86.3 mg
   c. 37.6 cm
   d. 54 μm
   e. 27 ns

Answer (a)

1.3×10^{-4} kg

Answer (b)

8.63×10^{-5} kg

Answer (c)

3.76×10^{-1} m

Answer (d)

5.4×10^{-5} m

Answer (e)

1×10^{9} s

3. Make the conversion indicated in each of the following:
   a. the length of a soccer field, 120 m (three significant figures), to feet
   b. the height of Mt. Kilimanjaro, at 19,565 ft the highest mountain in Africa, to kilometers
   c. the area of an 8.5 t 11-inch sheet of paper in cm^2
   d. the estimated mass of the atmosphere, 5.6 t 10^{15} tons, to kilograms
   e. the mass of a 5.00-grain aspirin tablet to milligrams (1 grain = 0.00229 oz)

Answer (a)

394 ft

Answer (b)

5.9634 km

Answer (c)

6.0×10^{2}

Answer (d)

5.1×10^{18} kg

Answer (e)

324 mg

4. 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?

Answer (a)

81.6 g

Answer (b)

17.6 g

5. Calculate these volumes the volume of 25 g iodine, density = 4.93 g/cm^3?

Answer

5.1 mL

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

Answer

5371 °F, 3239 K

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

Answer

−23 °C, 250 K

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.E: Essential Ideas of Chemistry- Homework is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

CHAPTER OVERVIEW

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.

2.1: Atomic Theory

2.2: Atomic Structure, Isotopes, and Atomic Mass

2.3: Chemical Formulas

2.E: Atoms, Molecules, and Ions- Homework

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 2: Atoms, Molecules, and Ions is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

2.1: 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
- 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

2.1.1: Introduction

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.

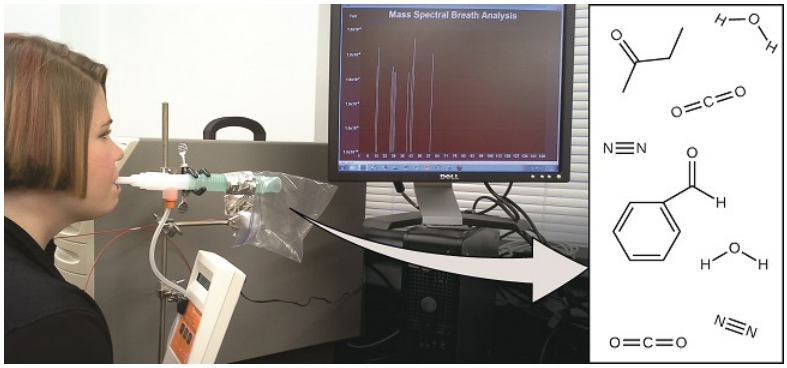


Figure 2.1.1: Analysis of molecules in an exhaled breath can provide valuable information, leading to early diagnosis of diseases or detection of environmental exposure to harmful substances. (credit: modification of work by Paul Flowers)

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.

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.

2.1.2: Atomic Theory in Ancient Greece - Aristotle and Democritus

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.

2.1.3: Atomic Theory in the Nineteenth Century - Dalton and Thompson

2.1.3.1: Evidence of the Atom

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 2.1.2). A macroscopic sample of an element contains an incredibly large number of atoms, all of which have identical chemical properties.

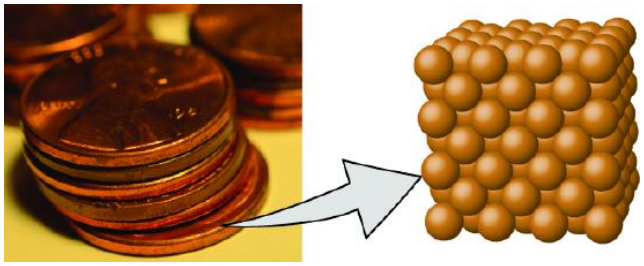


Figure 2.1.2: A pre-1982 copper penny (left) contains approximately 3×10^{22} copper atoms (several dozen are represented as brown spheres at the right), each of which has the same chemical properties. (credit: modification of work by “slgckgc”/Flickr)

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 2.1.3).

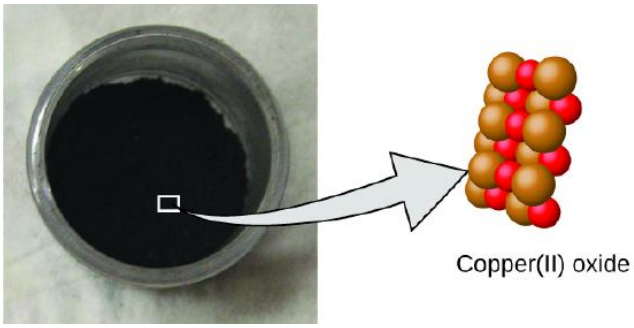


Figure 2.1.3: Copper(II) oxide, a powdery, black compound, results from the combination of two types of atoms—copper (brown spheres) and oxygen (red spheres)—in a 1:1 ratio. (credit: modification of work by “Chemicalinterest”/Wikimedia Commons)

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 2.1.4).*

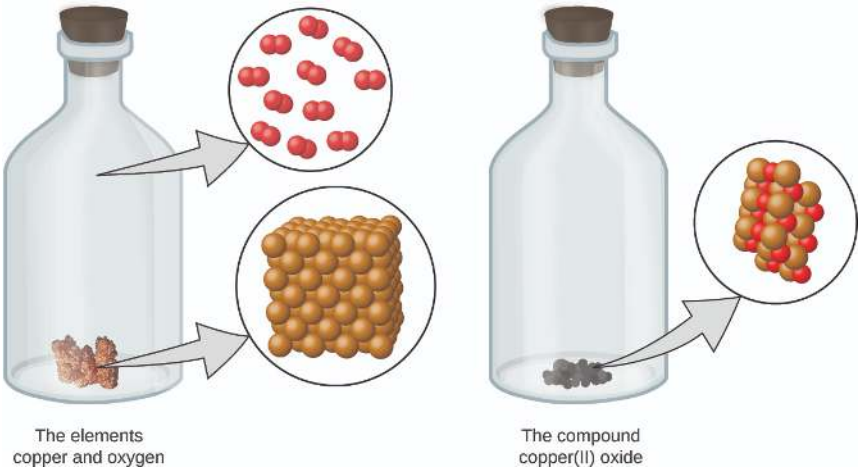


Figure 2.1.4: When the elements copper (a shiny, red-brown solid, shown here as brown spheres) and oxygen (a clear and colorless gas, shown here as red spheres) react, their atoms rearrange to form a compound containing copper and oxygen (a powdery, black solid). (credit copper: modification of work by http://images-of-elements.com/copper.php).

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 2.1.1: 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?



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 2.1.1

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



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.

2.1.3.2: Evidence of the Electron

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.

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 2.1.5).

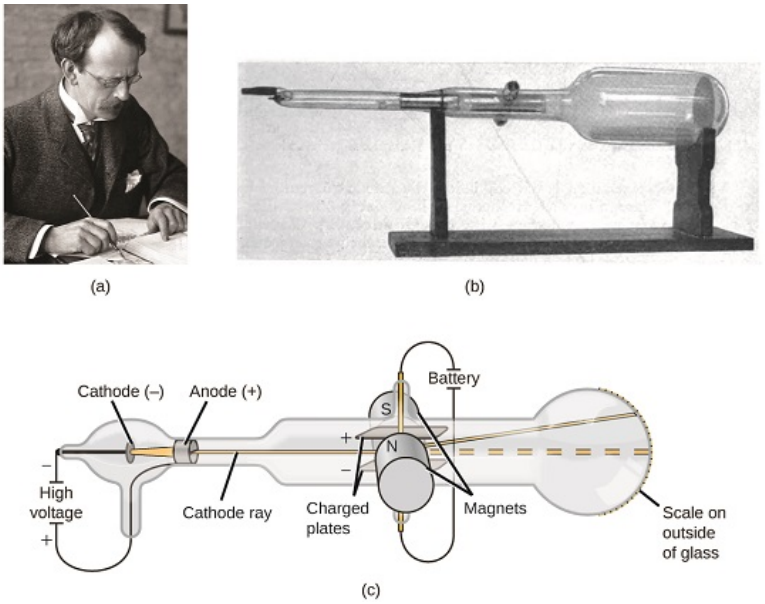


Figure 2.1.5: (a) J. J. Thomson produced a visible beam in a cathode ray tube. (b) This is an early cathode ray tube, invented in 1897 by Ferdinand Braun. (c) In the cathode ray, the beam (shown in yellow) comes from the cathode and is accelerated past the anode toward a fluorescent scale at the end 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).

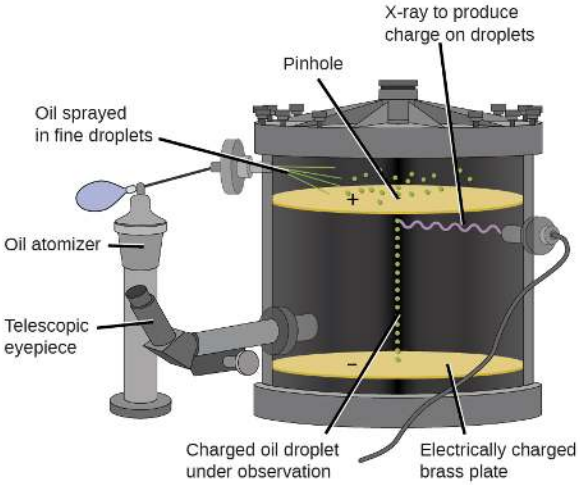
Based on his observations, here is what Thomson proposed and why: The particles are attracted by positive (+) charges and repelled by negative (−) charges, so they must be negatively charged (like charges repel and unlike charges attract); they are less massive than atoms and indistinguishable, regardless 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*."

2.1.4: Atomic Theory in the Twentieth Century - Millikan, Rutherford, and Chadwick

2.1.4.1: Mass of the Electron

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 2.1.6).



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 2.1.6: 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 2.1.7).

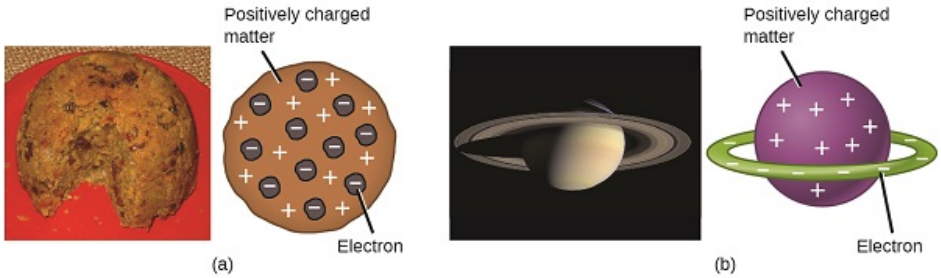


Figure 2.1.7: (a) Thomson suggested that atoms resembled plum pudding, an English dessert consisting of moist cake with embedded raisins ("plums"). (b) Nagaoka proposed that atoms resembled the planet Saturn, with a ring of electrons surrounding a positive "planet." (credit a: modification of work by "Man vyi"/Wikimedia Commons; credit b: modification of work by "NASA"/Wikimedia Commons).

2.1.4.2: The Nucleus

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 2.1.8). 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).

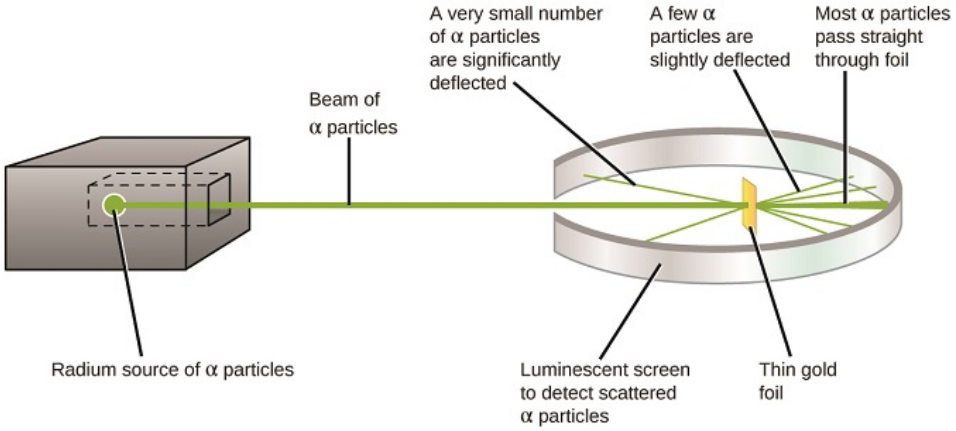


Figure 2.1.8: Geiger and Rutherford fired α particles at a piece of gold foil and detected where those particles went, as shown in this schematic diagram of their experiment. Most of the particles passed straight through the foil, but a few were deflected slightly and a very small number were significantly 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 2.1.9).

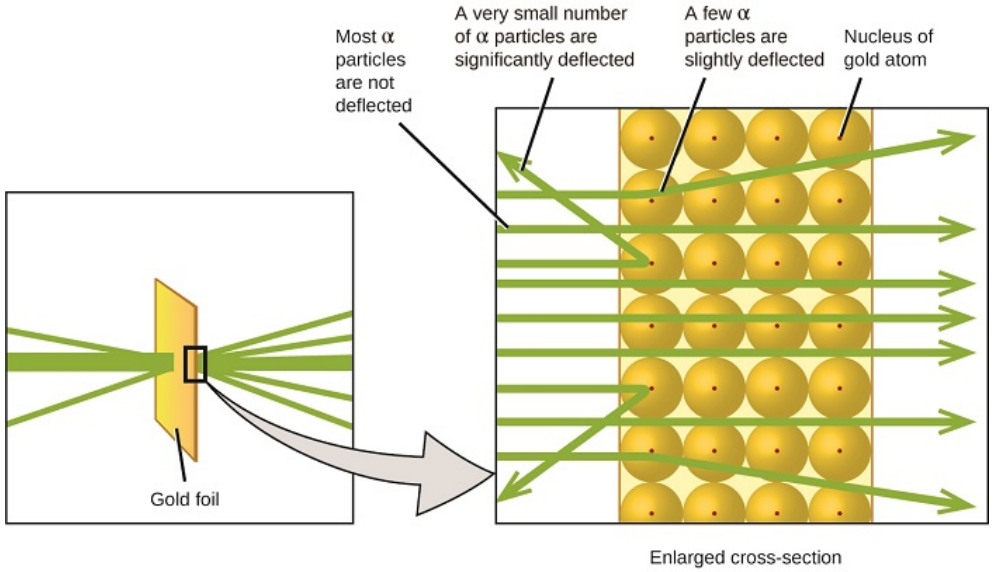
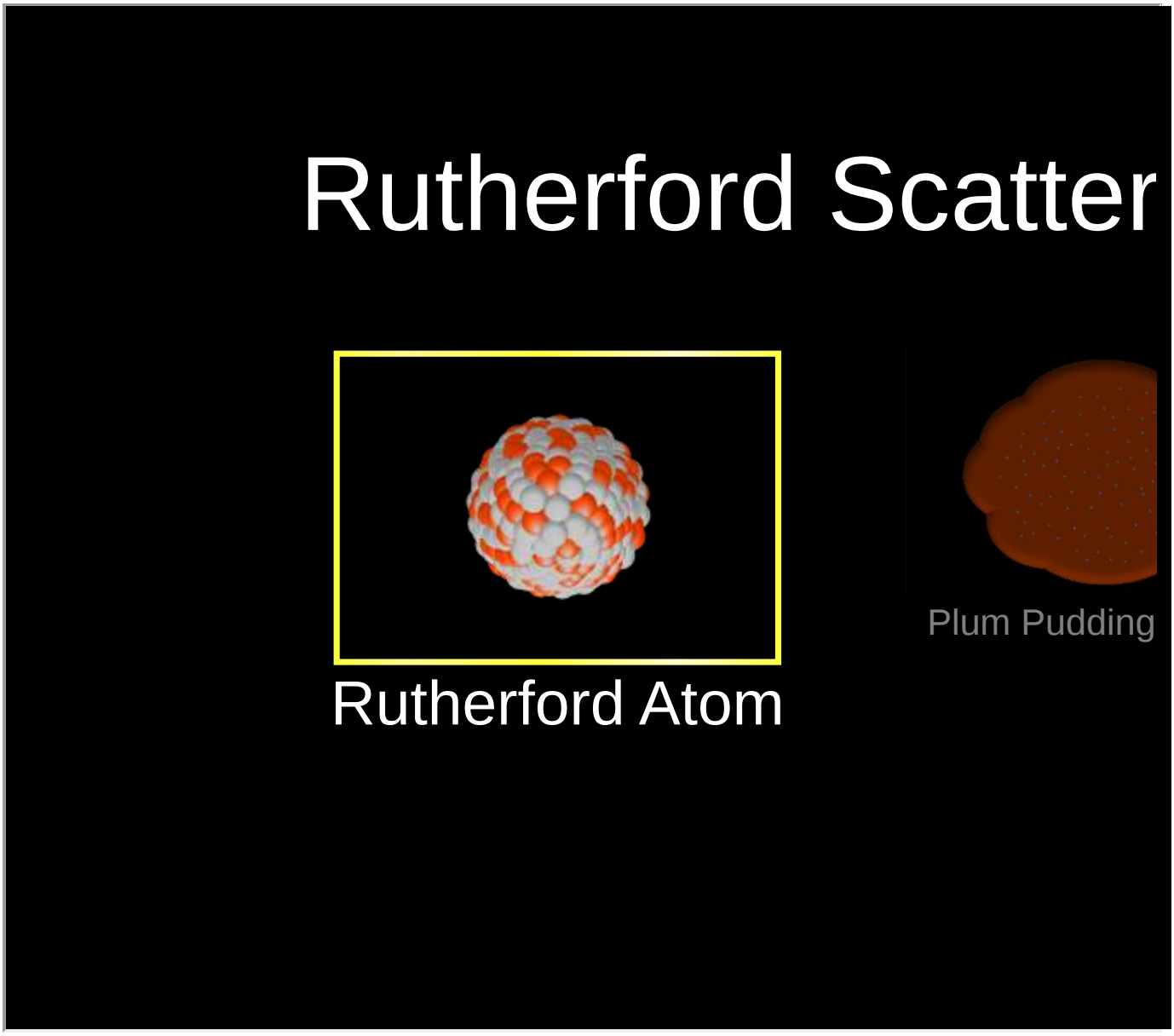


Figure 2.1.9: The α particles are deflected only when they collide with or pass close to the much heavier, positively charged gold nucleus. Because the nucleus is very small compared to the size of an atom, very few α particles are deflected. Most pass through the relatively large region occupied by 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.

2.1.4.3: PhET simulation



2.1.4.4: The Neutron

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.

2.1.5: Fundamental Experiments in Chemistry - Video

This project was preformed to supply **Libretext authors** with videos on General Chemistry topics which can be used to enhance their projects. Also, these videos are meant to act as a learning resource for **all General Chemistry students**.

Video Topics

Many concepts in chemistry are based on key experiments. Some of these experiments are discussed in this videos. In particular, Lavoisier's experiments determined the Law of Conservation of Mass which says mass is not gained or lost during a chemistry reaction. Proust's experiments came up with the Law of Definite Proportions which says elements will be in the same proportions in a given compound. J.J. Thomson discovered the electron and determined that it has a negative charge. Rutherford's experiment with gold foil led to the Theory of a Nuclear Atom.

Link to Video

Fundamental Experiments in Chemistry: https://youtu.be/IhqqLGKmah4



2.1.6: Attribution

- Prof. Steven Farmer (Sonoma State University)

2.1.7: 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.

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

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

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

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

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

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 2.1: Atomic Theory is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

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

2.2: Atomic Structure, Isotopes, and Atomic Mass

Learning Objectives

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

2.2.1: Structure of the Atom

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 2.2.1).



Figure 2.2.1: 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).

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 atomic mass unit (amu) was originally defined based on hydrogen, the lightest element, and oxygen. Because of this ambiguity it was redefined in 1961 as the unified atomic mass unit (u) with regard to the most abundant isotope of carbon, atoms of which are assigned masses of exactly 12 u. Thus, one u is exactly $1/12$ of the mass of one carbon-12 atom. The Dalton (Da) and the atomic mass unit (amu) are alternative units that are almost identical to the u. 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 u and a charge of 1+. A neutron is a slightly heavier particle with a mass 1.0087 u 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 u (it would take about 1800 electrons to equal the mass of one proton. The properties of these fundamental particles are summarized in Table 2.2.1. You may notice 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 u, slightly larger than the 12.00 u of an actual carbon-12 atom. This "missing" mass is known as the mass defect, it is related to the energy holding the atom together.

Table 2.2.1: Properties of Subatomic Particles

Name	Location	Charge (C)	Unit Charge	Mass (u)	Significance
electron	outside nucleus	-1.602×10^{-19}	1−	0.00055	charge = proton - electron

Name	Location	Charge (C)	Unit Charge	Mass (u)	Significance
proton	nucleus	1.602×10^{-19}	1+	1.00727	atomic number = proton
neutron	nucleus	0	0	1.00866	mass = proton + neutron

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 uncharged 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.

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

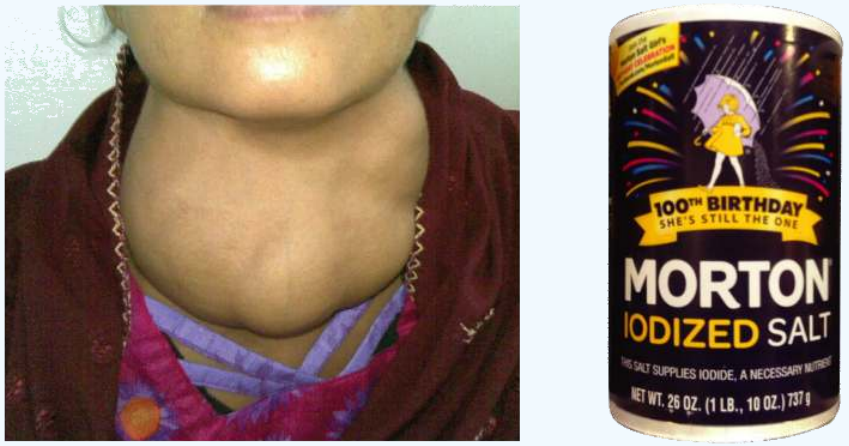
Atoms are electrically neutral if they contain the same number of positively charged protons and negatively charged electrons. When the numbers of these subatomic particles are *not* equal, the atom is electrically charged and is called an ion. The charge of an atom is defined as follows:

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

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 2.2.1: 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 2.2.2).



(a) (b)

Figure 2.2.2: (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)

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 2.2.1

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+

2.2.2: 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 2.2.3). 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 2.2.3: 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 2.2.2. 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 2.2.2: 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*)
copper	Cu (from *cuprum*)	silicon	Si
gold	Au (from *aurum*)	sodium	Na (from *natrium*)

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.

2.2.3: 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 2.2.4). 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 2.2.4 also shows how the charge of an atom is represented with the symbol for an element. In this example, the helium has a charge of +2 which is written as a superscript following the element symbol: $^{4}He^{2+}$. The magnesium isotope has a mass of 24 and a charge of +2, so it is written as $^{24}Mg^{2+}$.

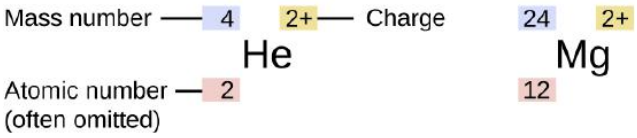


Figure 2.2.4: The symbol for an atom indicates the element via its usual two-letter symbol, the mass number as a left superscript, the atomic number as a left subscript (sometimes omitted), and the charge as a right superscript.

Information about the naturally occurring isotopes of elements with atomic numbers 1 through 5 is given in Table 2.2.2. 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 2.2.2: Nuclear Compositions of Atoms of the Very Light Elements

Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (u)	% Natural Abundance
hydrogen	$^{1}_{1}$H (protium)	1	1	0	1.0078	99.989
	$^{2}_{1}$H (deuterium)	1	1	1	2.0141	0.0115
	$^{3}_{1}$H (tritium)	1	1	2	3.01605	— (trace)
helium	$^{3}_{2}$He	2	2	1	3.01603	0.00013
	$^{4}_{2}$He	2	2	2	4.0026	100
lithium	$^{6}_{3}$Li	3	3	3	6.0151	7.59
	$^{7}_{3}$Li	3	3	4	7.0160	92.41
beryllium	$^{9}_{4}$Be	4	4	5	9.0122	100
boron	$^{10}_{5}$B	5	5	5	10.0129	19.9
	$^{11}_{5}$B	5	5	6	11.0093	80.1

2.2.4: Atomic Mass and Isotopes

Because each proton and each neutron contribute approximately one u 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.

$$\text{average mass} = \sum_i (\text{fractional abundance} \times \text{isotopic mass})_i \tag{2.2.1}$$

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 u, and the remaining 80.1% are ^{11}B with a mass of 11.0093 u. The average atomic mass for boron is calculated to be:

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

It is important to understand that no single boron atom weighs exactly 10.8 u; 10.8 u is the average mass of a large number of naturally occurring boron atoms. The individual boron atoms weigh either approximately 10 u or 11 u.

Example 2.2.2: 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 u), 0.47% ^{21}Ne (mass 20.9940 u), and 7.69% ^{22}Ne (mass 21.9914 u). What is the average mass of the neon in the solar wind?

Solution

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

The average mass of a neon atom in the solar wind is 20.15 u. The average mass of a terrestrial neon atom is 20.1796 u. This result demonstrates that we may find slight differences in the natural abundance of isotopes, depending on their origin. For some elements the differences in these isotope abundances are used to identify where the element came from. Neon from a meteorite has a different isotope distribution thane neon from the earth's crust. Lead from different mines can have different isotope distributions depending on the geology of the locations.

Exercise 2.2.2

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

Answer

24.31 u

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

Example 2.2.3: Calculation of Percent Abundance

Naturally occurring chlorine consists of ^{35}Cl (mass 34.96885 u) and ^{37}Cl (mass 36.96590 u), with an average mass of 35.453 u. 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.

$$\text{average mass} = (\text{fraction of } ^{35}\text{Cl} \times \text{mass of } ^{35}\text{Cl}) + (\text{fraction of } ^{37}\text{Cl} \times \text{mass of } ^{37}\text{Cl}) \tag{2.2.2}$$

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:

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

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 2.2.3

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

Answer

69.15% Cu-63 and 30.85% Cu-65

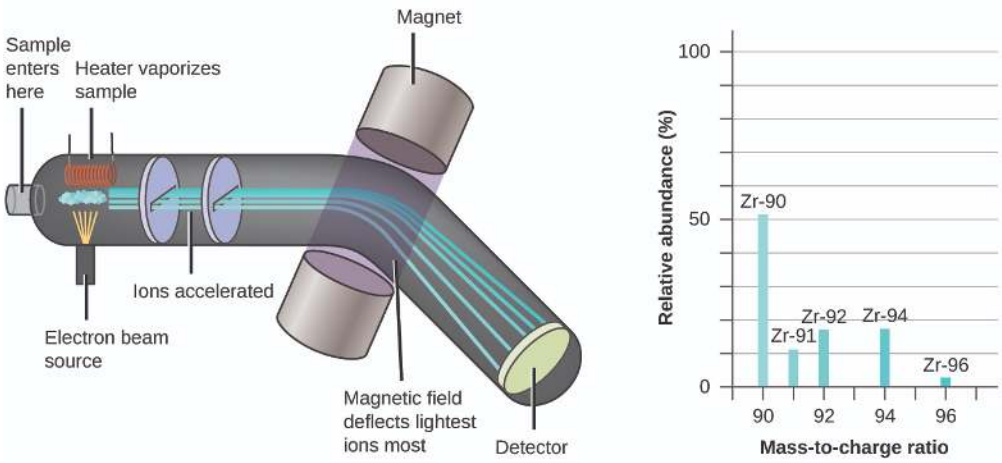


Figure 2.2.5: Analysis of zirconium in a mass spectrometer produces a mass spectrum with peaks showing the different isotopes of Zr.

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 2.2.5), 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* 2.2.1** *: Watch this video from the Royal Society for Chemistry for a brief description of the rudiments of mass spectrometry.*

2.2.5: Finding the Averaged Atomic Mass of an Element - Video

This project was preformed to supply **Libretext authors** with videos on General Chemistry topics which can be used to enhance their projects. Also, these videos are meant to act as a learning resource for **all General Chemistry students**.

Video Topics

Averaged Atomic Weight of an element is determined by the number of isotopes of the element and their relative abundance.

Link to Video

Finding the Averaged Atomic Weight of an Element: https://youtu.be/bmP6Gr9zJiQ



2.2.6: Attribution

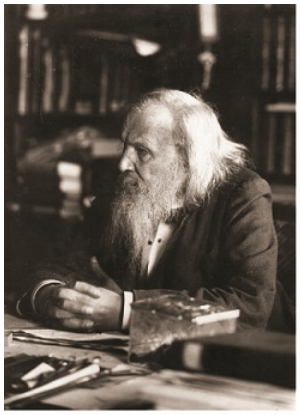
- Prof. Steven Farmer (Sonoma State University)

2.2.7: 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 2.2.6).



(a)

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

(b)

Figure 2.2.6: (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

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 2.2.2). 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.

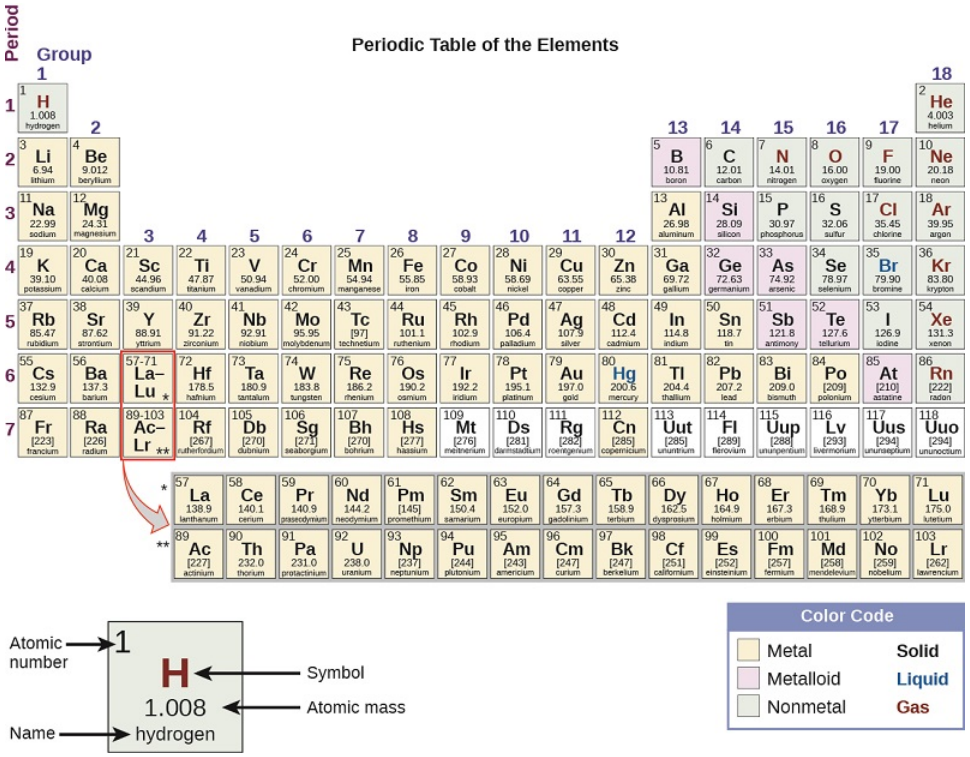


Figure 2.2.2: Elements in the periodic table are organized according to their properties.

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 2.2.7). 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.

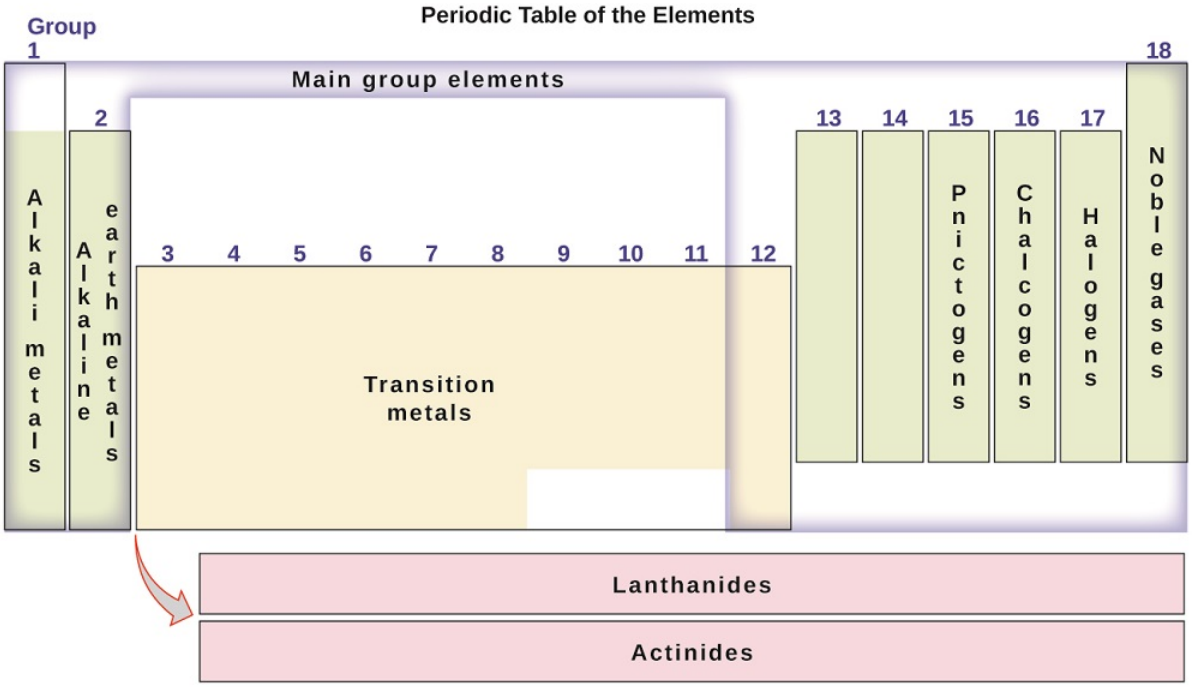


Figure 2.2.7: The periodic table organizes elements with similar properties into groups

Example 2.2.4: 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 2.2.4

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

https://chem.libretexts.org/@go/page/432409

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.

2.2.8: 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 unified atomic mass units (u), which is referred to as the atomic mass. A u 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 u. Neutrons are relatively heavy particles with no charge and a mass of 1.0087 u. Electrons are light particles with a charge of 1− and a mass of 0.00055 u. 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 u, 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.

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.

2.2.9: Key Equations

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

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

anion

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

atomic mass

average mass of atoms of an element, expressed in u

atomic number (Z)

number of protons in the nucleus of an atom

cation

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

chalcogen

element in group 16

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 $e = 1.602 \times 10^{-19}$ C

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

ion

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

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

mass number (A)

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

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

unified atomic mass unit (u)

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

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 2.2: Atomic Structure, Isotopes, and Atomic Mass is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

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

2.3: 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
- 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
- Derive names for common types of inorganic compounds using a systematic approach.
- Describe how to name binary covalent compounds including acids and oxyacids.

2.3.1: Elements, Molecules, and Compounds

2.3.1.1: Elements and Molecules

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 2.3.2).

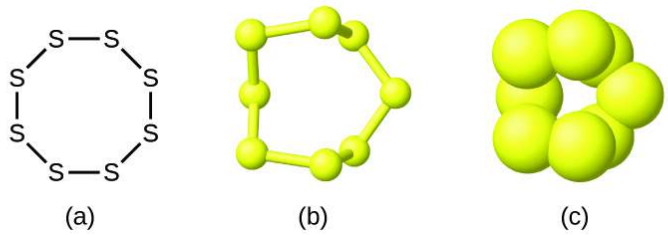


Figure 2.3.2: A molecule of sulfur is composed of eight sulfur atoms and is therefore written as S_8. It can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. Sulfur atoms are represented by yellow spheres.

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. 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 2.3.3).

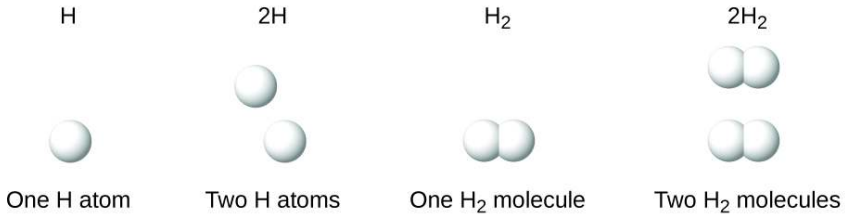


Figure 2.3.3: The symbols H, 2H, H_2, and $2H_2$ represent very different entities.

2.3.1.2: Compounds and Molecules

Compounds are formed when two or more elements chemically combine, resulting in the formation of bonds. If these two elements are non-metals the compound is a molecular compound. 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 2.3.1). 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.) These molecular compounds (covalent compounds) result when atoms share 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.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.

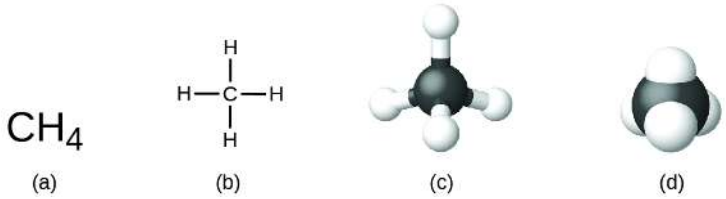


Figure 2.3.1: A methane molecule can be represented as (a) a molecular formula, (b) a structural formula, (c) a ball-and-stick model, and (d) a space-filling model. Carbon and hydrogen atoms are represented by black and white spheres, respectively.

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. We can also 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, 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 2.3.5).

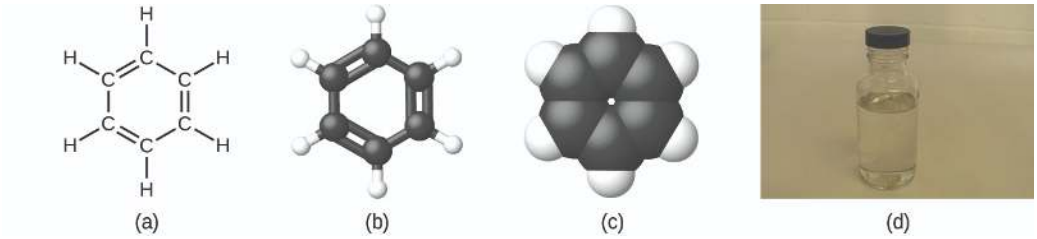


Figure 2.3.5: Benzene, C_6H_6, is produced during oil refining and has many industrial uses. A benzene molecule can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. (d) Benzene is a clear liquid. (credit d: modification of work by Sahar Atwa).

If we know a compound's formula, we can easily determine the empirical formula. 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 2.3.6) 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. The molecular formula is always a whole-number multiple of an empirical formula.

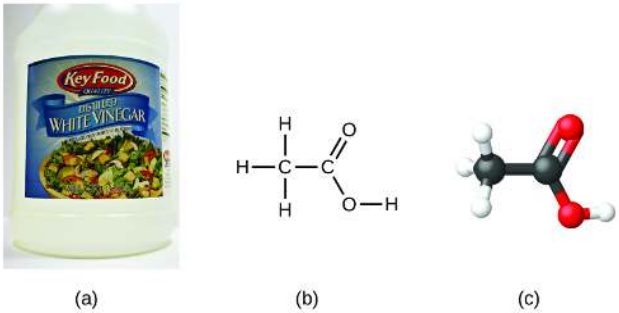


Figure 2.3.6: (a) Vinegar contains acetic acid, $C_2H_4O_2$, which has an empirical formula of CH_2O. It can be represented as (b) a structural formula and (c) as a ball-and-stick model. (credit a: modification of work by "HomeSpot HQ"/Flickr)

https://chem.libretexts.org/@go/page/432410

Example 2.3.1: 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 2.3.1

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 2.3.7). 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.

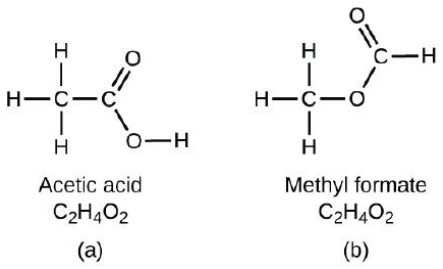


Figure 2.3.7: Molecules of (a) acetic acid and methyl formate (b) are structural isomers; they have the same formula ($C_2H_4O_2$) but different structures (and therefore different chemical properties).

Many types of isomers exist (Figure 2.3.8). 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.

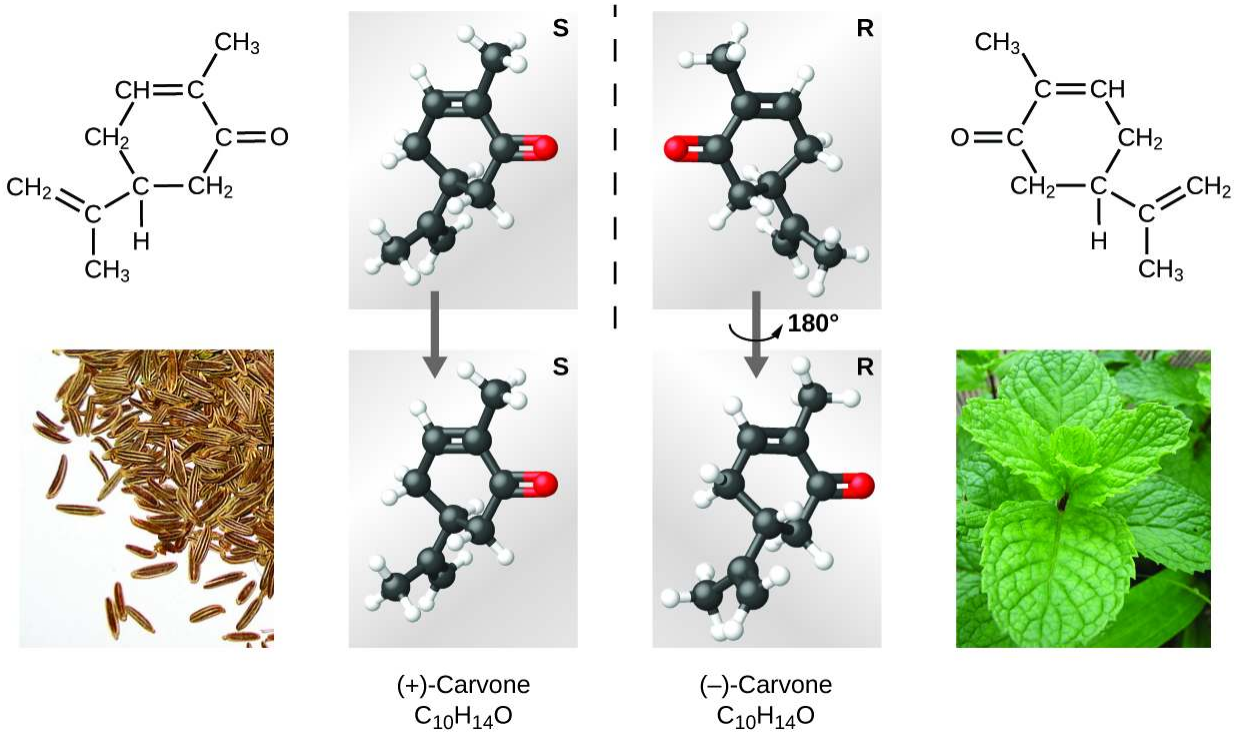


Figure 2.3.8: Molecules of carvone are spatial isomers; they only differ in the relative orientations of the atoms in space. (credit bottom left: modification of work by "Miansari66"/Wikimedia Commons; credit bottom right: modification of work by Forest & Kim Starr)

2.3.2: Naming Molecular Compounds

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 be called carbon oxide. To distinguish these two compounds prefixes are added 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 2.3.5.

Table 2.3.5: Nomenclature Prefixes

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 2.3.6.

Table 2.3.6: 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

Compound	Name
NO_2	nitrogen dioxide
N_2O_4	dinitrogen tetroxide
N_2O_5	dinitrogen pentoxide

Compound	Name
PF_5	phosphorus pentafluoride
P_4O_{10}	tetraphosphorus decaoxide
IF_7	iodine heptafluoride

There are a few common names that you may encounter as you continue your study of chemistry. For example, although the proper name for NO is nitrogen monoxide, it is often called nitric oxide. Similarly, dinitrogen monioxide, N_2O, may be called nitrous oxide. And H_2O is usually called water, not dihydrogen monoxide. Be careful when you encounter these common names to make sure you know what formula to use - it is a good idea to double check by looking these up.

Example 2.3.2: 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 2.3.2

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

2.3.3: Ionic Compounds

2.3.3.1: Introduction

Compounds are formed when two or more elements chemically combine, resulting in the formation of bonds. When two non-metals like hydrogen and oxygen react they form water molecules H_2O - which is a molecular compound. However, when a metal and a non-metal like sodium and chlorine react they form table salt which is an ionic compound. The result is not a molecule. This ionic compound has elements in a fixed ratio 1 Na to 1 Cl but the structure is very different from a molecular compound. The empirical formula for table salt is NaCl and the structure contains a large number of interconnected atoms. The empirical formula just indicates the types of atoms present and *the simplest whole-number ratio of the number of atoms (or ions) in the compound.*

Another example is titanium (IV) oxide. Titanium (IV) oxide is used as pigment in white paint and in the thick, white, blocking type of sunscreen. It has an empirical formula of TiO_2 that identifies the elements titanium (Ti) and oxygen (O) as the constituents of titanium (IV) oxide. The empirical formula shows there are twice as many oxygen atoms as titanium atoms. The structure, however, is shown in Figure 2.3.4*b*

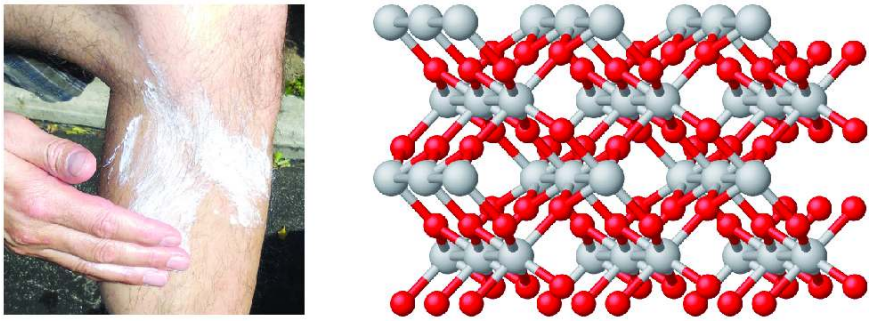


Figure 2.3.4: (a) The white compound titanium (IV) oxide provides effective protection from the sun. (b) A crystal of titanium (IV) oxide, TiO_2, contains titanium and oxygen in a ratio of 1 to 2. The titanium atoms are gray and the oxygen atoms are red. (credit a: modification of work by "osseous"/Flickr).

2.3.3.2: Forming Ions

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 2.3.5).

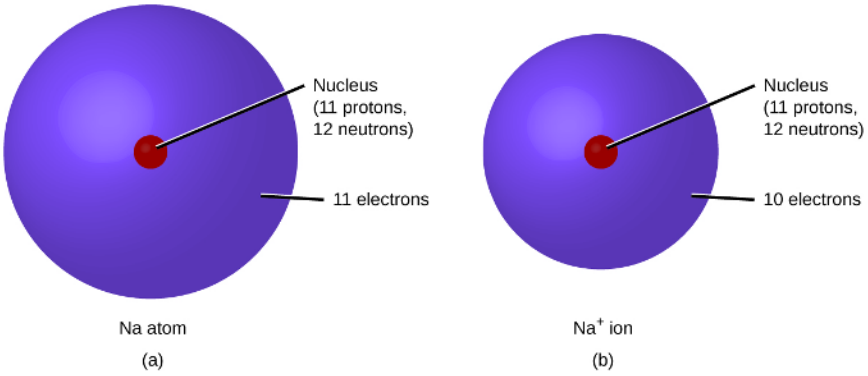


Figure 2.3.5: (a) A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. (b) A sodium cation (Na^+) has lost an electron, so it has one more proton (11) than electrons (10), giving it an overall positive charge, signified by a superscripted plus sign.

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 2.3.6). 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.

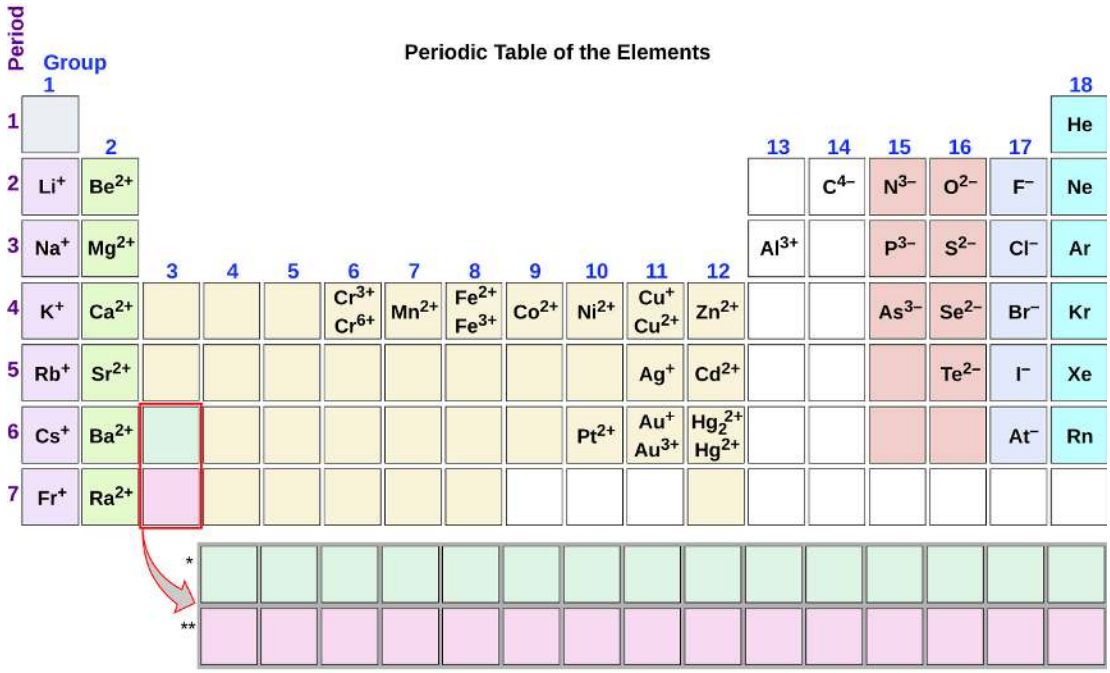


Figure 2.3.6: Some elements exhibit a regular pattern of ionic charge when they form ions.

Example 2.3.2: 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 2.3.2

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

Answer

Se^{2-}, the selenide ion

Example 2.3.3: 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 2.3.3

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.

2.3.3.3: Polyatomic Ions

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 2.3.1. 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 2.3.1: Common Polyatomic Ions

Name	Formula
ammonium	NH_4^+
hydronium	H_3O^+
hydroxide	OH^-
acetate	CH_3COO^-
cyanide	CN^-
carbonate	CO_3^{2-}
hydrogen carbonate (bicarbonate)	HCO_3^-
nitrate	NO_3^-
nitrite	NO_2^-
sulfate	SO_4^{2-}
hydrogen sulfate (bisulfate)	HSO_4^-
sulfite	SO_3^{2-}
hydrogen sulfite (bisulfite)	HSO_3^-

Name	Formula
phosphate	PO_4^{3-}
hydrogen phosphate (biphosphate)	HPO_4^{2-}
dihydrogen phosphate (dibiphosphate)	$H_2PO_4^-$

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. 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-}.

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.

2.3.3.4: Forming 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 2.3.7).

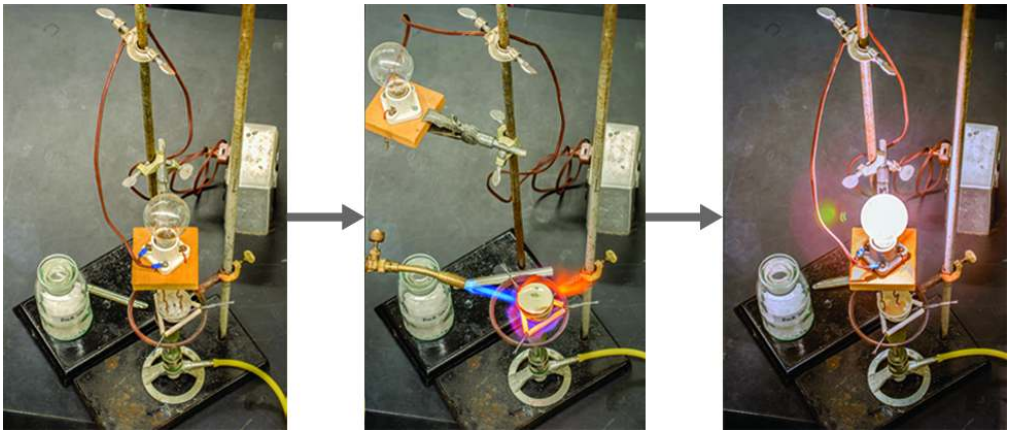


Figure 2.3.7: Sodium chloride melts at 801 °C and conducts electricity when molten. On the left a light bulb is connected to crucible filled with sodium chloride solid at room temperature. In the center figure the bunsen burner heats the sodium chloride. In the right figure the sodium chloride melts and as a liquid it conducts electricity so that the circut is complete and the light bulb turns on. (credit: modification of work by Mark Blaser and Matt Evans)

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 2.3.3: Predicting the Formula of an Ionic Compound

The gemstone sapphire (Figure 2.3.4) 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 2.3.4: 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 2.3.3

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 2.3.1) 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 2.3.4: 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 2.3.4

Predict the formula of the ionic compound formed between the lithium ion and the sulfate ion, SO_4^{2-} (Hint: Use the periodic table to predict the sign and the charge on the lithium ion.)

Answer

Li_2SO_4

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, $C_2O_4^{2-}$.

2.3.4: Naming Ionic Compounds

This section describes how to name simple ionic 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. There are different systems for ionic compounds where the metal always forms ions with the same charge vs metals that form ions with different charges.

2.3.4.1: Ionic Compounds Containing Metals With a Single Charge

The name of a binary compound containing monatomic ions consists of the name of the metal followed by the name of the nonmetal. The nonmetal has its ending replaced by the suffix *–ide*). Some examples are given in Table 2.3.2.

Table 2.3.2: 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

2.3.4.2: 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 a suffix is already present in the name of the anion. Examples are shown in Table 2.3.3.

Table 2.3.3: 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 2.3.3. 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 2.3.3: Everyday Ionic Compounds

Ionic Compound	Name	Use
NaCl	sodium chloride	ordinary table salt

$NaHCO_3$	sodium hydrogen carbonate or sodium bicarbonate	baking soda; used in cooking (and in antacids)
Na_2CO_3	sodium carbonate	washing soda; used in cleaning agents
$CaCO_3$	calcium carbonate	ingredient in antacids
$Mg(OH)_2$	magnesium hydroxide	ingredient in antacids
K_3PO_4	potassium phosphate	food additive (many purposes)
Na_2HPO_4	sodium hydrogen phosphate or sodium biphosphate	anti-caking agent; used in powdered products
Na_2SO_3	sodium sulfite	preservative

2.3.4.3: Compounds Containing a Metal Ion with a Variable Charge

Most of the transition metals 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 2.3.4.

Table 2.3.4: Names of Some Transition Metal Ionic Compounds

Transition Metal Ionic Compound	Name
$FeCl_3$	iron(III) chloride
$FeCl_2$	Iron (II) chloride
$Cu_3(PO_4)_2$	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. If you see one of these names, look it up to make sure you have the correct charge for the metal.

Example 2.3.1: 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 2.3.1

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

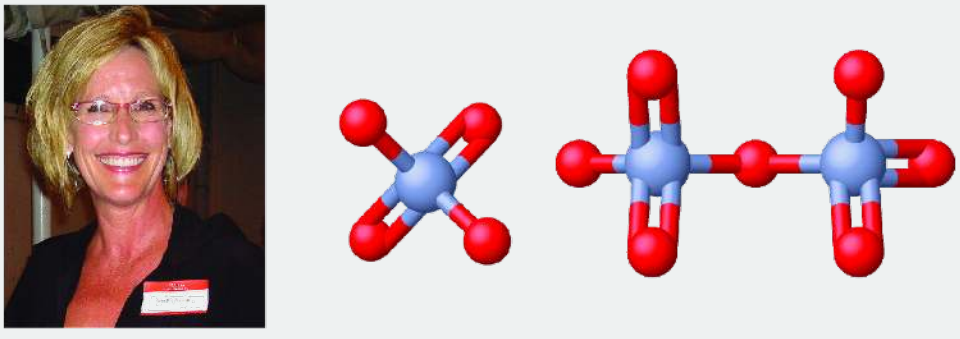
Cu_2O

Answer e

CrF_6

Erin Brokovich and Chromium Contamination

In the early 1990s, legal file clerk Erin Brockovich (Figure 2.3.2) 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 **2.3.2**: (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.

2.3.5: Distinguishing Ionic and Molecular Compounds

Since the systems for naming molecular compounds and ionic compounds are very different, it is important to know how to distinguish these two types of compounds. 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. Covalent compounds are usually formed by a combination of nonmetals

In contrast, ionic compounds are usually formed when a metal and a nonmetal combine. As a result, the periodic table helps distinguish these two types of compounds. 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 2.3.5: 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 2.3.5

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

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

2.3.6: Naming Acids

Acids are another important class of compounds. They share characteristics with both molecular and ionic compounds but they are named using a separate system of chemical nomenclature. If you are familiar with anions - both atomic and polyatomic - it is easy to identify when you need to name something as an acid because the cation is hydrogen. These compounds act as acids by releasing 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. The chemistry of acids is discussed in much greater detail in later chapters, but for now it is important that you know how to name these compounds.

2.3.6.1: Naming Binary Acids

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 2.3.5.

Table 2.3.5: 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
H_2S(*g*), hydrogen sulfide	H_2S(*aq*), hydrosulfuric acid

2.3.6.2: Naming Oxyacids

Oxyacids are compounds that contain hydrogen and a polyatomic ion with oxygen. These compounds 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). 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 2.3.6. 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 2.3.6: 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
H_2SO_4	sulfate	sulfuric acid

Formula	Anion Name	Acid Name
H_2SO_3	sulfite	sulfurous acid
H_3PO_4	phosphate	phosphoric acid

2.3.7: 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.

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.

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.

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

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

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

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.

monatomic ion

ion composed of a single atom

nomenclature

system of rules for naming objects of interest

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)

oxyanion

polyatomic anion composed of a central atom bonded to oxygen atoms

polyatomic ion

ion composed of more than one atom

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

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).
- 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).
- 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 2.3: Chemical Formulas is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

- **2.5: Chemical Formulas** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.
- **2.7: Molecular and Ionic Compounds** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.
- **2.8: Chemical Nomenclature** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.E: Atoms, Molecules, and Ions- Homework

2.E.1: For Chapter 2 you MUST know:

- The names and symbols for elements 1-36
- Know the polyatomic Ions. You MUST know ammonium (NH_4^+), acetate (CH_3COO^-), carbonate (CO_3^{2-}), hydroxide (OH^-), nitrate (NO_3^-), phosphate (PO_4^{3-}), and sulfate (SO_4^{2-}).

2.E.2: Turn in your answers for the following questions - show your work

1. How many protons, neutrons and electrons are present in one atom of the following:
    a. ^{1}H
    b. ^{2}H
    c. ^{3}H
    d. ^{79}Br
    e. $^{81}Br^{1-}$
    f. ^{262}Bh
2. What is the Atomic Weight of chlorine given that:
    - The exact mass of ^{35}Cl is 34.9689 and the relative abundance is 75.53%
    - The exact mass of ^{37}Cl is 36.9659 and the relative abundance is 24.47%
    - Is this the answer that you expected?
3. What is the Atomic Weight of ruthenium given the following information from WebElements, www.webelements.com. Is this the answer that you expected?
    - Isotope Abundance Exact Mass
    - ^{96}Ru 5.54% 95.907599
    - ^{98}Ru 1.87% 97.905287
    - ^{99}Ru 12.76% 98.9059389
    - ^{100}Ru 12.60% 99.9042192
    - ^{101}Ru 17.06% 100.9055819
    - ^{102}Ru 31.55% 101.9043485
    - ^{104}Ru 18.62% 103.905424
4. For the following molecules; write the chemical formula.
    a. carbon dioxide
    b. iron (II) chloride
    c. dinitrogen pentoxide
    d. iron (III) sulfate
5. Name the following compounds.
    a. KI
    b. CaF_2
    c. Cu_2SO_4
    d. N_2O
    e. LiOH
6. Give the chemical formula (or atomic symbol) and charge for the following ions:
    a. sulfate
    b. sulfite
    c. nitrate
    d. chloride
    e. nitride
    f. acetate
    g. carbonate

2.E.3: The Following Questions are for your practice - Do Not Turn In. They include answers so you can check your work

2.E.3.1: Atomic Structure and Symbolism

1. Write the symbol for each of the following ions:
   a. the ion with a 1+ charge, atomic number 55, and mass number 133
   b. the ion with atomic number 15, mass number 31, and a 3− charge

Answer A

$^{133}Cs^{+}$

Answer B

$^{31}P^{3-}$

2. Give the number of protons, electrons, and neutrons in neutral atoms of each of the following isotopes:
   a. $^{7}_{3}Li$
   b. $^{125}_{52}Te$

Answer A

3 protons, 3 electrons, 4 neutrons

Answer B

52 protons, 52 electrons, 73 neutrons

2.E.3.2: Chemical Formulas

1. Write the molecular and empirical formulas of the following compounds:
   a. 
   b. > 

Answer A

molecular CO_2, empirical CO_2

Answer B

molecular C_2H_2, empirical CH

2.E.3.3: The Periodic Table

1. 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. gold
   d. americium

Answer A

metal, inner transition metal

Answer B

nonmetal, representative element

Answer C

metal, transition metal

Answer D

metal, inner transition metal

2.E.3.4: Molecular and Ionic Compounds

1. Using the periodic table, predict whether the following chlorides are ionic or covalent: (a) KCl, (b) NCl_3, (c) ICl, and (d) PCl_5.

Answer A

ionic

Answer B

covalent

Answer C

covalent

Answer D

covalent

2.E.3.5: Chemical Nomenclature

1. Name the following compounds:
   a. CsCl
   b. BaO
   c. K_2S

Answer A

cesium chloride

Answer B

barium oxide

Answer C

potassium sulfide

2. Write the formulas of the following compounds:
   a. rubidium bromide
   b. magnesium selenide
   c. calcium chloride

Answer A

RbBr

Answer B

MgSe

Answer C

$CaCl_2$

3. Write the formulas of the following compounds
   a. chlorine dioxide
   b. dinitrogen tetraoxide
   c. potassium phosphide
   d. silver(I) sulfide

Answer A

ClO_2

Answer B

N_2O_4

Answer C

K_3P

Answer D

Ag_2S

4. Each of the following compounds contains a metal that can exhibit more than one ionic charge. Name these compounds:
   a. Cr_2O_3
   b. $FeCl_2$
   c. CrO_3

Answer A

chromium(III) oxide

Answer B

iron(II) chloride

Answer C

chromium(VI) oxide

This page titled 2.E: Atoms, Molecules, and Ions- Homework is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

CHAPTER OVERVIEW

3: Composition of Substances and Solutions

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

General Chemistry

Quantitative aspects of the composition of substances and mixtures are the subject of this chapter.

3.1: Formula Mass and the Mole Concept

3.2: Determining Empirical and Molecular Formulas

3.3: Percent Composition and Molecular Formula

3.4: Molarity

3.E: Composition of Substances and Solutions- Homework

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 3: Composition of Substances and Solutions is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

3.1: Formula Mass and the Mole Concept

Learning Objectives

- Calculate formula masses for covalent and ionic compounds
- Define the amount unit mole and the related quantity Avogadro's number
- Explain the relation between mass, moles, and numbers of atoms or molecules, and perform calculations deriving these quantities from one another

We can argue that modern chemical science began when scientists started exploring the quantitative as well as the qualitative aspects of chemistry. For example, Dalton's atomic theory was an attempt to explain the results of measurements that allowed him to calculate the relative masses of elements combined in various compounds. Understanding the relationship between the masses of atoms and the chemical formulas of compounds allows us to quantitatively describe the composition of substances.

3.1.1: Formula Mass

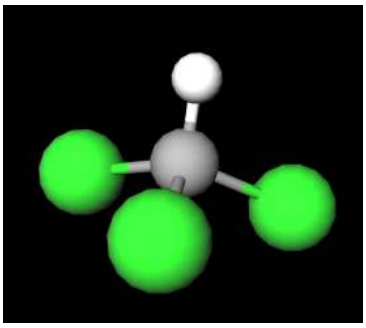
In an earlier chapter, we described the development of the unified atomic mass unit, the concept of average atomic masses, and the use of chemical formulas to represent the elemental makeup of substances. These ideas can be extended to calculate the formula mass of a substance by summing the average atomic masses of all the atoms represented in the substance's formula.

3.1.1.1: Formula Mass for Covalent Substances

For covalent substances, the formula represents the numbers and types of atoms composing a single molecule of the substance; therefore, the formula mass may be correctly referred to as a molecular mass. Consider chloroform ($CHCl_3$), a covalent compound once used as a surgical anesthetic and now primarily used in the production of tetrafluoroethylene, the building block for the "anti-stick" polymer, Teflon. The molecular formula of chloroform indicates that a single molecule contains one carbon atom, one hydrogen atom, and three chlorine atoms. The average molecular mass of a chloroform molecule is therefore equal to the sum of the average atomic masses of these atoms. Figure 3.1.1 outlines the calculations used to derive the molecular mass of chloroform, which is 119.37 u.

Figure 3.1.1: The average mass of a chloroform molecule, $CHCl_3$, is 119.37 u, which is the sum of the average atomic masses of each of its constituent atoms. The model shows the molecular structure of chloroform.

Element	Quantity	x	Average atomic mass (u)	=	Subtotal
C	1	x	12.01	=	12.01
H	1	x	1.008	=	1.008
Cl	3	x	35.45	=	106.35
Molecular Mass					119.37

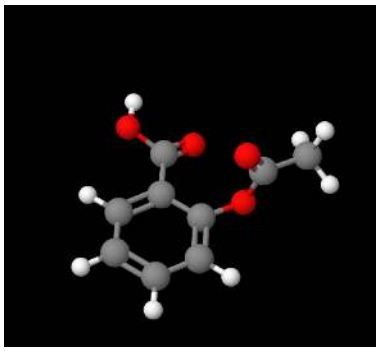


Likewise, the average molecular mass of an aspirin molecule, $C_9H_8O_4$, is the sum of the atomic masses of nine carbon atoms, eight hydrogen atoms, and four oxygen atoms, which amounts to 180.15 u (Figure 3.1.2).

Figure 3.1.2: The average mass of an aspirin molecule is 180.15 u. The model shows the molecular structure of aspirin, $C_9H_8O_4$.

Element	Quantity		Average atomic mass (u)		Subtotal
C	9	x	12.01	=	108.09

H	8	x	1.008	=	8.0064
O	4	x	16.00	=	64.00
Molecular Mass					180.15



Example 3.1.1: Computing Molecular Mass for a Covalent Compound

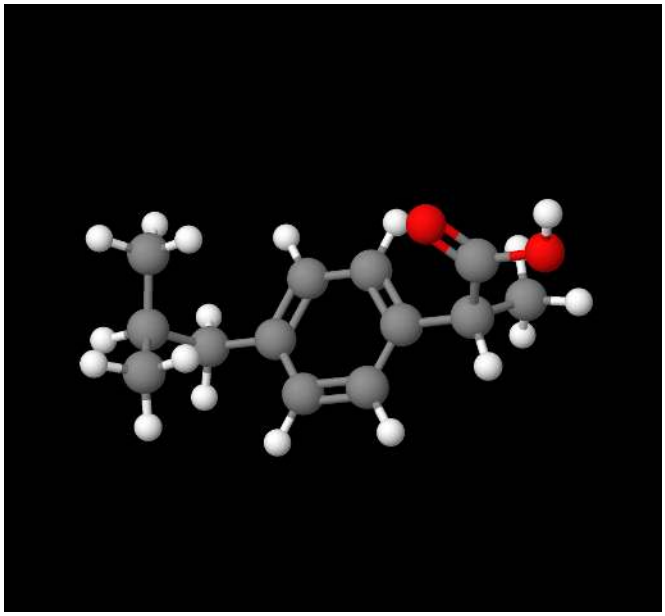
Ibuprofen, $C_{13}H_{18}O_2$, is a covalent compound and the active ingredient in several popular nonprescription pain medications, such as Advil and Motrin. What is the average molecular mass (u) for this compound?

Solution

Molecules of this compound are comprised of 13 carbon atoms, 18 hydrogen atoms, and 2 oxygen atoms. Following the approach described above, the average molecular mass for this compound is therefore:

Figure 3.1.2: The average mass of an aspirin molecule is 180.15 u. The model shows the molecular structure of aspirin, $C_9H_8O_4$.

Element	**Quantity**		**Average atomic mass (u)**		**Subtotal**
C	13	x	12.01	=	156.13
H	18	x	1.008	=	18.114
O	2	x	>16.00	=	32.00
Molecular Mass					206.27



Exercise 3.1.1

Acetaminophen, $C_8H_9NO_2$, is a covalent compound and the active ingredient in several popular nonprescription pain medications, such as Tylenol. What is the average molecular mass (u) for this compound?

Answer

151.16 u

3.1.1.2: Formula Mass for Ionic Compounds

Ionic compounds are composed of discrete cations and anions combined in ratios to yield electrically neutral bulk matter. The formula mass for an ionic compound is calculated in the same way as the formula mass for covalent compounds: by summing the average atomic masses of all the atoms in the compound's formula. Keep in mind, however, that the formula for an ionic compound does not represent the composition of a discrete molecule, so it may not correctly be referred to as the "molecular mass."

As an example, consider sodium chloride, NaCl, the chemical name for common table salt. Sodium chloride is an ionic compound composed of sodium cations, Na^+, and chloride anions, Cl^-, combined in a 1:1 ratio. The average formula mass for this compound is computed as 58.44 u (Figure 3.1.3).

Element	Quantity		Average atomic mass (u)		Subtotal
Na	1	x	22.99	=	22.99
Cl	1	x	35.45	=	35.45
Formula mass					58.44

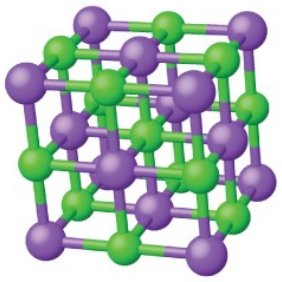


Figure 3.1.3: Table salt, NaCl, contains an array of sodium and chloride ions combined in a 1:1 ratio. Its average formula mass is 58.44 u.

Note that the average masses of neutral sodium and chlorine atoms were used in this computation, rather than the masses for sodium cations and chlorine anions. This approach is perfectly acceptable when computing the formula mass of an ionic compound. The mass of an electron at rest is 0.00055 u, so it is negligibly small with respect to the mass of an atom. For the numbers used here it does not change the least significant digit so the missing or additional electrons can be ignored. The few exceptions to this guideline are very light ions derived from elements with very precisely known atomic masses. In addition, even though a sodium cation has a slightly smaller mass than a sodium atom, this difference is offset by the increase in the mass of the chloride anion due to the extra electron.

Example 3.1.2: Computing Formula Mass for an Ionic Compound

Aluminum sulfate, $Al_2(SO_4)_3$, is an ionic compound that is used in the manufacture of paper and in various water purification processes. What is the average formula mass (u) of this compound?

Solution

The formula for this compound indicates it contains Al^{3+} and SO_4^{2-} ions combined in a 2:3 ratio. For purposes of computing an average formula mass, it is helpful to rewrite the formula in the simpler format, $Al_2S_3O_{12}$. Following the approach outlined above, the average formula mass for this compound is calculated as follows:

Element	Quantity		Average atomic mass (u)		Subtotal (u)
Al	2	x	26.98	=	53.96
S	3	x	32.06	=	96.18
O	12	x	16.00	=	192.00
				Formula mass	342.14



Exercise 3.1.2

Calcium phosphate, $Ca_3(PO_4)_2$, is an ionic compound and a common anti-caking agent added to food products. What is the average formula mass (u) of calcium phosphate?

Answer

310.18 u

3.1.2: The Mole

The identity of a substance is defined not only by the types of atoms or ions it contains, but by the quantity of each type of atom or ion. For example, water, H_2O, and hydrogen peroxide, H_2O_2, are alike in that their respective molecules are composed of hydrogen and oxygen atoms. However, because a hydrogen peroxide molecule contains two oxygen atoms, as opposed to the water molecule, which has only one, the two substances exhibit very different properties. Water is critical to staying hydrated and drinking it is healthy. Hydrogen peroxide is used to clean cuts and drinking it is a bad idea. Today, we possess sophisticated instruments that allow the direct measurement of these defining microscopic traits; however, the same traits were originally derived from the measurement of macroscopic properties (the masses and volumes of bulk quantities of matter) using relatively simple tools (balances and volumetric glassware). This experimental approach required the introduction of a new unit for amount of substances, the *mole*, which remains indispensable in modern chemical science.

The mole is an amount of substance similar to familiar units like pair, dozen, gross, etc. It provides a specific measure of *the number* of atoms or molecules in a bulk sample of matter. One Latin connotation for the word “mole” is “large mass” or “bulk,” which is consistent with its use as the name for this unit. The mole provides a link between an easily measured macroscopic property, bulk mass, and an extremely important fundamental property, number of atoms, molecules, and so forth. The sumbol for the amount of substance is *n*. Like the symbol for distance is *d*.

The unit for the amount of substance is the mole, and the symbol for the unit is mol - like the unit for distance is meter and the symbol for the unit is m. The number of entities composing a mole is defined as $6.02214076 \times 10^{23}$, a fundamental constant named **Avogadro’s number** (N_A) or the Avogadro constant in honor of Italian scientist Amedeo Avogadro. This constant is properly reported with an explicit unit of mol^{-1} or “per mole”.

Consistent with its definition as an amount unit, 1 mole of any element contains the same number of atoms as 1 mole of any other element. The masses of 1 mole of different elements, however, are different, since the masses of the individual atoms are drastically different. The molar mass is the mass in grams of 1 mole of that substance, a property expressed in units of grams per mole (g/mol). Figure 3.1.4 shows 1 mole of several different elements. Molar mass can be for an element, a molecule, or the formula for an ionic compound.

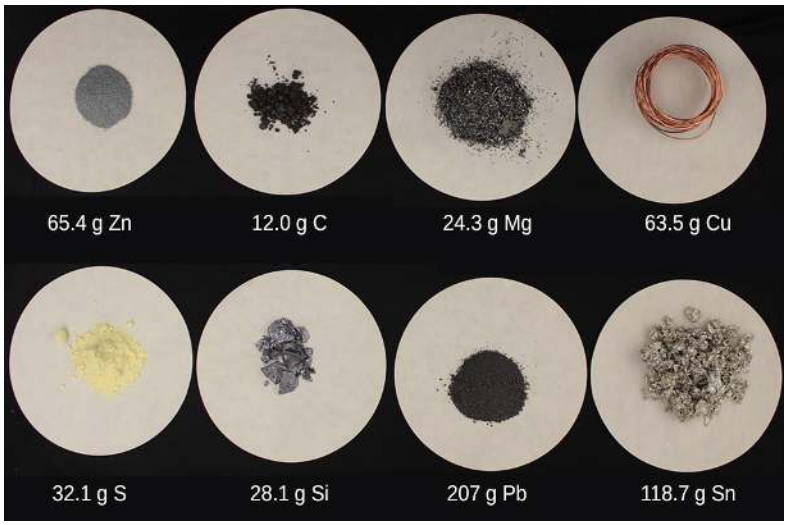


Figure 3.1.4: Each sample contains 6.02×10^{23} atoms —1.00 mol of atoms. From left to right (top row): 65.4 g zinc, 12.0 g carbon, 24.3 g magnesium, and 63.5 g copper. From left to right (bottom row): 32.1 g sulfur, 28.1 g silicon, 207 g lead, and 118.7 g tin. (credit: modification of work by Mark Ott).

The definition of the mole is historically related to the unified atomic mass unit, based on the mass of ^{12}C. As a result, the molar mass of any substance is numerically equivalent to its average average formula mass in u. Per the definition of the unified atomic mass, a single ^{12}C atom weighs 12 u (its atomic mass is 12 u). According to the definition of the mole, 12 g of ^{12}C contains 1 mole of ^{12}C atoms so its molar mass is 12 g/mol. This relationship holds for all elements, since their atomic masses are measured relative to ^{12}C. Extending this principle, the molar mass of a compound in grams is likewise numerically equivalent to its average formula mass in unified atomic mass units (Figure 3.1.5).



(Figure 3.1.5). Each sample contains 6.02×10^{23} molecules or formula units—1.00 mol of the compound or element. Clock-wise from the upper left: 130.2 g of $C_8H_{17}OH$ (1-octanol, formula mass 130.2 amu), 454.4 g of HgI_2 (mercury(II) iodide, formula mass 454.4 amu), 32.0 g of CH_3OH (methanol, formula mass 32.0 amu) and 256.5 g of S_8 (sulfur, formula mass 256.5 amu). (credit: Sahar Atwa)

Table 3.1.1: Mass of one mole of elements

Element	Average Atomic Mass (u)	Molar Mass (g/mol)	Atoms/Mole
C	12.01	12.01	6.022×10^{23}
H	1.008	1.008	6.022×10^{23}

Element	Average Atomic Mass (u)	Molar Mass (g/mol)	Atoms/Mole
O	16.00	16.00	6.022×10^{23}
Na	22.99	22.99	6.022×10^{23}
Cl	35.45	35.45	6.022×10^{23}

While average atomic mass and molar mass are numerically equivalent, keep in mind that they are vastly different in terms of scale, as represented by the vast difference in the magnitudes of their respective units (u versus g). To appreciate the enormity of the mole, consider a small drop of water after a rainfall. Although this represents just a tiny fraction of 1 mole of water (~18 g), it contains more water molecules than can be clearly imagined. If the molecules were distributed equally among the roughly seven billion people on earth, each person would receive more than 100 billion molecules.



Video 3.1.1: The mole is used in chemistry to represent 6.022×10^{23} of something, but it can be difficult to conceptualize such a large number. Watch this video and then complete the "Think" questions that follow. Explore more about the mole by reviewing the information under "Dig Deeper."

The relationships between formula mass, the mole, and Avogadro's number can be applied to compute various quantities that describe the composition of substances and compounds. For example, if we know the mass and chemical composition of a substance, we can determine the number of moles and calculate number of atoms or molecules in the sample. Likewise, if we know the number of moles of a substance, we can derive the number of atoms or molecules and calculate the substance's mass.

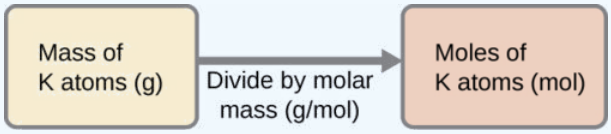
Example 3.1.3: Deriving Moles from Grams for an Element

According to nutritional guidelines from the US Department of Agriculture, the estimated average requirement for dietary potassium is 4.7 g. What is the estimated average requirement of potassium in moles?

Solution

The mass of K is provided, and the corresponding amount of K in moles is requested. Referring to the periodic table, the atomic mass of K is 39.10 u, and so its molar mass is 39.10 g/mol. The given mass of K (4.7 g) is a bit more than one-tenth the molar mass (39.10 g), so a reasonable "ballpark" estimate of the number of moles would be slightly greater than 0.1 mol.

The molar amount of a substance may be calculated by dividing its mass (g) by its molar mass (g/mol):



The factor-label method supports this mathematical approach since the unit "g" cancels and the answer has units of "mol:"

$$4.7 \ \cancel{\text{g}}\text{K}\left(\frac{\text{mol K}}{39.10 \ \cancel{\text{g}}}\right) = 0.12 \text{ mol K}$$

The calculated magnitude (0.12 mol K) is consistent with our ballpark expectation, since it is a bit greater than 0.1 mol.

Exercise 3.1.3: Beryllium

Beryllium is a light metal used to fabricate transparent X-ray windows for medical imaging instruments. How many moles of Be are in a thin-foil window weighing 3.24 g?

Answer

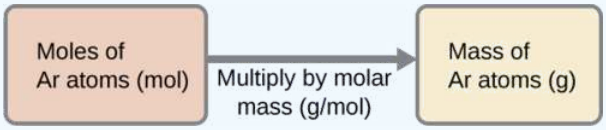
0.360 mol

Example 3.1.4: Deriving Grams from Moles for an Element

A liter of air contains 9.2×10^{-4} mol argon. What is the mass of Ar in a liter of air?

Solution

The molar amount of Ar is provided and must be used to derive the corresponding mass in grams. Since the amount of Ar is less than 1 mole, the mass will be less than the mass of 1 mole of Ar, approximately 40 g. The molar amount in question is approximately one-one thousandth (~10^{-3}) of a mole, and so the corresponding mass should be roughly one-one thousandth of the molar mass (~0.04 g):



In this case, logic dictates (and the factor-label method supports) multiplying the provided amount (mol) by the molar mass (g/mol):

$$9.2 \times 10^{-4} \ \cancel{\text{mol}}\ \text{Ar} \left(\frac{39.95\ \text{g}}{\cancel{\text{mol}}\ \text{Ar}} \right) = 0.037\ \text{g Ar}$$

The result is in agreement with our expectations, around 0.04 g Ar.

Exercise 3.1.4

What is the mass of 2.561 mol of gold?

Answer

504.4 g

Example 3.1.6: Deriving Number of Atoms from Mass for an Element

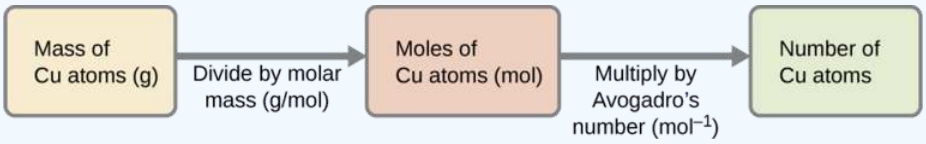
Copper is commonly used to fabricate electrical wire (Figure 3.1.6). How many copper atoms are in 5.00 g of copper wire?



Figure 3.1.6: Copper wire is composed of many, many atoms of Cu. (credit: Emilian Robert Vicol)

Solution

The number of Cu atoms in the wire may be conveniently derived from its mass by a two-step computation: first calculating the molar amount of Cu, and then using Avogadro's number (N_A) to convert this molar amount to number of Cu atoms:



Considering that the provided sample mass (5.00 g) is a little less than one-tenth the mass of 1 mole of Cu (~64 g), a reasonable estimate for the number of atoms in the sample would be on the order of one-tenth N_A, or approximately 10^{22} Cu atoms. Carrying out the two-step computation yields:

$$5.00\ \cancel{\text{g}}\ \text{Cu}\left(\frac{\cancel{\text{mol}}\ \text{Cu}}{63.55\ \cancel{\text{g}}}\right)\left(\frac{6.022\times10^{23}\ \text{atoms}}{\cancel{\text{mol}}}\right)=4.74\times10^{22}\ \text{atoms of copper} \tag{3.1.1}$$

The factor-label method yields the desired cancellation of units, and the computed result is on the order of 10^{22} as expected.

? Exercise 3.1.6

A prospector panning for gold in a river collects 15.00 g of pure gold. How many Au atoms are in this quantity of gold?

Answer

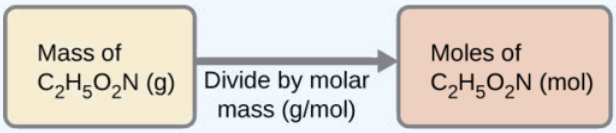
$4.586\times10^{22}\ Au$ atoms

✓ Example 3.1.7: Deriving Moles from Grams for a Compound

Our bodies synthesize protein from amino acids. One of these amino acids is glycine, which has the molecular formula $C_2H_5O_2N$. How many moles of glycine molecules are contained in 28.35 g of glycine?

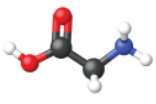
Solution

We can derive the number of moles of a compound from its mass following the same procedure we used for an element in Example 3.1.6:



The molar mass of glycine is required for this calculation, and it is computed in the same fashion as its molecular mass. One mole of glycine, $C_2H_5O_2N$, contains 2 moles of carbon, 5 moles of hydrogen, 2 moles of oxygen, and 1 mole of nitrogen:

Element	Quantity (mol element/ mol compound)		Molar mass (g/mol element)		Subtotal (g/mol compound)
C	2	×	12.01	=	24.02
H	5	×	1.008	=	5.040
O	2	×	16.00	=	32.00
N	1	×	14.007	=	14.007
Molecular mass (g/mol compound)					75.07



The provided mass of glycine (~28 g) is a bit more than one-third the molar mass (~75 g/mol), so we would expect the computed result to be a bit greater than one-third of a mole (~0.33 mol). Dividing the compound's mass by its molar mass yields:

$$28.35\ \cancel{\text{g}}\ \text{glycine}\left(\frac{\text{mol glycine}}{75.07\ \cancel{\text{g}}}\right)=0.378\ \text{mol glycine}$$

This result is consistent with our rough estimate.

Exercise 3.1.7

How many moles of sucrose, $C_{12}H_{22}O_{11}$, are in a 25-g sample of sucrose?

Answer

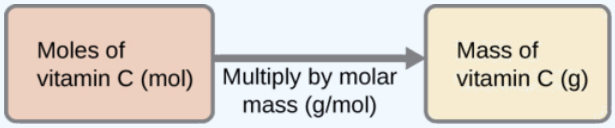
0.073 mol

Example 3.1.8: Deriving Grams from Moles for a Compound

Vitamin C is a covalent compound with the molecular formula $C_6H_8O_6$. The recommended daily dietary allowance of vitamin C for children aged 4–8 years is 1.42×10^{-4} mol. What is the mass of this allowance in grams?

Solution

As for elements, the mass of a compound can be derived from its molar amount as shown:



The molar mass for this compound is computed to be 176.124 g/mol. The given number of moles is a very small fraction of a mole (~10^{-4} or one-ten thousandth); therefore, we would expect the corresponding mass to be about one-ten thousandth of the molar mass (~0.02 g). Performing the calculation, we get:

$$1.42 \times 10^{-4} \cancel{\text{ mol}} \text{ vitamin C} \left(\frac{176.124 \text{ g}}{\cancel{\text{mol}} \text{ vitamin C}} \right) = 0.0250 \text{ g vitamin C}$$

This is consistent with the anticipated result.

Exercise 3.1.8

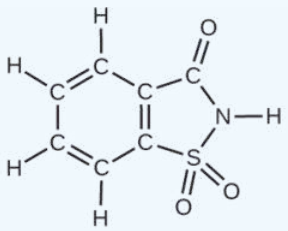
What is the mass of 0.443 mol of hydrazine, N_2H_4?

Answer

14.2 g

Example 3.1.9: Deriving the Number of Molecules from the Compound Mass

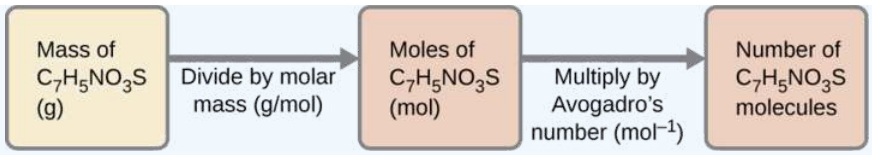
A packet of an artificial sweetener contains 40.0 mg of saccharin ($C_7H_5NO_3S$), which has the structural formula:



Given that saccharin has a molar mass of 183.18 g/mol, how many saccharin molecules are in a 40.0-mg (0.0400-g) sample of saccharin? How many carbon atoms are in the same sample?

Solution

The number of molecules in a given mass of compound is computed by first deriving the number of moles, as demonstrated in Example 3.1.8, and then multiplying by Avogadro's number:



Using the provided mass and molar mass for saccharin yields:

$$0.0400\ \cancel{\text{g}}\ \text{C}_7\text{H}_5\text{NO}_3\text{S}\left(\frac{\cancel{\text{mol}}\ \text{C}_7\text{H}_5\text{NO}_3\text{S}}{183.18\ \cancel{\text{g}}\ \text{C}_7\text{H}_5\text{NO}_3\text{S}}\right)\left(\frac{6.022\times10^{23}\ \text{C}_7\text{H}_5\text{NO}_3\text{S molecules}}{1\ \cancel{\text{mol}}\ \text{C}_7\text{H}_5\text{NO}_3\text{S}}\right) \tag{3.1.2}$$
$$= 1.31\times10^{20}\ \text{C}_7\text{H}_5\text{NO}_3\text{S molecules}$$

The compound's formula shows that each molecule contains seven carbon atoms, and so the number of C atoms in the provided sample is:

$$1.31\times10^{20}\ \text{C}_7\text{H}_5\text{NO}_3\text{S molecules}\left(\frac{7\ \text{C atoms}}{1\ \text{C}_7\text{H}_5\text{NO}_3\text{S molecule}}\right) = 9.20\times10^{21}\ \text{C atoms}$$

Exercise 3.1.9

How many C_4H_{10} molecules are contained in 9.213 g of this compound? How many hydrogen atoms?

Answer

- 9.545×10^{22} molecules C_4H_{10}
- 9.545×10^{23} atoms H

This project was preformed to supply **Libretext authors** with videos on General Chemistry topics which can be used to enhance their projects. Also, these videos are meant to act as a learning resource for **all General Chemistry students**.

Video Topics

This video shows the relation ship between grams, mols, and number of atoms of a given sample of an element. Molar mass and Avogadro's Number are used to convert between these factors.

Link to Video

Conversions Between Grams, Mol, & Atoms: https://youtu.be/rOvErpAnoCg



3.1.3: Summary

The formula mass of a substance is the sum of the average atomic masses of each atom represented in the chemical formula and is expressed in atomic mass units. The formula mass of a covalent compound is also called the molar mass. A convenient amount unit for expressing very large numbers of atoms or molecules is the mole. Experimental measurements have determined the number of entities composing 1 mole of substance to be 6.022×10^{23}, a quantity called Avogadro's number. The mass in grams of 1 mole of substance is its molar mass. Due to the use of the same reference substance in defining the atomic mass unit and the mole, the formula mass (u) and molar mass (g/mol) for any substance are numerically equivalent (for example, one H_2O molecule weighs approximately 18 u and 1 mole of H_2O molecules weighs approximately 18 g).

Glossary

Avogadro's number (N_A)
: experimentally determined value of the number of entities comprising 1 mole of substance, equal to 6.022×10^{23} mol^{-1}

formula mass
: sum of the average masses for all atoms represented in a chemical formula; for covalent compounds, this is also the molecular mass

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

molar mass
: mass in grams of 1 mole of a substance

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).
- Prof. Steven Farmer (Sonoma State University)

This page titled 3.1: Formula Mass and the Mole Concept is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

- **3.1: Formula Mass and the Mole Concept** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

3.2: Determining Empirical and Molecular Formulas

Learning Objectives

- Compute the percent composition of a compound
- Determine the empirical formula of a compound
- Determine the molecular formula of a compound

In the previous section, we discussed the relationship between the bulk mass of a substance and the number of atoms or molecules it contains (moles). Given the chemical formula of the substance, we were able to determine the amount of the substance (moles) from its mass, and vice versa. But what if the chemical formula of a substance is unknown? In this section, we will explore how to apply these very same principles in order to derive the chemical formulas of unknown substances from experimental mass measurements.

3.2.1: Percent Composition

The elemental makeup of a compound defines its chemical identity, and chemical formulas are the most succinct way of representing this elemental makeup. When a compound's formula is unknown, measuring the mass of each of its constituent elements is often the first step in the process of determining the formula experimentally. The results of these measurements permit the calculation of the compound's percent composition, defined as the percentage by mass of each element in the compound. For example, consider a gaseous compound composed solely of carbon and hydrogen. The percent composition of this compound could be represented as follows:

$$\%\mathrm{H} = \frac{\text{mass H}}{\text{mass compound}} \times 100\% \tag{3.2.1}$$

$$\%\mathrm{C} = \frac{\text{mass C}}{\text{mass compound}} \times 100\% \tag{3.2.2}$$

If analysis of a 10.0-g sample of this gas showed it to contain 2.5 g H and 7.5 g C, the percent composition would be calculated to be 25% H and 75% C:

$$\%\mathrm{H} = \frac{2.5\ \text{g H}}{10.0\ \text{g compound}} \times 100\% = 25\% \tag{3.2.3}$$

$$\%\mathrm{C} = \frac{7.5\ \text{g C}}{10.0\ \text{g compound}} \times 100\% = 75\% \tag{3.2.4}$$

Example 3.2.1: Calculation of Percent Composition

Analysis of a 12.04-g sample of a liquid compound composed of carbon, hydrogen, and nitrogen showed it to contain 7.34 g C, 1.85 g H, and 2.85 g N. What is the percent composition of this compound?

Solution

To calculate percent composition, we divide the experimentally derived mass of each element by the overall mass of the compound, and then convert to a percentage:

$$\%\mathrm{C} = \frac{7.34\ \text{g C}}{12.04\ \text{g compound}} \times 100\% = 61.0\%$$

$$\%\mathrm{H} = \frac{1.85\ \text{g H}}{12.04\ \text{g compound}} \times 100\% = 15.4\%$$

$$\%\mathrm{N} = \frac{2.85\ \text{g N}}{12.04\ \text{g compound}} \times 100\% = 23.7\%$$

The analysis results indicate that the compound is 61.0% C, 15.4% H, and 23.7% N by mass.

Exercise 3.2.1

A 24.81-g sample of a gaseous compound containing only carbon, oxygen, and chlorine is determined to contain 3.01 g C, 4.00 g O, and 17.81 g Cl. What is this compound's percent composition?

Answer

12.1% C, 16.1% O, 71.8% Cl

3.2.2: Determining Percent Composition from Formula Mass

Percent composition is also useful for evaluating the relative abundance of a given element in different compounds of known formulas. As one example, consider the common nitrogen-containing fertilizers ammonia (NH_3), ammonium nitrate (NH_4NO_3), and urea (CH_4N_2O). The element nitrogen is the active ingredient for agricultural purposes, so the mass percentage of nitrogen in the compound is a practical and economic concern for consumers choosing among these fertilizers. For these sorts of applications, the percent composition of a compound is easily derived from its average formula mass and the average atomic masses of its constituent elements. A molecule of NH_3 contains one N atom weighing 14.01 u and three H atoms weighing a total of (3 × 1.008 u) = 3.024 u. The average formula mass of ammonia is therefore (14.01 u+ 3.024 u) = 17.03 u, and its percent composition is:

$$\%\mathrm{N} = \frac{14.01\ \mathrm{u\ N}}{17.03\ \mathrm{u\ NH_3}} \times 100\% = 82.27\% \tag{3.2.5}$$

$$\%\mathrm{H} = \frac{3.024\ \mathrm{u\ H}}{17.03\ \mathrm{u\ NH_3}} \times 100\% = 17.76\% \tag{3.2.6}$$

This same approach may be taken considering a pair of molecules, a dozen molecules, or a mole of molecules, etc. The latter amount is most convenient and would simply involve the use of molar masses instead of atomic and formula masses, as demonstrated Example 3.2.2. As long as we know the chemical formula of the substance in question, we can easily derive percent composition from the formula mass or molar mass.

Example 3.2.2: Determining Percent Composition from a Molecular Formula

Aspirin is a compound with the molecular formula $C_9H_8O_4$. What is its percent composition?

Solution

To calculate the percent composition, we need to know the masses of C, H, and O in a known mass of $C_9H_8O_4$. It is convenient to consider 1 mol of $C_9H_8O_4$ and use its molar mass (180.159 g/mole, determined from the chemical formula) to calculate the percentages of each of its elements:

$$\%\mathrm{C} = \frac{9\ \mathrm{mol\ C} \times \mathrm{molar\ mass\ C}}{\mathrm{molar\ mass\ C_9H_{18}O_4}} \times 100 = \frac{9 \times 12.01\ \mathrm{g/mol}}{180.159\ \mathrm{g/mol}} \times 100 = \frac{108.09\ \mathrm{g/mol}}{180.159\ \mathrm{g/mol}} \times 100$$

$$\%\mathrm{C} = 60.00\,\%\,\mathrm{C}$$

$$\%\mathrm{H} = \frac{8\ \mathrm{mol\ H} \times \mathrm{molar\ mass\ H}}{\mathrm{molar\ mass\ C_9H_{18}O_4}} \times 100 = \frac{8 \times 1.008\ \mathrm{g/mol}}{180.159\ \mathrm{g/mol}} \times 100 = \frac{8.064\ \mathrm{g/mol}}{180.159\ \mathrm{g/mol}} \times 100$$

$$\%\mathrm{H} = 4.476\,\%\,\mathrm{H}$$

$$\%\mathrm{O} = \frac{4\ \mathrm{mol\ O} \times \mathrm{molar\ mass\ O}}{\mathrm{molar\ mass\ C_9H_{18}O_4}} \times 100 = \frac{4 \times 16.00\ \mathrm{g/mol}}{180.159\ \mathrm{g/mol}} \times 100 = \frac{64.00\ \mathrm{g/mol}}{180.159\ \mathrm{g/mol}} \times 100$$

$$\%\mathrm{O} = 35.52\%$$

Note that these percentages sum to equal 100.00% when appropriately rounded.

Exercise 3.2.2

To three significant digits, what is the mass percentage of iron in the compound Fe_2O_3?

Answer

69.9% Fe

3.2.3: Determination of Empirical Formulas

As previously mentioned, the most common approach to determining a compound's chemical formula is to first measure the masses of its constituent elements. However, we must keep in mind that chemical formulas represent the relative *numbers*, not masses, of atoms in the substance. Therefore, any experimentally derived data involving mass must be used to derive the corresponding numbers of atoms in the compound. To accomplish this, we can use molar masses to convert the mass of each element to a number of moles. We then consider the moles of each element relative to each other, converting these numbers into a whole-number ratio that can be used to derive the empirical formula of the substance. Consider a sample of compound determined to contain 1.71 g C and 0.287 g H. The corresponding numbers of atoms (in moles) are:

$$1.71 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 0.142 \text{ mol C} \tag{3.2.7}$$

$$0.287 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 0.284 \text{ mol H} \tag{3.2.8}$$

Thus, we can accurately represent this compound with the formula $C_{0.142}H_{0.284}$. Of course, per accepted convention, formulas contain whole-number subscripts, which can be achieved by dividing each subscript by the smaller subscript:

$$\text{C}_{\frac{0.142}{0.142}}\ \text{H}_{\frac{0.284}{0.142}}\ \text{or}\ \text{CH}_2 \tag{3.2.9}$$

(Recall that subscripts of "1" are not written, but rather assumed if no other number is present.)

The empirical formula for this compound is thus CH_2. This may or not be the compound's *molecular formula* as well; however, we would need additional information to make that determination (as discussed later in this section).

Consider as another example a sample of compound determined to contain 5.31 g Cl and 8.40 g O. Following the same approach yields a tentative empirical formula of:

$$\text{Cl}_{0.150}\text{O}_{0.525} = \text{Cl}_{\frac{0.150}{0.150}}\ \text{O}_{\frac{0.525}{0.150}} = \text{ClO}_{3.5} \tag{3.2.10}$$

In this case, dividing by the smallest subscript still leaves us with a decimal subscript in the empirical formula. To convert this into a whole number, we must multiply each of the subscripts by two, retaining the same atom ratio and yielding Cl_2O_7 as the final empirical formula.

Procedure

In summary, empirical formulas are derived from experimentally measured element masses by:

1. Deriving the number of moles of each element from its mass
2. Dividing each element's molar amount by the smallest molar amount to yield subscripts for a tentative empirical formula
3. Multiplying all coefficients by an integer, if necessary, to ensure that the smallest whole-number ratio of subscripts is obtained

Figure 3.2.1 outlines this procedure in flow chart fashion for a substance containing elements A and X.

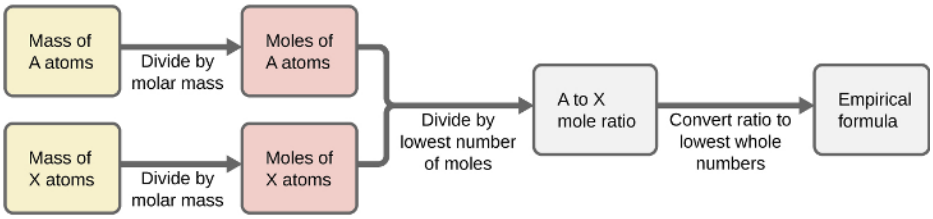


Figure 3.2.1: The empirical formula of a compound can be derived from the masses of all elements in the sample.

Example 3.2.3: Determining an Empirical Formula from Masses of Elements

A sample of the black mineral hematite (Figure 3.2.2), an oxide of iron found in many iron ores, contains 34.97 g of iron and 15.03 g of oxygen. What is the empirical formula of hematite?



Figure 3.2.2: Hematite is an iron oxide that is used in jewelry. (credit: Mauro Cateb)

Solution

For this problem, we are given the mass in grams of each element. Begin by finding the moles of each:

$$34.97 \text{ g Fe} \left(\frac{\text{mol Fe}}{55.85 \text{ g}} \right) = 0.6261 \text{ mol Fe}$$

$$15.03 \text{ g O} \left(\frac{\text{mol O}}{16.00 \text{ g}} \right) = 0.9394 \text{ mol O}$$

Next, derive the iron-to-oxygen molar ratio by dividing by the lesser number of moles:

$$\frac{0.6261}{0.6261} = 1.000 \text{ mol Fe}$$

$$\frac{0.9394}{0.6261} = 1.500 \text{ mol O}$$

The ratio is 1.000 mol of iron to 1.500 mol of oxygen ($Fe_1O_{1.5}$). Finally, multiply the ratio by two to get the smallest possible whole number subscripts while still maintaining the correct iron-to-oxygen ratio:

$$2(Fe_1O_{1.5}) = Fe_2O_3$$

The empirical formula is Fe_2O_3.

Exercise 3.2.3

What is the empirical formula of a compound if a sample contains 0.130 g of nitrogen and 0.370 g of oxygen?

Answer

N_2O_5



***Video* 3.2.1** *: Additional worked examples illustrating the derivation of empirical formulas are presented in the brief video clip.*

3.2.4: Summary

The chemical identity of a substance is defined by the types and relative numbers of atoms composing its fundamental entities (molecules in the case of covalent compounds, ions in the case of ionic compounds). A compound's percent composition provides the mass percentage of each element in the compound, and it is often experimentally determined and used to derive the compound's empirical formula. The empirical formula mass of a covalent compound may be compared to the compound's molecular or molar mass to derive a molecular formula.

3.2.5: Key Equations

- $\%\mathrm{X} = \dfrac{\text{mass X}}{\text{mass compound}} \times 100\%$
- $\dfrac{\text{molecular or molar mass}\left(\text{u or } \dfrac{\text{g}}{\text{mol}}\right)}{\text{empirical formula mass}\left(\text{u or } \dfrac{\text{g}}{\text{mol}}\right)} = n\,\text{formula units/molecule}$
- $(\mathrm{A_xB_y})_n = \mathrm{A_{nx}B_{ny}}$

Glossary

percent composition

percentage by mass of the various elements in a compound

empirical formula mass

sum of average atomic masses for all atoms represented in an empirical formula

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 3.2: Determining Empirical and Molecular Formulas is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

- **3.2: Determining Empirical and Molecular Formulas** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

3.3: Percent Composition and Molecular Formula

Deriving Empirical Formulas from Percent Composition

Finally, with regard to deriving empirical formulas, consider instances in which a compound's percent composition is available rather than the absolute masses of the compound's constituent elements. In such cases, the percent composition can be used to calculate the masses of elements present in any convenient mass of compound; these masses can then be used to derive the empirical formula in the usual fashion.

Example 3.3.4: Determining an Empirical Formula from Percent Composition

The bacterial fermentation of grain to produce ethanol forms a gas with a percent composition of 27.29% C and 72.71% O (Figure 3.3.3). What is the empirical formula for this gas?



Figure 3.3.3: An oxide of carbon is removed from these fermentation tanks through the large copper pipes at the top. (credit: "Dual Freq"/Wikimedia Commons)

Solution

Since the scale for percentages is 100, it is most convenient to calculate the mass of elements present in a sample weighing 100 g. The calculation is "most convenient" because, per the definition for percent composition, the mass of a given element in grams is numerically equivalent to the element's mass percentage. This numerical equivalence results from the definition of the "percentage" unit, whose name is derived from the Latin phrase *per centum* meaning "by the hundred." Considering this definition, the mass percentages provided may be more conveniently expressed as fractions:

$$27.29\,\%\,\mathrm{C} = \frac{27.29\ \mathrm{g\ C}}{100\ \mathrm{g\ compound}}$$

$$72.71\,\%\,\mathrm{O} = \frac{72.71\ \mathrm{g\ O}}{100\ \mathrm{g\ compound}}$$

The molar amounts of carbon and hydrogen in a 100-g sample are calculated by dividing each element's mass by its molar mass:

$$27.29\ \mathrm{g\ C}\left(\frac{\mathrm{mol\ C}}{12.01\ \mathrm{g}}\right) = 2.272\ \mathrm{mol\ C}$$

$$72.71\ \mathrm{g\ O}\left(\frac{\mathrm{mol\ O}}{16.00\ \mathrm{g}}\right) = 4.544\ \mathrm{mol\ O}$$

Coefficients for the tentative empirical formula are derived by dividing each molar amount by the lesser of the two:

$$\frac{2.272\ \mathrm{mol\ C}}{2.272} = 1$$

$$\frac{4.544\ \mathrm{mol\ O}}{2.272} = 2$$

Since the resulting ratio is one carbon to two oxygen atoms, the empirical formula is CO_2.

Exercise 3.3.4

What is the empirical formula of a compound containing 40.0% C, 6.71% H, and 53.28% O?

Answer

CH_2O

Derivation of Molecular Formulas

Recall that empirical formulas are symbols representing the *relative* numbers of a compound's elements. Determining the *absolute* numbers of atoms that compose a single molecule of a covalent compound requires knowledge of both its empirical formula and its molecular mass or molar mass. These quantities may be determined experimentally by various measurement techniques. Molar mass, for example, is often derived from the mass spectrum of the compound (see discussion of this technique in the previous chapter on atoms and molecules). Molar mass can be measured by a number of experimental methods, many of which will be introduced in later chapters of this text.

Molecular formulas are derived by comparing the compound's molecular or molar mass to its empirical formula mass. As the name suggests, an empirical formula mass is the sum of the average atomic masses of all the atoms represented in an empirical formula. If we know the molar mass of the substance, we can divide this by the empirical formula mass in order to identify the number of empirical formula units per molecule, which we designate as *n*:

$$\frac{\text{molecular or molar mass}\left(\text{u or }\frac{\text{g}}{\text{mol}}\right)}{\text{empirical formula mass}\left(\text{u or }\frac{\text{g}}{\text{mol}}\right)} = n\,\text{formula units/molecule} \tag{3.3.1}$$

The molecular formula is then obtained by multiplying each subscript in the empirical formula by *n*, as shown by the generic empirical formula A_xB_y:

$$(\mathrm{A_xB_y})_\mathrm{n} = \mathrm{A_{nx}B_{nx}} \tag{3.3.2}$$

For example, consider a covalent compound whose empirical formula is determined to be CH_2O. The averge empirical formula mass for this compound is approximately 30 u (the sum of 12 u for one C atom, 2 u for two H atoms, and 16 u for one O atom). If the compound's molecular mass is determined to be 180 u, this indicates that molecules of this compound contain six times the number of atoms represented in the empirical formula:

$$\frac{180\ \text{u/molecule}}{30\ \frac{\text{u}}{\text{formula unit}}} = 6\ \text{formula units/molecule} \tag{3.3.3}$$

Molecules of this compound are then represented by molecular formulas whose subscripts are six times greater than those in the empirical formula:

$$(\mathrm{CH_2O})_6 = \mathrm{C_6H_{12}O_6} \tag{3.3.4}$$

Note that this same approach may be used when the molar mass (g/mol) instead of the average molecular mass (u) is used. In this case, we are merely considering one mole of empirical formula units and molecules, as opposed to single units and molecules.

Example 3.3.5: Determination of the Molecular Formula for Nicotine

Nicotine, an alkaloid in the nightshade family of plants that is mainly responsible for the addictive nature of cigarettes, contains 74.02% C, 8.710% H, and 17.27% N. If 40.57 g of nicotine contains 0.2500 mol nicotine, what is the molecular formula?

Solution

Determining the molecular formula from the provided data will require comparison of the compound's empirical formula mass to its molar mass. As the first step, use the percent composition to derive the compound's empirical formula. Assuming a convenient, a 100-g sample of nicotine yields the following molar amounts of its elements:

$$(74.02\ \text{g C})\left(\frac{1\ \text{mol C}}{12.01\ \text{g C}}\right) = 6.163\ \text{mol C} \tag{3.3.5}$$

$$(8.710\ \text{g H})\left(\frac{1\ \text{mol H}}{1.01\ \text{g H}}\right) = 8.624\ \text{mol H} \tag{3.3.6}$$

$$(17.27\ \text{g N})\left(\frac{1\ \text{mol N}}{14.01\ \text{g N}}\right) = 1.233\ \text{mol N} \tag{3.3.7}$$

Next, we calculate the molar ratios of these elements relative to the least abundant element, N.

$$6.163\ \text{mol C}/\ 1.233\ \text{mol N} = 5$$

$$8.264\ \text{mol H}/\ 1.233\ \text{mol N} = 7$$

$$1.233\ \text{mol N}/\ 1.233\ \text{mol N} = 1$$

$$1.233/1.233 = 1.000\ \text{mol N}$$

$$6.163/1.233 = 4.998\ \text{mol C}$$

$$8.624/1.233 = 6.994\ \text{mol H}$$

The C-to-N and H-to-N molar ratios are adequately close to whole numbers, and so the empirical formula is C_5H_7N. The empirical formula mass for this compound is therefore 81.13 u/formula unit, or 81.13 g/mol formula unit.

We calculate the molar mass for nicotine from the given mass and molar amount of compound:

$$\frac{40.57\ \text{g nicotine}}{0.2500\ \text{mol nicotine}} = \frac{162.3\ \text{g}}{\text{mol}}$$

Comparing the molar mass and empirical formula mass indicates that each nicotine molecule contains two formula units:

$$\frac{162.3\ \text{g/mol}}{81.13\ \dfrac{\text{g}}{\text{formula unit}}} = 2\ \text{formula units/molecule}$$

Thus, we can derive the molecular formula for nicotine from the empirical formula by multiplying each subscript by two:

$$(C_5H_7N)_2 = C_{10}H_{14}N_2$$

? Exercise 3.3.5

What is the molecular formula of a compound with a percent composition of 49.47% C, 5.201% H, 28.84% N, and 16.48% O, and an average molecular mass of 194.2 u?

Answer

$C_8H_{10}N_4O_2$

Summary

The chemical identity of a substance is defined by the types and relative numbers of atoms composing its fundamental entities (molecules in the case of covalent compounds, ions in the case of ionic compounds). A compound's percent composition provides the mass percentage of each element in the compound, and it is often experimentally determined and used to derive the compound's empirical formula. The empirical formula mass of a covalent compound may be compared to the compound's molecular or molar mass to derive a molecular formula.

Key Equations

- $\%\text{X} = \dfrac{\text{mass X}}{\text{mass compound}} \times 100\%$
- $\dfrac{\text{molecular or molar mass}\left(\text{u or } \dfrac{\text{g}}{\text{mol}}\right)}{\text{empirical formula mass}\left(\text{u or } \dfrac{\text{g}}{\text{mol}}\right)} = n\,\text{formula units/molecule}$
- $(A_xB_y)_n = A_{nx}B_{ny}$

Glossary

percent composition

percentage by mass of the various elements in a compound

empirical formula mass

sum of average atomic masses for all atoms represented in an empirical formula

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).

3.3: Percent Composition and Molecular Formula is shared under a CC BY license and was authored, remixed, and/or curated by LibreTexts.

- **3.2: Determining Empirical and Molecular Formulas** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

3.4: Molarity

Learning Objectives

- Describe the fundamental properties of solutions
- Calculate solution concentrations using molarity
- Perform dilution calculations using the dilution equation

In preceding sections, we focused on the composition of substances: samples of matter that contain only one type of element or compound. However, mixtures—samples of matter containing two or more substances physically combined—are more commonly encountered in nature than are pure substances. Similar to a pure substance, the relative composition of a mixture plays an important role in determining its properties. The relative amount of oxygen in a planet's atmosphere determines its ability to sustain aerobic life. The relative amounts of iron, carbon, nickel, and other elements in steel (a mixture known as an "alloy") determine its physical strength and resistance to corrosion. The relative amount of the active ingredient in a medicine determines its effectiveness in achieving the desired pharmacological effect. The relative amount of sugar in a beverage determines its sweetness (Figure 3.4.1). In this section, we will describe one of the most common ways in which the relative compositions of mixtures may be quantified.



Figure 3.4.1: Sugar is one of many components in the complex mixture known as coffee. The amount of sugar in a given amount of coffee is an important determinant of the beverage's sweetness. (credit: Jane Whitney)

3.4.1: Solutions

We have previously defined solutions as homogeneous mixtures, meaning that the composition of the mixture (and therefore its properties) is uniform throughout its entire volume. The relative amount of a given solution component is known as its concentration. Often, though not always, a solution contains one component with a concentration that is significantly greater than that of all other components. This component is called the solvent and may be viewed as the medium in which the other components are dispersed, or dissolved. Solutions in which water is the solvent are, of course, very common on our planet. A solution in which water is the solvent is called an aqueous solution.

A solute is a component of a solution that is typically present at a much lower concentration than the solvent. Solute concentrations are often described with qualitative terms such as dilute (of relatively low concentration) and concentrated (of relatively high concentration).

Concentrations may be quantitatively assessed using a wide variety of measurement units, each convenient for particular applications. Molarity (M) is a useful concentration unit for many applications in chemistry. Molarity is defined as the number of moles of solute in exactly 1 liter (1 L) of the solution:

$$M = \frac{\text{mol solute}}{\text{L solution}} \tag{3.4.1}$$

3.4.1.1: Calculating Molarity

Example 3.4.1: Calculating Molar Concentrations

A 355-mL soft drink sample contains 0.133 mol of sucrose (table sugar). What is the molar concentration of sucrose in the beverage?

Solution

Since the molar amount of solute and the volume of solution are both given, the molarity can be calculated using the definition of molarity. Per this definition, the solution volume must be converted from mL to L:

$$\begin{aligned} M &= \frac{mol\ solute}{L\ solution} \\ &= \frac{0.133\ mol}{355\ mL \times \dfrac{1\ L}{1000\ mL}} \\ &= 0.375\ M \end{aligned}$$

Exercise 3.4.1

A teaspoon of table sugar contains about 0.01 mol sucrose. What is the molarity of sucrose if a teaspoon of sugar has been dissolved in a cup of tea with a volume of 200 mL?

Answer

0.05 M

3.4.1.2: Calculating Moles

Example 3.4.2: Deriving Moles and Volumes from Molar Concentrations

How much sugar (mol) is contained in a modest sip (~10 mL) of the soft drink from Example 3.4.1?

Solution

In this case, we can rearrange the definition of molarity to isolate the quantity sought, moles of sugar. We then substitute the value for molarity that we derived in Example 3.4.2, 0.375 *M*:

$$M = \frac{\text{mol solute}}{\text{L solution}}$$

$$\text{mol solute} = \text{M} \times \text{L solution}$$

$$\text{mol solute} = 0.375\ \frac{\text{mol sugar}}{\text{L}} \times \left(10\ \text{mL} \times \frac{1\ \text{L}}{1000\ \text{mL}}\right) \qquad = 0.004\ \text{mol sugar}$$

Exercise 3.4.2

What volume (mL) of the sweetened tea described in Example 3.4.1 contains the same amount of sugar (mol) as 10 mL of the soft drink in this example?

Answer

80 mL

3.4.1.3: Calculating molarity from mass

Example 3.4.3: Calculating Molar Concentrations from the Mass of Solute

Distilled white vinegar (Figure 3.4.2) is a solution of acetic acid, CH_3CO_2H, in water. A 0.500-L vinegar solution contains 25.2 g of acetic acid. What is the concentration of the acetic acid solution in units of molarity?



Figure 3.4.3: Distilled white vinegar is a solution of acetic acid in water.

Solution

As in previous examples, the definition of molarity is the primary equation used to calculate the quantity sought. In this case, the mass of solute is provided instead of its molar amount, so we must use the solute's molar mass to obtain the amount of solute in moles:

$$M = \frac{\text{mol solute}}{\text{L solution}} = \frac{25.2\ \text{g}\ \text{CH}_3\text{CO}_2\text{H} \times \dfrac{1\ \text{mol}\ \text{CH}_3\text{CO}_2\text{H}}{60.052\ \text{g}\ \text{CH}_3\text{CO}_2\text{H}}}{0.500\ \text{L solution}} = 0.839\ M$$

$$M = \frac{0.839\ \text{mol solute}}{1.00\ \text{L solution}}$$

Exercise 3.4.3

Calculate the molarity of 6.52 g of $CoCl_2$ (128.9 g/mol) dissolved in an aqueous solution with a total volume of 75.0 mL.

Answer

0.674 M

3.4.1.4: Calculating mass from molarity

Example 3.4.4: Determining the Mass of Solute in a Given Volume of Solution

How many grams of NaCl are contained in 0.250 L of a 5.30-*M* solution?

Solution

The volume and molarity of the solution are specified, so the amount (mol) of solute is easily computed as demonstrated in Example 3.4.3:

$$M = \frac{\text{mol solute}}{\text{L solution}} \tag{3.4.2}$$

$$\text{mol solute} = M \times \text{L solution} \tag{3.4.3}$$

$$\text{mol solute} = 5.30\ \frac{\text{mol NaCl}}{\text{L}} \times 0.250\ \text{L} = 1.325\ \text{mol NaCl} \tag{3.4.4}$$

Finally, this molar amount is used to derive the mass of NaCl:

$$1.325 \text{ mol NaCl} \times \frac{58.44 \text{ g NaCl}}{\text{mol NaCl}} = 77.4 \text{ g NaCl} \tag{3.4.5}$$

Exercise 3.4.4

How many grams of $CaCl_2$ (110.98 g/mol) are contained in 250.0 mL of a 0.200-M solution of calcium chloride?

Answer

5.55 g $CaCl_2$

When performing calculations stepwise, as in Example 3.4.3, it is important to refrain from rounding any intermediate calculation results, which can lead to rounding errors in the final result. In Example 3.4.4, the molar amount of NaCl computed in the first step, 1.325 mol, would be properly rounded to 1.32 mol if it were to be reported; however, although the last digit (5) is not significant, it must be retained as a guard digit in the intermediate calculation. If we had not retained this guard digit, the final calculation for the mass of NaCl would have been 77.1 g, a difference of 0.3 g.

In addition to retaining a guard digit for intermediate calculations, we can also avoid rounding errors by performing computations in a single step (Example 3.4.5). This eliminates intermediate steps so that only the final result is rounded.

3.4.1.5: Calculating volume

Example 3.4.5: Determining the Volume of Solution

In Example 3.4.3, we found the typical concentration of vinegar to be 0.839 *M*. What volume of vinegar contains 75.6 g of acetic acid?

Solution

First, use the molar mass to calculate moles of acetic acid from the given mass:

$$\text{g solute} \times \frac{\text{mol solute}}{\text{g solute}} = \text{mol solute} \tag{3.4.6}$$

Then, use the molarity of the solution to calculate the volume of solution containing this molar amount of solute:

$$\text{mol solute} \times \frac{\text{L solution}}{\text{mol solute}} = \text{L solution} \tag{3.4.7}$$

Combining these two steps into one yields:

$$\text{g solute} \times \frac{\text{mol solute}}{\text{g solute}} \times \frac{\text{L solution}}{\text{mol solute}} = \text{L solution} \tag{3.4.8}$$

$$75.6 \text{ g } CH_3CO_2H \left(\frac{\text{mol } CH_3CO_2H}{60.05 \text{ g}}\right)\left(\frac{\text{L solution}}{0.839 \text{ mol } CH_3CO_2H}\right) = 1.50 \text{ L solution} \tag{3.4.9}$$

Exercise 3.4.5:

What volume of a 1.50-M KBr solution contains 66.0 g KBr?

Answer

0.370 L

3.4.1.6: Video



Calculations Involving Molarity (M): https://youtu.be/TVTCvKoSR-Q

3.4.2: Dilution of Solutions

Dilution is the process whereby the concentration of a solution is lessened by the addition of solvent. For example, we might say that a glass of iced tea becomes increasingly diluted as the ice melts. The water from the melting ice increases the volume of the solvent (water) and the overall volume of the solution (iced tea), thereby reducing the relative concentrations of the solutes that give the beverage its taste (Figure 3.4.2).

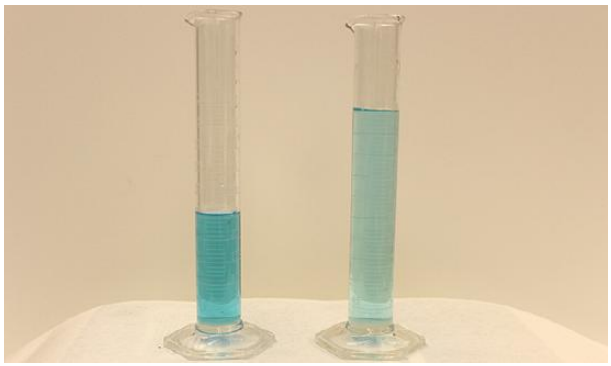


Figure 3.4.2: Both solutions contain the same mass of copper nitrate. The solution on the right is more dilute because the copper nitrate is dissolved in more solvent. (credit: Mark Ott).

Dilution is also a common means of preparing solutions of a desired concentration. By adding solvent to a measured portion of a more concentrated *stock solution*, we can achieve a particular concentration. For example, commercial pesticides are typically sold as solutions in which the active ingredients are far more concentrated than is appropriate for their application. Before they can be used on crops, the pesticides must be diluted. This is also a very common practice for the preparation of a number of common laboratory reagents (Figure 3.4.3).



Figure 3.4.3: A solution of $KMnO_4$ is prepared by mixing water with 4.74 g of KMnO4 in a flask. (credit: modification of work by Mark Ott)

A simple mathematical relationship can be used to relate the volumes and concentrations of a solution before and after the dilution process. According to the definition of molarity, the molar amount of solute in a solution is equal to the product of the solution's molarity and its volume in liters:

$$n = ML \tag{3.4.10}$$

Expressions like these may be written for a solution before and after it is diluted:

$$n_1 = M_1 L_1 \tag{3.4.11}$$

$$n_2 = M_2 L_2 \tag{3.4.12}$$

where the subscripts "1" and "2" refer to the solution before and after the dilution, respectively. Since the dilution process *does not change the amount of solute in the solution*, $n_1 = n_2$. Thus, these two equations may be set equal to one another:

$$M_1 L_1 = M_2 L_2 \tag{3.4.13}$$

This relation is commonly referred to as the dilution equation. Although we derived this equation using molarity as the unit of concentration and liters as the unit of volume, other units of concentration and volume may be used, so long as the units properly cancel per the factor-label method. Reflecting this versatility, the dilution equation is often written in the more general form:

$$C_1 V_1 = C_2 V_2 \tag{3.4.14}$$

where C and V are concentration and volume, respectively.

3.4.2.1: Dilution Calculations: molarity

Example 3.4.6: Determining the Concentration of a Diluted Solution

If 0.850 L of a 5.00-*M* solution of copper nitrate, $Cu(NO_3)_2$, is diluted to a volume of 1.80 L by the addition of water, what is the molarity of the diluted solution?

Solution

We are given the volume and concentration of a stock solution, V_1 and C_1, and the volume of the resultant diluted solution, V_2. We need to find the concentration of the diluted solution, C_2. We thus rearrange the dilution equation in order to isolate C_2:

$$C_1 V_1 = C_2 V_2$$

$$C_2 = \frac{C_1 V_1}{V_2}$$

Since the stock solution is being diluted by more than two-fold (volume is increased from 0.85 L to 1.80 L), we would expect the diluted solution's concentration to be less than one-half 5 *M*. We will compare this ballpark estimate to the calculated result to check for any gross errors in computation (for example, such as an improper substitution of the given quantities). Substituting the given values for the terms on the right side of this equation yields:

$$C_2 = \frac{0.850\ \text{L} \times 5.00\ \dfrac{\text{mol}}{\text{L}}}{1.80\ \text{L}} = 2.36\ M$$

This result compares well to our ballpark estimate (it's a bit less than one-half the stock concentration, 5 *M*).

Exercise 3.4.6

What is the concentration of the solution that results from diluting 25.0 mL of a 2.04-M solution of CH_3OH to 500.0 mL?

Answer

0.102 M CH_3OH

3.4.2.2: Dilution Calcuations: Volume

Example 3.4.7: Volume of a Diluted Solution

What volume of 0.12 *M* HBr can be prepared from 11 mL (0.011 L) of 0.45 *M* HBr?

Solution

We are given the volume and concentration of a stock solution, V_1 and C_1, and the concentration of the resultant diluted solution, C_2. We need to find the volume of the diluted solution, V_2. We thus rearrange the dilution equation in order to isolate V_2:

$$C_1V_1 = C_2V_2$$

$$V_2 = \frac{C_1V_1}{C_2}$$

Since the diluted concentration (0.12 *M*) is slightly more than one-fourth the original concentration (0.45 *M*), we would expect the volume of the diluted solution to be roughly four times the original volume, or around 44 mL. Substituting the given values and solving for the unknown volume yields:

$$V_2 = \frac{(0.45\ M)(0.011\ \text{L})}{(0.12\ M)}$$

$$V_2 = 0.041\ \text{L}$$

The volume of the 0.12-*M* solution is 0.041 L (41 mL). The result is reasonable and compares well with our rough estimate.

Exercise 3.4.7

A laboratory experiment calls for 0.125 M HNO_3. What volume of 0.125 M HNO_3 can be prepared from 0.250 L of 1.88 M HNO_3?

Answer

3.76 L

3.4.2.3: Dilution Calculations: Design

Example 3.4.8: Volume of a Concentrated Solution Needed for Dilution

What volume of 1.59 *M* KOH is required to prepare 5.00 L of 0.100 *M* KOH?

Solution

We are given the concentration of a stock solution, C_1, and the volume and concentration of the resultant diluted solution, V_2 and C_2. We need to find the volume of the stock solution, V_1. We thus rearrange the dilution equation in order to isolate V_1:

$$C_1V_1 = C_2V_2$$

$$V_1 = \frac{C_2V_2}{C_1}$$

Since the concentration of the diluted solution 0.100 *M* is roughly one-sixteenth that of the stock solution (1.59 *M*), we would expect the volume of the stock solution to be about one-sixteenth that of the diluted solution, or around 0.3 liters. Substituting the given values and solving for the unknown volume yields:

$$V_1 = \frac{(0.100\ M)(5.00\ \text{L})}{1.59\ M}$$

$$V_1 = 0.314\ \text{L}$$

Thus, we would need 0.314 L of the 1.59-*M* solution to prepare the desired solution. This result is consistent with our rough estimate.

? Exercise 3.4.8

What volume of a 0.575-M solution of glucose, $C_6H_{12}O_6$, can be prepared from 50.00 mL of a 3.00-M glucose solution?

Answer

0.261 L

3.4.2.4: Video



Calculations Involving Dilution: https://youtu.be/Yq3cNk29_Ao

3.4.3: Summary

Solutions are homogeneous mixtures. Many solutions contain one component, called the solvent, in which other components, called solutes, are dissolved. An aqueous solution is one for which the solvent is water. The concentration of a solution is a measure of the relative amount of solute in a given amount of solution. Concentrations may be measured using various units, with one very useful unit being molarity, defined as the number of moles of solute per liter of solution. The solute concentration of a solution may be decreased by adding solvent, a process referred to as dilution. The dilution equation is a simple relation between concentrations and volumes of a solution before and after dilution.

3.4.4: Key Equations

- $M = \frac{\text{mol solute}}{\text{L solution}}$
- $C_1V_1 = C_2V_2$

Glossary

aqueous solution
solution for which water is the solvent

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

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

dissolved

describes the process by which solute components are dispersed in a solvent

molarity (*M*)

unit of concentration, defined as the number of moles of solute dissolved in 1 liter of solution

solute

solution component present in a concentration less than that of the solvent

solvent

solution component present in a concentration that is higher relative to other components

---

This page titled 3.4: Molarity is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

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

3.E: Composition of Substances and Solutions- Homework

3.E.1: For Chapter 3 you MUST know:

- The additional polyatomic ions: cyanide (CN^-), nitrite (NO_2^-), and sulfite (SO_3^{2-}).

3.E.2: Turn in your answers for the following questions - show your work

1. For the following molecules; write the chemical formula, determine the molecular weight and determine the number of moles in exactly 1 gram.
    a. carbon dioxide
    b. iron (II) chloride
    c. dinitrogen pentoxide
    d. iron (III) sulfate
2. Name the following compounds, determine the molecular weight and determine how many moles in 8.35 grams of the compound.
    a. KI
    b. CaF_2
    c. Cu_2SO_4
    d. N_2O
    e. LiOH
3. Give the chemical formula (or atomic symbol), molecular (or atomic) weight, and charge for the following ions:
    a. sulfate
    b. sulfite
    c. nitrate
    d. chloride
    e. nitride
    f. acetate
    g. carbonate
4. Calculate the number of moles in:
    a. 45.3594 g of Ne
    b. 0.198669 g of Ne
5. Calculate the mass of:
    a. 2.00 mole of Fe
    b. 4.362×10^{-5} mol of Fe
6. Describe how to prepare 250 mL of 0.12 M lithium chloride solution from solid lithium chloride.
7. Describe how to prepare 100 mL of 0.012 M lithium chloride solution from a 0.12 M lithium chloride solution.

3.E.3: The Following Questions are for your practice - Do Not Turn In. They include answers so you can check your work

3.E.3.1: 3.1: Formula Mass and the Mole Concept

1. What is the total mass (amu) of carbon in each of the following molecules?
    a. CH_4
    b. $C_{12}H_{10}O_6$

    (a)

    12.01 amu

    (b)

    144.12 amu

2. Calculate the molecular or formula mass of each of the following:

a. P_4
b. H_2O
c. $Ca(NO_3)_2$

(a)

123.896 amu

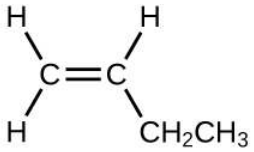
(b)

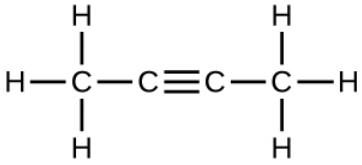
18.015 amu

(c)

164.086 amu

3. Determine the molecular mass of the following compounds:

a. 

b. 

(a)

56.107 amu

(b)

54.091 amu

4. Calculate the molar mass of each of the following:

a. S_8
b. C_5H_{12}

(a)

256.528 g/mol

(b)

72.150 g mol^{-1}

5. Determine the mass of each of the following:

a. 0.0146 mol KOH
b. 10.2 mol ethane, C_2H_6

(a)

0.819 g

(b)

307 g

3.E.3.2: 3.2: Determining Empirical and Molecular Formulas

answer

$Mg_3Si_2H_3O_8$ (empirical formula), $Mg_6Si_4H_6O_{16}$ (molecular formula)

1. Calculate the percent composition of ammonia, NH_3 to four significant figures:

answer

% N = 82.24%; % H = 17.76%

2. A compound of carbon and hydrogen contains 92.3% C and has a molar mass of 78.1 g/mol. What is its molecular formula?

answer

C_6H_6

3. Determine the empirical and molecular formula for chrysotile asbestos. Chrysotile has the following percent composition: 28.03% Mg, 21.60% Si, 1.16% H, and 49.21% O. The molar mass for chrysotile is 520.8 g/mol.

3.E.3.3: 3.3: Molarity

1. Determine the molarity for 0.444 mol of $CoCl_2$ in 0.654 L of solution

answer

0.679 *M*

2. Determine the molarity for 98.0 g of phosphoric acid, H_3PO_4, in 1.00 L of solution

answer

1.00 *M*

3. Calculate the number of moles and the mass of the solute in 2.00 L of 18.5 *M* H_2SO_4, concentrated sulfuric acid:

answer

37.0 mol H_2SO_4; 3.63×10^3 g H_2SO_4

4. Calculate the molarity of 0.195 g of cholesterol, $C_{27}H_{46}O$, in 0.100 L of serum, the average concentration of cholesterol in human serum

answer

5.04×10^{-3} *M*

5. What is the molarity of the diluted solution when 1.00 L of a 0.250-*M* solution of $Fe(NO_3)_3$ is diluted to a final volume of 2.00 L?

answer

0.125 *M*

6. What volume of a 0.20-*M* K_2SO_4 solution contains 57 g of K_2SO_4?

answer

1.6 L

This page titled 3.E: Composition of Substances and Solutions- Homework is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

CHAPTER OVERVIEW

4: Stoichiometry of Chemical Reactions

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

General Chemistry

This chapter will describe how to symbolize chemical reactions using chemical equations, how to classify some common chemical reactions by identifying patterns of reactivity, and how to determine the quantitative relations between the amounts of substances involved in chemical reactions—that is, the reaction *stoichiometry*.

4.1: Writing and Balancing Chemical Equations
4.2: Reaction Stoichiometry
4.3: Classifying Chemical Reactions - Precipitation Reactions
4.4: Classifying Chemical Reactions - Acid Base Reactions
4.5: Classifying Chemical Reactions - Combustion Reactions
4.E: Stoichiometry of Chemical Reactions- Homework

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 4: Stoichiometry of Chemical Reactions is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

4.1: Writing and Balancing Chemical Equations

Learning Objectives

- Derive chemical equations from narrative descriptions of chemical reactions.
- Write and balance chemical equations in molecular, total ionic, and net ionic formats.

4.1.1: Introduction

Solid-fuel rockets are a central feature in the world's space exploration programs, including the new Space Launch System being developed by the National Aeronautics and Space Administration (NASA) to replace the retired Space Shuttle fleet (Figure 4.1.1). The engines of these rockets rely on carefully prepared solid mixtures of chemicals combined in precisely measured amounts. Igniting the mixture initiates a vigorous chemical reaction that rapidly generates large amounts of gaseous products. These gases are ejected from the rocket engine through its nozzle, providing the thrust needed to propel heavy payloads into space. Both the nature of this chemical reaction and the relationships between the amounts of the substances being consumed and produced by the reaction are critically important considerations that determine the success of the technology. This chapter will describe how to symbolize chemical reactions using chemical equations, how to classify some common chemical reactions by identifying patterns of reactivity, and how to determine the quantitative relations between the amounts of substances involved in chemical reactions—that is, the reaction *stoichiometry*.



Figure 4.1.1: Many modern rocket fuels are solid mixtures of substances combined in carefully measured amounts and ignited to yield a thrust-generating chemical reaction. (credit: modification of work by NASA)

The preceding chapter introduced the use of element symbols to represent individual atoms. When atoms gain or lose electrons to yield ions, or combine with other atoms to form molecules, their symbols are modified or combined to generate chemical formulas that appropriately represent these species. Extending this symbolism to represent both the identities and the relative quantities of substances undergoing a chemical (or physical) change involves writing and balancing a chemical equation. Consider as an example the reaction between one methane molecule (CH_4) and two diatomic oxygen molecules (O_2) to produce one carbon dioxide molecule (CO_2) and two water molecules (H_2O). The chemical equation representing this process is provided in the upper half of Figure 4.1.2, with space-filling molecular models shown in the lower half of the figure.

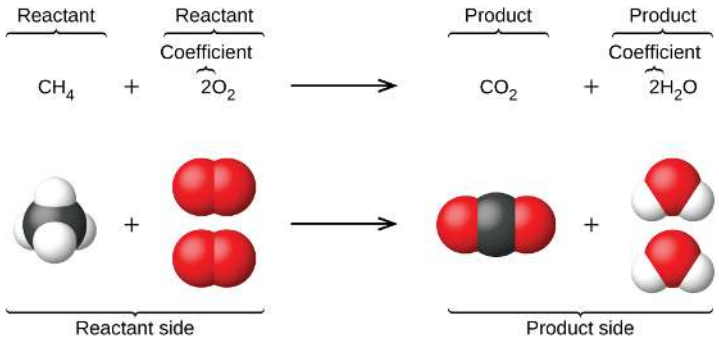


Figure 4.1.2: The reaction between methane and oxygen to yield carbon dioxide and water (shown at bottom) may be represented by a chemical equation using formulas (top).

This example illustrates the fundamental aspects of any chemical equation:

1. The substances undergoing reaction are called reactants, and their formulas are placed on the left side of the equation.
2. The substances generated by the reaction are called products, and their formulas are placed on the right sight of the equation.
3. Plus signs (+) separate individual reactant and product formulas, and an arrow (⟶) separates the reactant and product (left and right) sides of the equation.
4. The relative numbers of reactant and product species are represented by coefficients (numbers placed immediately to the left of each formula). A coefficient of 1 is typically omitted.

It is common practice to use the smallest possible whole-number coefficients in a chemical equation, as is done in this example. Realize, however, that these coefficients represent the *relative* numbers of reactants and products, and, therefore, they may be correctly interpreted as ratios. Methane and oxygen react to yield carbon dioxide and water in a 1:2:1:2 ratio. This ratio is satisfied if the numbers of these molecules are, respectively, 1-2-1-2, or 2-4-2-4, or 3-6-3-6, and so on (Figure 4.1.3). Likewise, these coefficients may be interpreted with regard to any amount (number) unit, and so this equation may be correctly read in many ways, including:

- *One* methane molecule and *two* oxygen molecules react to yield *one* carbon dioxide molecule and *two* water molecules.
- *One dozen* methane molecules and *two dozen* oxygen molecules react to yield *one dozen* carbon dioxide molecules and *two dozen* water molecules.
- *One mole* of methane molecules and *2 moles* of oxygen molecules react to yield *1 mole* of carbon dioxide molecules and *2 moles* of water molecules.

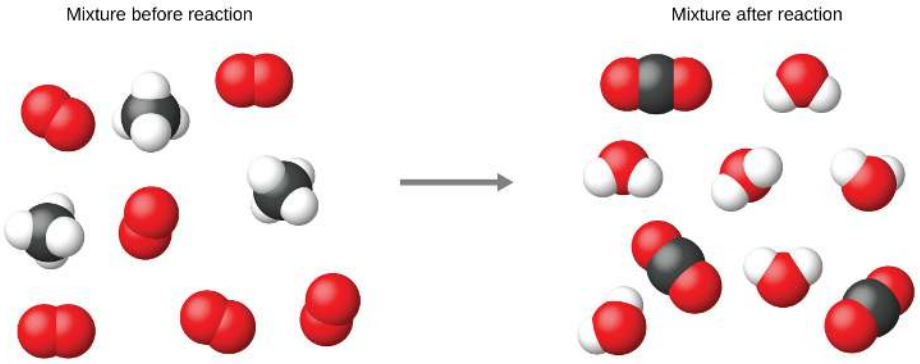


Figure 4.1.3: Regardless of the absolute number of molecules involved, the ratios between numbers of molecules of each species that react (the reactants) and molecules of each species that form (the products) are the same and are given in the chemical equation.

4.1.2: Balancing Equations

When a chemical equation is balanced it means that equal numbers of atoms for each element involved in the reaction are represented on the reactant and product sides. This is a requirement the equation must satisfy to be consistent with the law of conservation of matter. It may be confirmed by simply summing the numbers of atoms on either side of the arrow and comparing

these sums to ensure they are equal. Note that the number of atoms for a given element is calculated by multiplying the coefficient of any formula containing that element by the element's subscript in the formula. If an element appears in more than one formula on a given side of the equation, the number of atoms represented in each must be computed and then added together. For example, both product species in the example reaction, CO_2 and H_2O, contain the element oxygen, and so the number of oxygen atoms on the product side of the equation is

$$\left(1\ \cancel{CO_2\ \text{molecule}} \times \frac{2\ \text{O atoms}}{\cancel{CO_2\ \text{molecule}}}\right) + \left(2\ \cancel{H_2O\ \text{molecule}} \times \frac{1\ \text{O atom}}{\cancel{H_2O\ \text{molecule}}}\right) = 4\ \text{O atoms}$$

The equation for the reaction between methane and oxygen to yield carbon dioxide and water is confirmed to be balanced per this approach, as shown here:

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$$

Equation for the reaction

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$$

Element	Reactants	Products	Balanced?
C	1 × 1 = 1	1 × 1 = 1	1 = 1, yes
H	4 × 1 = 4	2 × 2 = 4	4 = 4, yes
O	2 × 2 = 4	(1 × 2) + (2 × 1) = 4	4 = 4, yes

A balanced chemical equation often may be derived from a qualitative description of some chemical reaction by a fairly simple approach known as balancing by inspection. Consider as an example the decomposition of water to yield molecular hydrogen and oxygen. This process is represented qualitatively by an *unbalanced* chemical equation:

$$H_2O \rightarrow H_2 + O_2 \qquad \text{(unbalanced)}$$

Comparing the number of H and O atoms on either side of this equation confirms its imbalance:

Comparisons between H and O atoms

Element	Reactants	Products	Balanced?
H	1 × 2 = 2	1 × 2 = 2	2 = 2, yes
O	1 × 1 = 1	1 × 2 = 2	1 ≠ 2, no

The numbers of H atoms on the reactant and product sides of the equation are equal, but the numbers of O atoms are not. To achieve balance, the *coefficients* of the equation may be changed as needed. Keep in mind, of course, that the *formula subscripts* define, in part, the identity of the substance, and so these cannot be changed without altering the qualitative meaning of the equation. For example, changing the reactant formula from H_2O to H_2O_2 would yield balance in the number of atoms, but doing so also changes the reactant's identity (it's now hydrogen peroxide and not water). The O atom balance may be achieved by changing the coefficient for H_2O to 2.

$$2\,H_2O \rightarrow H_2 + O_2 \qquad \text{(unbalanced)}$$

O atom balance may be achieved by changing the coefficient for H2O to 2

Element	Reactants	Products	Balanced?
H	**2** × 2 = 4	1 × 2 = 2	4 ≠ 2, no
O	2 × 1 = 2	1 × 2 = 2	2 = 2, yes

The H atom balance was upset by this change, but it is easily reestablished by changing the coefficient for the H_2 product to 2.

$$2\,H_2O \rightarrow 2\,H_2 + O_2 \qquad \text{(balanced)}$$

H atom balance upset but easily reestablished by changing the coefficient for the H2 product to 2.

Element	Reactants	Products	Balanced?
H	2 × 2 = 4	**2** × 2 = 2	4 = 4, yes
O	2 × 1 = 2	1 × 2 = 2	2 = 2, yes

These coefficients yield equal numbers of both H and O atoms on the reactant and product sides, and the balanced equation is, therefore:

$$2\,H_2O \rightarrow 2\,H_2 + O_2$$

Example 4.1.1: Balancing Chemical Equations

Write a balanced equation for the reaction of molecular nitrogen (N_2) and oxygen (O_2) to form dinitrogen pentoxide.

Solution

First, write the unbalanced equation.

$$N_2 + O_2 \rightarrow N_2O_5 \qquad \text{(unbalanced)}$$

Next, count the number of each type of atom present in the unbalanced equation.

Unbalanced Equation

Element	Reactants	Products	Balanced?
N	1 × 2 = 2	1 × 2 = 2	2 = 2, yes
O	1 × 2 = 2	1 × 5 = 5	2 ≠ 5, no

Though nitrogen is balanced, changes in coefficients are needed to balance the number of oxygen atoms. To balance the number of oxygen atoms, a reasonable first attempt would be to change the coefficients for the O_2 and N_2O_5 to integers that will yield 10 O atoms (the least common multiple for the O atom subscripts in these two formulas).

$$N_2 + 5\,O_2 \rightarrow 2\,N_2O_5 \qquad \text{(unbalanced)}$$

$$N_2 + 5\,O_2 \rightarrow 2\,N_2O_5 \qquad \text{(unbalanced)}$$

Element	Reactants	Products	Balanced?
N	1 × 2 = 2	**2** × 2 = 4	2 ≠ 4, no
O	**5** × 2 = 10	**2** × 5 = 10	10 = 10, yes

The N atom balance has been upset by this change; it is restored by changing the coefficient for the reactant N_2 to 2.

$$2\,N_2 + 5\,O_2 \rightarrow 2\,N_2O_5$$

N atom balance upset but restored by changing the coefficient for the reactant N2 to 2.

Element	Reactants	Products	Balanced?
N	**2** × 2 = 4	2 × 2 = 4	4 = 4, yes
O	5 × 2 = 10	2 × 5 = 10	10 = 10, yes

The numbers of N and O atoms on either side of the equation are now equal, and so the equation is balanced.

Exercise 4.1.1

Write a balanced equation for the decomposition of ammonium nitrate to form molecular nitrogen, molecular oxygen, and water. (Hint: Balance oxygen last, since it is present in more than one molecule on the right side of the equation.)

Answer

$$2\,NH_4NO_3 \rightarrow 2\,N_2 + O_2 + 4\,H_2O$$



It is sometimes convenient to use fractions instead of integers as intermediate coefficients in the process of balancing a chemical equation. When balance is achieved, all the equation's coefficients may then be multiplied by a whole number to convert the fractional coefficients to integers without upsetting the atom balance. For example, consider the reaction of ethane (C_2H_6) with oxygen to yield H_2O and CO_2, represented by the unbalanced equation:

$$C_2H_6 + O_2 \rightarrow H_2O + CO_2 \qquad \text{(unbalanced)}$$

Following the usual inspection approach, one might first balance C and H atoms by changing the coefficients for the two product species, as shown:

$$C_2H_6 + O_2 \rightarrow 3\,H_2O + 2\,CO_2 \qquad \text{(unbalanced)}$$

This results in seven O atoms on the product side of the equation, an odd number—no integer coefficient can be used with the O_2 reactant to yield an odd number, so a fractional coefficient, $\frac{7}{2}$, is used instead to yield a provisional balanced equation:

$$C_2H_6 + \tfrac{7}{2}O_2 \rightarrow 3\,H_2O + 2\,CO_2$$

A conventional balanced equation with integer-only coefficients is derived by multiplying each coefficient by 2:

$$2\,C_2H_6 + 7\,O_2 \rightarrow 6\,H_2O + 4\,CO_2$$

Finally with regard to balanced equations, recall that convention dictates use of the *smallest whole-number coefficients*. Although the equation for the reaction between molecular nitrogen and molecular hydrogen to produce ammonia is, indeed, balanced,

$$3\,N_2 + 9\,H_2 \rightarrow 6\,NH_3$$

the coefficients are not the smallest possible integers representing the relative numbers of reactant and product molecules. Dividing each coefficient by the greatest common factor, 3, gives the preferred equation:

$$N_2 + 3\,H_2 \rightarrow 2\,NH_3$$

Phet Simulation

Use this interactive tutorial for additional practice balancing equations.

4.1.3: Additional Information in Chemical Equations

The physical states of reactants and products in chemical equations very often are indicated with a parenthetical abbreviation following the formulas. Common abbreviations include *s* for solids, *l* for liquids, *g* for gases, and *aq* for substances dissolved in water (*aqueous solutions*, as introduced in the preceding chapter). These notations are illustrated in the example equation here:

$$2\,\mathrm{Na(s)} + 2\,\mathrm{H_2O(l)} \rightarrow 2\,\mathrm{NaOH(aq)} + \mathrm{H_2(g)}$$

This equation represents the reaction that takes place when sodium metal is placed in water. The solid sodium reacts with liquid water to produce molecular hydrogen gas and the ionic compound sodium hydroxide (a solid in pure form, but readily dissolved in water).

Special conditions necessary for a reaction are sometimes designated by writing a word or symbol above or below the equation's arrow. For example, a reaction carried out by heating may be indicated by the uppercase Greek letter delta (Δ) over the arrow.

$$\mathrm{CaCO_3}(s) \xrightarrow{\Delta} \mathrm{CaO}(s) + \mathrm{CO_2}(g)$$

Other examples of these special conditions will be encountered in more depth in later chapters.

4.1.4: Equations for Ionic Reactions

Given the abundance of water on earth, it stands to reason that a great many chemical reactions take place in aqueous media. When ions are involved in these reactions, the chemical equations may be written with various levels of detail appropriate to their intended use. To illustrate this, consider a reaction between ionic compounds taking place in an aqueous solution. When aqueous solutions of $\mathrm{CaCl_2}$ and $\mathrm{AgNO_3}$ are mixed, a reaction takes place producing aqueous $\mathrm{Ca(NO_3)_2}$ and solid AgCl:

$$\mathrm{CaCl_2}(aq) + 2\,\mathrm{AgNO_3}(aq) \rightarrow \mathrm{Ca(NO_3)_2}(aq) + 2\,\mathrm{AgCl}(s)$$

This balanced equation, derived in the usual fashion, is called a molecular equation because it doesn't explicitly represent the ionic species that are present in solution. When ionic compounds dissolve in water, they may *dissociate* into their constituent ions, which are subsequently dispersed homogenously throughout the resulting solution (a thorough discussion of this important process is provided in the chapter on solutions). Ionic compounds dissolved in water are, therefore, more realistically represented as dissociated ions, in this case:

$$\mathrm{CaCl_2}(aq) \rightarrow \mathrm{Ca^{2+}}(aq) + 2\,\mathrm{Cl^-}(aq)$$

$$2\,\mathrm{AgNO_3}(aq) \rightarrow 2\,\mathrm{Ag^+}(aq) + 2\,\mathrm{NO_3^-}(aq)$$

$$\mathrm{Ca(NO_3)_2}(aq) \rightarrow \mathrm{Ca^{2+}}(aq) + 2\,\mathrm{NO_3^-}(aq)$$

Unlike these three ionic compounds, AgCl does not dissolve in water to a significant extent, as signified by its physical state notation, *(s)*.

Explicitly representing all dissolved ions results in a complete ionic equation. In this particular case, the formulas for the dissolved ionic compounds are replaced by formulas for their dissociated ions:

$$\mathrm{Ca^{2+}}(aq) + 2\,\mathrm{Cl^-}(aq) + 2\,\mathrm{Ag^+}(aq) + 2\,\mathrm{NO_3^-}(aq) \rightarrow \mathrm{Ca^{2+}}(aq) + 2\,\mathrm{NO_3^-}(aq) + 2\,\mathrm{AgCl}(s)$$

Examining this equation shows that two chemical species are present in identical form on both sides of the arrow, $\mathrm{Ca^{2+}(aq)}$ and $\mathrm{NO_3^-}(aq)$. These spectator ions—ions whose presence is required to maintain charge neutrality—are neither chemically nor physically changed by the process, and so they may be eliminated from the equation to yield a more succinct representation called a net ionic equation:

$$\cancel{\mathrm{Ca^{2+}}(aq)} + 2\,\mathrm{Cl^-}(aq) + 2\,\mathrm{Ag^+}(aq) + \cancel{2\,\mathrm{NO_3^-}(aq)} \rightarrow \cancel{\mathrm{Ca^{2+}}(aq)} + \cancel{2\,\mathrm{NO_3^-}(aq)} + 2\,\mathrm{AgCl}(s)$$

$$2\,\mathrm{Cl^-}(aq) + 2\,\mathrm{Ag^+}(aq) \rightarrow 2\,\mathrm{AgCl}(s)$$

Following the convention of using the smallest possible integers as coefficients, this equation is then written:

$$Cl^-(aq) + Ag^+(aq) \rightarrow AgCl(s)$$

This net ionic equation indicates that solid silver chloride may be produced from dissolved chloride and silver(I) ions, regardless of the source of these ions. These molecular and complete ionic equations provide additional information, namely, the ionic compounds used as sources of Cl^- and Ag^+.

Example 4.1.2: Molecular and Ionic Equations

When carbon dioxide is dissolved in an aqueous solution of sodium hydroxide, the mixture reacts to yield aqueous sodium carbonate and liquid water. Write balanced molecular, complete ionic, and net ionic equations for this process.

Solution

Begin by identifying formulas for the reactants and products and arranging them properly in chemical equation form:

$$CO_2(aq) + NaOH(aq) \rightarrow Na_2CO_3(aq) + H_2O(l) \qquad \text{(unbalanced)}$$

Balance is achieved easily in this case by changing the coefficient for NaOH to 2, resulting in the molecular equation for this reaction:

$$CO_2(aq) + 2\,NaOH(aq) \rightarrow Na_2CO_3(aq) + H_2O(l)$$

The two dissolved ionic compounds, NaOH and Na_2CO_3, can be represented as dissociated ions to yield the complete ionic equation:

$$CO_2(aq) + 2\,Na^+(aq) + 2\,OH^-(aq) \rightarrow 2\,Na^+(aq) + CO_3^{2-}(aq) + H_2O(l)$$

Finally, identify the spectator ion(s), in this case $Na^+(aq)$, and remove it from each side of the equation to generate the net ionic equation:

$$CO_2(aq) + \cancel{2\,Na^+(aq)} + 2\,OH^-(aq) \rightarrow \cancel{2\,Na^+(aq)} + CO_3^{2-}(aq) + H_2O(l)$$

$$CO_2(aq) + 2\,OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l)$$

Exercise 4.1.2

Diatomic chlorine and sodium hydroxide (lye) are commodity chemicals produced in large quantities, along with diatomic hydrogen, via the electrolysis of brine, according to the following unbalanced equation:

$$NaCl(aq) + H_2O(l) \xrightarrow{electricity} NaOH(aq) + H_2(g) + Cl_2(g)$$

Write balanced molecular, complete ionic, and net ionic equations for this process.

Answer

Balanced molecular equation:

$$2\,NaCl(aq) + 2\,H_2O(l) \longrightarrow 2\,NaOH(aq) + H_2(g) + Cl_2(g)$$

Balanced ionic equation:

$$2\,Na^+(aq) + 2\,Cl^-(aq) + 2\,H_2O(l) \longrightarrow 2\,Na^+(aq) + 2\,OH^-(aq) + H_2(g) + Cl_2(g)$$

Balanced net ionic equation:

$$2\,Cl^-(aq) + 2\,H_2O(l) \longrightarrow 2\,OH^-(aq) + H_2(g) + Cl_2(g)$$

4.1.5: Key Concepts and Summary

Chemical equations are symbolic representations of chemical and physical changes. Formulas for the substances undergoing the change (reactants) and substances generated by the change (products) are separated by an arrow and preceded by integer coefficients indicating their relative numbers. Balanced equations are those whose coefficients result in equal numbers of atoms for each element in the reactants and products. Chemical reactions in aqueous solution that involve ionic reactants or products may be represented more realistically by complete ionic equations and, more succinctly, by net ionic equations.

Glossary

balanced equation
chemical equation with equal numbers of atoms for each element in the reactant and product

chemical equation
symbolic representation of a chemical reaction

coefficient
number placed in front of symbols or formulas in a chemical equation to indicate their relative amount

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

molecular equation
chemical equation in which all reactants and products are represented as neutral substances

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)

product
substance formed by a chemical or physical change; shown on the right side of the arrow in a chemical equation

reactant
substance undergoing a chemical or physical change; shown on the left side of the arrow in a chemical equation

spectator ion
ion that does not undergo a chemical or physical change during a reaction, but its presence is required to maintain charge neutrality

---

This page titled 4.1: Writing and Balancing Chemical Equations is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

- **4.2: Writing and Balancing Chemical Equations** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.
- **4.1: Prelude to Stoichiometry** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

4.2: Reaction Stoichiometry

Learning Objectives

- Explain the concept of stoichiometry as it pertains to chemical reactions
- Use balanced chemical equations to derive stoichiometric factors relating amounts of reactants and products
- Perform stoichiometric calculations involving mass, moles, and solution molarity
- Explain the concepts of theoretical yield, atom economy, and limiting reactants/reagents.
- Derive the theoretical yield for a reaction under specified conditions.
- Calculate the percent yield for a reaction.
- Calculate the atom economy for a reaction.

The relative amounts of reactants and products represented in a balanced chemical equation are often referred to as *stoichiometric amounts*. All the exercises of the preceding module involved stoichiometric amounts of reactants. For example, when calculating the amount of product generated from a given amount of reactant, it was assumed that any other reactants required were available in stoichiometric amounts (or greater). In this module, more realistic situations are considered, in which reactants are not present in stoichiometric amounts.

Stoichiometry

A balanced chemical equation provides a great deal of information in a very succinct format. Chemical formulas provide the identities of the reactants and products involved in the chemical change, allowing classification of the reaction. Coefficients provide the relative numbers of these chemical species, allowing a quantitative assessment of the relationships between the amounts of substances consumed and produced by the reaction. These quantitative relationships are known as the reaction's stoichiometry, a term derived from the Greek words *stoicheion* (meaning "element") and *metron* (meaning "measure"). In this module, the use of balanced chemical equations for various stoichiometric applications is explored.

The general approach to using stoichiometric relationships is similar in concept to the way people go about many common activities. Cooking, for example, offers an appropriate comparison. Suppose a recipe for making eight pancakes calls for 1 cup pancake mix, $\frac{3}{4}$ cup milk, and one egg. The "equation" representing the preparation of pancakes per this recipe is

$$1 \text{ cup mix} + \frac{3}{4} \text{ cup milk} + 1 \text{ egg} \rightarrow 8 \text{ pancakes} \tag{4.2.1}$$

If two dozen pancakes are needed for a big family breakfast, the ingredient amounts must be increased proportionally according to the amounts given in the recipe. For example, the number of eggs required to make 24 pancakes is

$$24 \ \cancel{\text{pancakes}} \times \frac{1 \text{ egg}}{8 \ \cancel{\text{pancakes}}} = 3 \text{ eggs} \tag{4.2.2}$$

Balanced chemical equations are used in much the same fashion to determine the amount of one reactant required to react with a given amount of another reactant, or to yield a given amount of product, and so forth. The coefficients in the balanced equation are used to derive stoichiometric factors that permit computation of the desired quantity. To illustrate this idea, consider the production of ammonia by reaction of hydrogen and nitrogen:

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightarrow 2\,\mathrm{NH_3}(g) \tag{4.2.3}$$

This equation shows that ammonia molecules are produced from hydrogen molecules in a 2:3 ratio, and stoichiometric factors may be derived using any amount (number) unit:

$$\frac{2\,\mathrm{NH_3} \text{ molecules}}{3\,\mathrm{H_2} \text{ molecules}} \text{ or } \frac{2 \text{ doz } \mathrm{NH_3} \text{ molecules}}{3 \text{ doz } \mathrm{H_2} \text{ molecules}} \text{ or } \frac{2 \text{ mol } \mathrm{NH_3} \text{ molecules}}{3 \text{ mol } \mathrm{H_2} \text{ molecules}} \tag{4.2.4}$$

These stoichiometric factors can be used to compute the number of ammonia molecules produced from a given number of hydrogen molecules, or the number of hydrogen molecules required to produce a given number of ammonia molecules. Similar factors may be derived for any pair of substances in any chemical equation.

Example 4.2.1: Moles of Reactant Required in a Reaction

How many moles of I_2 are required to react with 0.429 mol of Al according to the following equation (see Figure 4.2.1)?

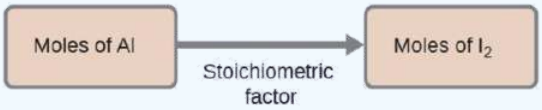
$$2\ \mathrm{Al} + 3\ \mathrm{I_2} \rightarrow 2\ \mathrm{AlI_3} \tag{4.2.5}$$



Figure 4.2.1: Aluminum and iodine react to produce aluminum iodide. The heat of the reaction vaporizes some of the solid iodine as a purple vapor. (credit: modification of work by Mark Ott)

Solution

Referring to the balanced chemical equation, the stoichiometric factor relating the two substances of interest is $\frac{3\ \mathrm{mol\ I_2}}{2\ \mathrm{mol\ Al}}$. The molar amount of iodine is derived by multiplying the provided molar amount of aluminum by this factor:



$$\mathrm{mol\ I_2} = 0.429\ \cancel{\mathrm{mol\ Al}} \times \frac{3\ \mathrm{mol\ I_2}}{2\ \cancel{\mathrm{mol\ Al}}}$$

$$= 0.644\ \mathrm{mol\ I_2}$$

Exercise 4.2.1

How many moles of $Ca(OH)_2$ are required to react with 1.36 mol of H_3PO_4 to produce $Ca_3(PO_4)_2$ according to the equation $3\ \mathrm{Ca(OH)_2} + 2\ \mathrm{H_3PO_4} \rightarrow \mathrm{Ca_3(PO_4)_2} + 6\ \mathrm{H_2O}$?

Answer

2.04 mol

These examples illustrate the ease with which the amounts of substances involved in a chemical reaction of known stoichiometry may be related. Directly measuring numbers of atoms and molecules is, however, not an easy task, and the practical application of stoichiometry requires that we use the more readily measured property of mass.

Example 4.2.2: Relating Masses of Reactants and Products

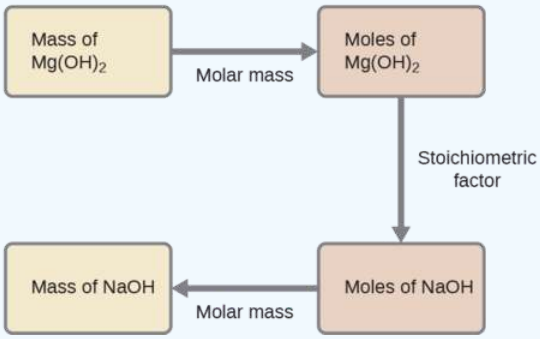
What mass of sodium hydroxide, NaOH, would be required to produce 16 g of the antacid milk of magnesia [magnesium hydroxide, $Mg(OH)_2$] by the following reaction?

$$\mathrm{MgCl_2}(aq) + 2\ \mathrm{NaOH}(aq) \rightarrow \mathrm{Mg(OH)_2}(s) + 2\ \mathrm{NaCl}(aq)$$

Solution

The approach used previously in Examples 4.2.1 and 4.2.2 is likewise used here; that is, we must derive an appropriate stoichiometric factor from the balanced chemical equation and use it to relate the amounts of the two substances of interest. In

this case, however, masses (not molar amounts) are provided and requested, so additional steps of the sort learned in the previous chapter are required. The calculations required are outlined in this flowchart:



$$16\ \text{g}\ \cancel{\text{Mg(OH)}_2} \times \frac{1\ \text{mol}\ \cancel{\text{Mg(OH)}_2}}{58.3\ \text{g}\ \cancel{\text{Mg(OH)}_2}} \times \frac{2\ \text{mol}\ \cancel{\text{NaOH}}}{1\ \text{mol}\ \cancel{\text{Mg(OH)}_2}} \times \frac{40.0\ \text{g NaOH}}{\text{mol}\ \cancel{\text{NaOH}}} = 22\ \text{g NaOH}$$

Exercise 4.2.2

What mass of gallium oxide, Ga_2O_3, can be prepared from 29.0 g of gallium metal? The equation for the reaction is $4\,Ga + 3\,O_2 \rightarrow 2\,Ga_2O_3$.

Answer

39.0 g

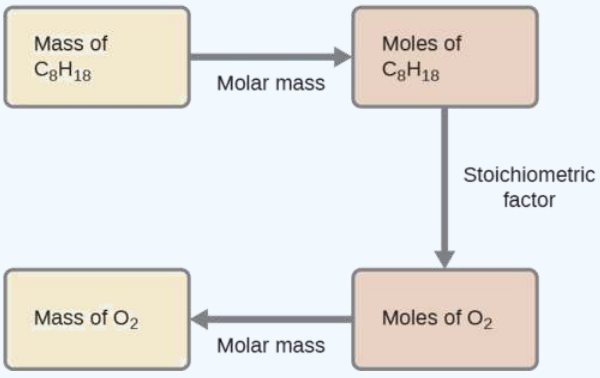
Example 4.2.3: Relating Masses of Reactants

What mass of oxygen gas, O_2, from the air is consumed in the combustion of 702 g of octane, C_8H_{18}, one of the principal components of gasoline?

$$2\,C_8H_{18} + 25\,O_2 \rightarrow 16\,CO_2 + 18\,H_2O$$

Solution

The approach required here is the same as for the Example 4.2.3, differing only in that the provided and requested masses are both for reactant species.



$$702\ \text{g}\ \cancel{\text{C}_8\text{H}_{18}} \times \frac{1\ \text{mol}\ \cancel{\text{C}_8\text{H}_{18}}}{114.23\ \text{g}\ \cancel{\text{C}_8\text{H}_{18}}} \times \frac{25\ \text{mol}\ \cancel{\text{O}_2}}{2\ \text{mol}\ \cancel{\text{C}_8\text{H}_{18}}} \times \frac{32.00\ \text{g O}_2}{\text{mol}\ \cancel{\text{O}_2}} = 2.46 \times 10^3\ \text{g O}_2$$

Exercise 4.2.3

What mass of CO is required to react with 25.13 g of Fe_2O_3 according to the equation $\mathrm{Fe_2O_3 + 3\,CO \rightarrow 2\,Fe + 3\,CO_2}$?

Answer

13.22 g

4.2.1: Limiting Reactant

Consider another food analogy, making grilled cheese sandwiches (Figure 4.2.2):

$$1 \text{ slice of cheese} + 2 \text{ slices of bread} \rightarrow 1 \text{ sandwich} \tag{4.2.6}$$

Stoichiometric amounts of sandwich ingredients for this recipe are bread and cheese slices in a 2:1 ratio. Provided with 28 slices of bread and 11 slices of cheese, one may prepare 11 sandwiches per the provided recipe, using all the provided cheese and having six slices of bread left over. In this scenario, the number of sandwiches prepared has been *limited* by the number of cheese slices, and the bread slices have been provided in *excess*.

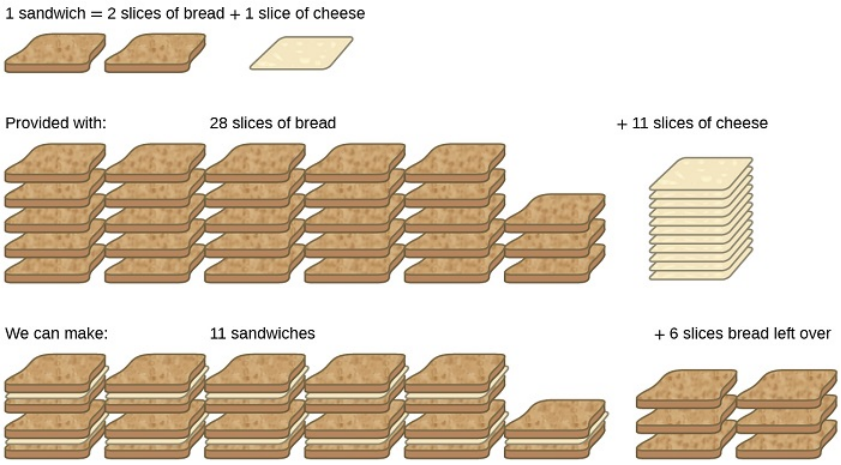


Figure 4.2.2: Sandwich making can illustrate the concepts of limiting and excess reactants.

Consider this concept now with regard to a chemical process, the reaction of hydrogen with chlorine to yield hydrogen chloride:

$$\mathrm{H_2}(g) + \mathrm{Cl_2}(g) \rightarrow 2\,\mathrm{HCl}(g)$$

The balanced equation shows the hydrogen and chlorine react in a 1:1 stoichiometric ratio. If these reactants are provided in any other amounts, one of the reactants are entirely consumed and limit the amount of product generated. This substance is the limiting reactant. Any substances that are left over are the excess reactant. Identifying the limiting and excess reactants for a given situation requires computing the molar amounts of each reactant provided and comparing them to the stoichiometric amounts represented in the balanced chemical equation.

For example, imagine combining 6 moles of H_2 and 4 moles of Cl_2. Identifying the limiting reactant involves comparing the amount of product expected for the complete reaction of each reactant. Each reactant amount is used to separately calculate the amount of product that would be formed per the reaction's stoichiometry. The reactant yielding the lesser amount of product is the limiting reactant.

For the example in the previous paragraph, the complete reaction of the hydrogen would yield

$$\text{mol HCl produced} = 6 \text{ mol } \mathrm{H_2} \times \frac{2 \text{ mol HCl}}{1 \text{ mol } \mathrm{H_2}} = 12 \text{ mol HCl}$$

The complete reaction of the provided chlorine would produce

$$\text{mol HCl produced} = 4 \text{ mol } Cl_2 \times \frac{2 \text{ mol HCl}}{1 \text{ mol } Cl_2} = 8 \text{ mol HCl}$$

The chlorine will be completely consumed once 8 moles of HCl have been produced. Since enough hydrogen was provided to yield 12 moles of HCl, there will be non-reacted hydrogen remaining once this reaction is complete. Chlorine, therefore, is the limiting reactant and hydrogen is the excess reactant (Figure 4.2.3). To determine the amount of excess reactant that remains, the amount of hydrogen consumed in the reaction can be subtracted from the starting quantity of hydrogen.

The amount of hydrogen consumed is

$$\text{mol } H_2 \text{ produced} = 8 \text{ mol HCl} \times \frac{1 \text{ mol } H_2}{2 \text{ mol HCl}} = 4 \text{ mol } H_2$$

Subtract the hydrogen consumed from the starting quantity

$$\text{mole of excess } H_2 = 6 \text{ mol } H_2 \text{ starting } - 4 \text{ mol } H_2 \text{ consumed } = 2 \text{ mol } H_2 \text{ excess}$$

Figure 4.2.3 provides a visual representation for the initial and final conditions for this reaction.

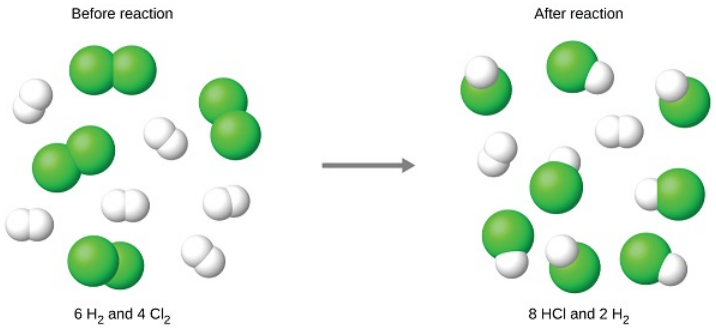


Figure 4.2.3: When H_2 and Cl_2 are combined in nonstoichiometric amounts, one of these reactants will limit the amount of HCl that can be produced. This illustration shows a reaction in which hydrogen is present in excess and chlorine is the limiting reactant.

A useful way to summarize the calculations required for determining the reaction yield is an Initial, Change, Final (ICF) table. This format helps organize the problem and shows the connections for solving a wide range of stoichiometry problems. Set up a table where the first row is the balanced chemical equation, in the second row you list all the initial amounts - in moles, in the third row you list the change that occurs in the reaction, and in the fourth row you list the final amounts remaining when the reaction is complete. This layout makes it easy to see if you make any mistakes - like picking the wrong limiting reagent. And clarifies all the interrelationships needed to solve a wide range of problems. An example is shown in Table 4.2.1 for the reaction of H_2 and Cl_2:

Table 4.2.1: ICF table for reaction of H_2 and Cl_2

	H_2	Cl_2	→	HCl
Initial	6	4		0
Change	4	4		8
Final	2	0		8

Example 4.2.4: Identifying the Limiting Reactant

Silicon nitride is a very hard, high-temperature-resistant ceramic used as a component of turbine blades in jet engines. It is prepared according to the following equation:

$$3\,Si(s) + 2\,N_2(g) \rightarrow Si_3N_4(s)$$

Which is the limiting reactant when 2.00 g of Si and 1.50 g of N_2 react?

Solution

Compute the provided molar amounts of reactants, and then compare these amounts to the balanced equation to identify the limiting reactant.

$$\text{mol Si} = 2.00\ \cancel{\text{g Si}} \times \frac{1\ \text{mol Si}}{28.09\ \cancel{\text{g Si}}} = 0.0712\ \text{mol Si}$$

$$\text{mol } N_2 = 1.50\ \cancel{\text{g } N_2} \times \frac{1\ \text{mol } N_2}{28.02\ \cancel{\text{g } N_2}} = 0.0535\ \text{mol } N_2$$

Compute the amount of product expected for complete reaction of each of the provided reactants. The 0.0712 moles of silicon would yield

$$\text{mol } Si_3N_4 \text{ produced} = 0.0712\ \text{mol Si} \times \frac{1\ \text{mol } Si_3N_4}{3\ \text{mol Si}} = 0.0237\ \text{mol } Si_3N_4$$

while the 0.0535 moles of nitrogen would produce

$$\text{mol } Si_3N_4 \text{ produced} = 0.0535\ \text{mol } N_2 \times \frac{1\ \text{mol } Si_3N_4}{2\ \text{mol } N_2} = 0.0268\ \text{mol } Si_3N_4$$

Since silicon yields the lesser amount of product, it is the limiting reactant.

This is summarized in the ICF table shown below. In the Change row, always use the stoichiometric coefficients from the balanced equation to go from one column to another.

	3 Si	2 N_2	→	Si_3N_4
Initial (grams)	2.00 g	1.50 g		0 g
Initial (moles)	0.0712 mol	0.0535 mol		0 mol
Change (moles)	0.0712 mol	0.0475 mol		0.0237 mol
Final (moles)	0 mol	0.0060 mol		0.0237 mol

? Exercise 4.2.4

Which is the limiting reactant when 5.00 g of H_2 and 10.0 g of O_2 react and form water?

Answer

O_2

4.2.2: Stoichiometry Calculations - Video

This project was preformed to supply **Libretext authors** with videos on General Chemistry topics which can be used to enhance their projects. Also, these videos are meant to act as a learning resource for **all General Chemistry students**.

Video Topics

This video discusses finding the mols and masses of reactants and products of a reaction by using stoichiometric factors (Mol Ratios). A reaction's stoichiometry can be used to create mole ratio conversion factor which link reactants and products. These types of calculation are a simplified version of the Limiting Reactant Problems which will come later.

Link to Video

Finding Mols and Masses of Reactants and Products Using Stoichiometric Factors (Mol Ratios): https://youtu.be/74mHV0CZcjw



4.2.2.1: Attribution

- Prof. Steven Farmer (Sonoma State University)

4.2.3: Percent Yield

The amount of product that *may be* produced by a reaction under specified conditions, as calculated per the stoichiometry of an appropriate balanced chemical equation, is called the theoretical yield of the reaction. The amount of product obtained when a reaction is actually carried out is the actual yield. The actual yield is often less than the theoretical yield. This may happen because a reaction also produces other side reactions and generates other products. It could also occur because some reactions do not go to completion and some of the limiting reagent remains when the reaction stops. And finally some products are difficult to collect and so some of the product is lost, which also reduces the actual yield. The extent to which a reaction's theoretical yield is achieved is commonly expressed as its percent yield:

$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

Actual and theoretical yields may be expressed as masses or molar amounts (or any other appropriate property; e.g., volume, if the product is a gas). As long as both yields are expressed using the same units, these units will cancel when percent yield is calculated.

Example 4.2.5: Calculation of Percent Yield

Upon reaction of 1.274 g of copper sulfate with excess zinc metal, 0.392 g copper metal was obtained according to the equation:

$$\mathrm{CuSO_4}(aq) + \mathrm{Zn}(s) \rightarrow \mathrm{Cu}(s) + \mathrm{ZnSO_4}(aq)$$

What is the percent yield?

Solution

The provided information identifies copper sulfate as the limiting reactant, and so the theoretical yield is found by the approach illustrated in the previous module, as shown here:

$$1.274\ \text{g}\ \cancel{\mathrm{CuSO_4}} \times \frac{1\ \text{mol}\ \cancel{\mathrm{CuSO_4}}}{159.62\ \text{g}\ \cancel{\mathrm{CuSO_4}}} \times \frac{1\ \text{mol}\ \cancel{\mathrm{Cu}}}{1\ \text{mol}\ \cancel{\mathrm{CuSO_4}}} \times \frac{63.55\ \text{g Cu}}{1\ \text{mol}\ \cancel{\mathrm{Cu}}} = 0.5072\ \text{g Cu}$$

Using this theoretical yield and the provided value for actual yield, the percent yield is calculated to be

$$\text{percent yield} = \left(\frac{\text{actual yield}}{\text{theoretical yield}}\right) \times 100$$

$$\text{percent yield} = \left(\frac{0.392 \text{ g Cu}}{0.5072 \text{ g Cu}}\right) \times 100$$
$$= 77.3\%$$

Exercise 4.2.5

What is the percent yield of a reaction that produces 12.5 g of the gas Freon CF_2Cl_2 from 32.9 g of CCl_4 and excess HF?

$$CCl_4 + 2\,HF \rightarrow CF_2Cl_2 + 2\,HCl$$

Answer

48.3%

4.2.4: Atom Economy

The purposeful design of chemical products and processes that minimize the use of environmentally hazardous substances and the generation of waste is known as *green chemistry*. Green chemistry is a philosophical approach that is being applied to many areas of science and technology, and its practice is summarized by guidelines known as the "Twelve Principles of Green Chemistry". One of the 12 principles is aimed specifically at maximizing the efficiency of processes for synthesizing chemical products. The *atom economy* of a process is a measure of this efficiency, defined as the percentage by mass of the desired product of a synthesis relative to the masses of *all* the reactants used:

$$\text{atom economy} = \frac{\text{mass of product}}{\text{mass of reactants}} \times 100\%$$

Though the definition of atom economy at first glance appears very similar to that for percent yield, be aware that this property represents a difference in the *theoretical* efficiencies of *different* chemical processes. The percent yield of a given chemical process, on the other hand, evaluates the efficiency of a process by comparing the yield of product actually obtained to the maximum yield predicted by stoichiometry.

The synthesis of the common nonprescription pain medication, ibuprofen, nicely illustrates the success of a green chemistry approach (Figure 4.2.3). First marketed in the early 1960s, ibuprofen was produced using a six-step synthesis that required 514 g of reactants to generate each mole (206 g) of ibuprofen, an atom economy of 40%. In the 1990s, an alternative process was developed by the BHC Company (now BASF Corporation) that requires only three steps and has an atom economy of ~80%, nearly twice that of the original process. The BHC process generates significantly less chemical waste; uses less-hazardous and recyclable materials; and provides significant cost-savings to the manufacturer (and, subsequently, the consumer). In recognition of the positive environmental impact of the BHC process, the company received the Environmental Protection Agency's Greener Synthetic Pathways Award in 1997.



Figure 4.2.3: (a) Ibuprofen is a popular nonprescription pain medication commonly sold as 200 mg tablets. (b) The BHC process for synthesizing ibuprofen requires only three steps and exhibits an impressive atom economy. (credit a: modification of work by Derrick Coetzee)

Example 4.2.6: Calculation of Atom Economy

Plants use carbon dioxide and water to produce fructose ($C_6H_{12}O_6$) and oxygen gas. Write a balanced chemical equation that describes this reaction and determine the atom economy for the production of fructose.

Solution

$$6CO_2(g) + 6H_2O(g) \rightarrow C_6H_{12}O_6(s) + 6O_2(aq) \tag{4.2.7}$$

To determine the atom economy calculate the mass of the desired product using the stoichiometry for the balanced reaction.

This reaction produces 1 mole of fructose with a molar mass of 180.16 g/mol, for a total mass of 180.16 g

This reaction uses 6 moles of carbon dioxide (44.01 g/mol) and 6 moles of water (18.01 g/mol) for a total mass of 372.12 g

The atom economy is:

$$\frac{180.16g}{372.12g} \times 100 = 48.14 \tag{4.2.8}$$

Exercise 4.2.6

Write a balanced chemical equation and determine the atom economy for the production of sucrose $C_{12}H_{22}O_{11}$ and oxygen gas from carbon dioxide and water.

Answer

47.13%

4.2.4.1: Airbags

Airbags (Figure 4.2.4) are a safety feature provided in most automobiles since the 1990s. The effective operation of an airbag requires that it be rapidly inflated with an appropriate amount (volume) of gas when the vehicle is involved in a collision. This requirement is satisfied in many automotive airbag systems through use of explosive chemical reactions, one common choice

being the decomposition of sodium azide, NaN_3. When sensors in the vehicle detect a collision, an electrical current is passed through a carefully measured amount of NaN_3 to initiate its decomposition:

$$2\,\mathrm{NaN_3}(s) \rightarrow 3\,\mathrm{N_2}(g) + 2\,\mathrm{Na}(s)$$

This reaction is very rapid, generating gaseous nitrogen that can deploy and fully inflate a typical airbag in a fraction of a second (~0.03–0.1 s). Among many engineering considerations, the amount of sodium azide used must be appropriate for generating enough nitrogen gas to fully inflate the air bag and ensure its proper function. For example, a small mass (~100 g) of NaN_3 will generate approximately 50 L of N_2.



Figure 4.2.4: Airbags deploy upon impact to minimize serious injuries to passengers. (credit: Jon Seidman)

4.2.5: Summary

When reactions are carried out using less-than-stoichiometric quantities of reactants, the amount of product generated will be determined by the limiting reactant. The amount of product generated by a chemical reaction is its actual yield. This yield is often less than the amount of product predicted by the stoichiometry of the balanced chemical equation representing the reaction (its theoretical yield). The extent to which a reaction generates the theoretical amount of product is expressed as its percent yield.

A balanced chemical equation may be used to describe a reaction's stoichiometry (the relationships between amounts of reactants and products). Coefficients from the equation are used to derive stoichiometric factors that subsequently may be used for computations relating reactant and product masses, molar amounts, and other quantitative properties.

4.2.6: Key Equations

$$\text{percent yield} = \left(\frac{\text{actual yield}}{\text{theoretical yield}}\right) \times 100$$

$$\text{atom economy} = \left(\frac{\text{mass desired product}}{\text{mass all reactants}}\right) \times 100$$

Glossary

actual yield
: amount of product formed in a reaction

excess reactant

reactant present in an amount greater than required by the reaction stoichiometry

limiting reactant

reactant present in an amount lower than required by the reaction stoichiometry, thus limiting the amount of product generated

percent yield

measure of the efficiency of a reaction, expressed as a percentage of the theoretical yield

stoichiometric factor

ratio of coefficients in a balanced chemical equation, used in computations relating amounts of reactants and products

stoichiometry

relationships between the amounts of reactants and products of a chemical reaction

theoretical yield

amount of product that may be produced from a given amount of reactant(s) according to the reaction stoichiometry

---

This page titled 4.2: Reaction Stoichiometry is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

- **4.4: Reaction Stoichiometry** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.
- **4.5: Reaction Yields** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

4.3: Classifying Chemical Reactions - Precipitation Reactions

Learning Objectives

- Predict the solubility of common inorganic compounds by using solubility rules
- Identify when a precipitation reaction will occur
- Write a balanced chemical equation that describes what happens when a precipitation reaction occurs
- Solve stoichiometry problems with precipitation reactions

Humans interact with one another in various and complex ways, and we classify these interactions according to common patterns of behavior. When two humans exchange information, we say they are communicating. When they exchange blows with their fists or feet, we say they are fighting. Faced with a wide range of varied interactions between chemical substances, scientists have likewise found it convenient (or even necessary) to classify chemical interactions by identifying common patterns of reactivity. This module will provide an introduction to precipitation reactions, one of the most prevalent types of chemical reactions.

4.3.1: Precipitation Reactions and Solubility Rules

A precipitation reaction is one in which dissolved substances react to form one (or more) solid products. Many reactions of this type involve the exchange of ions between ionic compounds in aqueous solution and are sometimes referred to as *double displacement*, *double replacement*, or *metathesis* reactions. These reactions are common in nature and are responsible for the formation of coral reefs in ocean waters and kidney stones in animals. They are used widely in industry for production of a number of commodity and specialty chemicals. Precipitation reactions also play a central role in many chemical analysis techniques, including spot tests used to identify metal ions and *gravimetric methods* for determining the composition of matter.

The extent to which a substance may be dissolved in water, or any solvent, is quantitatively expressed as its solubility, defined as the maximum concentration of a substance that can be achieved under specified conditions. Substances with relatively large solubilities are said to be soluble. A substance will precipitate when solution conditions are such that its concentration exceeds its solubility. Substances with relatively low solubilities are said to be insoluble, and these are the substances that readily precipitate from solution. For purposes of predicting the identities of solids formed by precipitation reactions, one may simply refer to patterns of solubility that have been observed for many ionic compounds (Table 4.3.1).

Table 4.3.1: Solubilities of Common Ionic Compounds in Water

Always Soluble compounds contain	
• alkali metal cations (Li^+, Na^+, K^+) • ammonium ion (NH_4^+) • acetate $(C_2H_3O_2^-)$ ion • nitrate (NO_3^-) ion	
Usually Soluble compounds contain	**Except if they also contain**
• halide ions (F^-, Cl^-, Br^-, and I^-) • sulfate (SO_4^{2-}) ion	• halides of Ag^+ and Pb^{2+} • sulfates of Ag^+ and Pb^{2+} and Ba^{2+}, Ca^{2+}, and Sr^{2+}
Usually Insoluble compounds contain	**Exceptions include**
• carbonate ion ((CO_3^{2-})) • phosphate ion ((PO_4^{3-})) • hydroxide ion (OH^-)	• carbonate with alkali metals or ammonium (NH_4^+) • phosphate with alkali metals or ammonium (NH_4^+) • hydroxides with alkali metals or ammonium (NH_4^+), Ba^{2+}, or Sr^{2+}

A vivid example of precipitation is shown in Figure 4.3.1 when solutions of potassium iodide and lead nitrate are mixed, resulting in the formation of solid lead iodide. Lead iodide is a bright yellow solid that was formerly used as an artist's pigment known as iodine yellow. The properties of pure PbI_2 crystals make them useful for fabrication of X-ray and gamma ray detectors. The balanced chemical reaction is:

$$2\,\mathrm{KI}(aq) + \mathrm{Pb(NO_3)_2}(aq) \rightarrow \mathrm{PbI_2}(s) + 2\,\mathrm{KNO_3}(aq) \tag{4.3.1}$$

The formation of the precipitate observed in Figure 4.3.1 is consistent with the solubility guidelines: The only insoluble compound among all those involved is lead iodide, one of the exceptions to the general solubility of iodide salts.

The net ionic equation for this reaction is:

$$\mathrm{Pb^{2+}}(aq) + 2\,\mathrm{I^-}(aq) \rightarrow \mathrm{PbI_2}(s) \tag{4.3.2}$$



Figure 4.3.1: A precipitate of PbI_2 forms when solutions containing Pb^{2+} and I^- are mixed. (credit: Der Kreole/Wikimedia Commons)

The solubility guidelines in Table 4.3.1 will predict if a precipitation reaction occurs when solutions of soluble ionic compounds are mixed together. To do this, first identify all the ions present in the solution and then consider if any possible cation/anion combination forms an insoluble compound. For example, mixing solutions of silver nitrate and sodium fluoride will yield a solution containing Ag^+, NO_3^-, Na^+, and F^- ions. The possible combinations include the two ionic compounds originally present in the solutions, $AgNO_3$ and NaF, which are both soluble in water. And two additional ionic compounds $NaNO_3$ and AgF. The solubility guidelines state all nitrate salts are soluble, so $NaNO_3$ will not form a precipitate. However, Ag^+ is an exception for halide ions so AgF forms a precipitate. The reaction is described by the following equations:

$$\mathrm{NaF}(aq) + \mathrm{AgNO_3}(aq) \rightarrow \mathrm{AgF}(s) + \mathrm{NaNO_3}(aq) \quad \text{(molecular)} \tag{4.3.3}$$

$$\mathrm{Na^+}(aq) + \mathrm{F^-}(aq) + \mathrm{Ag^+}(aq) + \mathrm{NO_3^-}(aq) \rightarrow \mathrm{AgF}(s) + \mathrm{Na^+}(aq) + \mathrm{NO_3^-}(aq) \quad \text{(complete ionic)} \tag{4.3.4}$$

$$\mathrm{Ag^+}(aq) + \mathrm{F^-}(aq) \rightarrow \mathrm{AgF}(s) \quad \text{(net ionic)} \tag{4.3.5}$$

Example 4.3.1: Predicting Precipitation Reactions

Predict the result of mixing reasonably concentrated solutions of the following ionic compounds. If precipitation is expected, write a balanced net ionic equation for the reaction.

a. potassium sulfate and barium nitrate
b. lithium chloride and silver acetate
c. lead nitrate and ammonium carbonate

Solution

(a) The two possible products for this combination are KNO_3 and $BaSO_4$. The solubility guidelines indicate $BaSO_4$ is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is

$$\mathrm{Ba^{2+}}(aq) + \mathrm{SO_4^{2-}}(aq) \rightarrow \mathrm{BaSO_4}(s)$$

(b) The two possible products for this combination are $LiC_2H_3O_2$ and AgCl. The solubility guidelines indicate AgCl is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

(c) The two possible products for this combination are $PbCO_3$ and NH_4NO_3. The solubility guidelines indicate $PbCO_3$ is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is

$$Pb^{2+}(aq) + CO_3^{2-}(aq) \rightarrow PbCO_3(s)$$

? Exercise 4.3.1

Which solution could be used to precipitate the barium ion, Ba^{2+}, in a water sample: sodium chloride, sodium hydroxide, or sodium sulfate? What is the formula for the expected precipitate?

Answer

sodium sulfate, $BaSO_4$

4.3.2: Solubility of Ionic Compounds - Video

Video Topics

This video discusses how to predict if a given ionic compound is soluble or insoluble in water. Solubility rules make these prediction based on the species making up the ionic compound. If the ionic compound is soluble it will disassociate in water to form strong electrolyte aqueous solution.

Link to Video

Predicting the Solubility of Ionic Compounds: https://youtu.be/U3QNwnfmvGU



4.3.3: Determining the Products of a Precipitation Reaction - Video

Video Topics

During a precipitation reaction, also called a double substitution reaction, the ions of two soluble ionic compounds recombine to form an insoluble ionic compound and a precipitate (solid) forms. This video discusses how to determining the molecular formula of the precipitate given the ionic species present in the reactants. In particular, combining different charged species to create a neutral compounds will be discussed.

Link to Video

Determining the Products for Precipitation Reactions: https://youtu.be/r0kYeZVuTAM



4.3.4: Determining the Net Ionic Equation - Video

Determining Net Ionic Equation for a Precipitation Reaction: https://youtu.be/AMJz1Sdz8IA



4.3.5: Gravimetric Analysis

A gravimetric analysis is one in which a sample is subjected to some treatment that causes a change in the physical state of the analyte that permits its separation from the other components of the sample. Mass measurements of the sample, the isolated analyte, or some other component of the analysis system, used along with the known stoichiometry of the compounds involved, permit calculation of the analyte concentration. Gravimetric methods were the first techniques used for quantitative chemical analysis, and they remain important tools in the modern chemistry laboratory.

The required change of state in a gravimetric analysis may be achieved by various physical and chemical processes. For example, the moisture (water) content of a sample is routinely determined by measuring the mass of a sample before and after it is subjected to a controlled heating process that evaporates the water. Also common are gravimetric techniques in which the analyte is subjected to a precipitation reaction of the sort described earlier in this chapter. The precipitate is typically isolated from the reaction mixture

by filtration, carefully dried, and then weighed (Figure 4.3.2). The mass of the precipitate may then be used, along with relevant stoichiometric relationships, to calculate analyte concentration.



Figure 4.3.2: Precipitate may be removed from a reaction mixture by filtration.

Example 4.3.2: Gravimetric Analysis

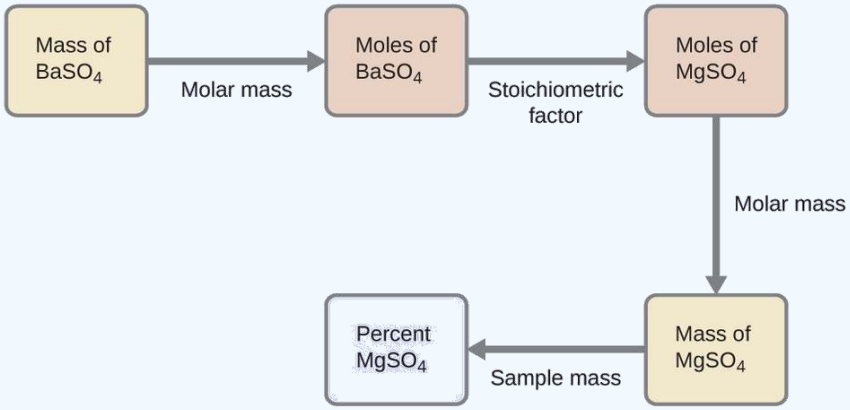
A 0.4550-g solid mixture containing $MgSO_4$ is dissolved in water and treated with an excess of $Ba(NO_3)_2$, resulting in the precipitation of 0.6168 g of $BaSO_4$.

$$MgSO_4(aq) + Ba(NO_3)_2(aq) \rightarrow BaSO_4(s) + Mg(NO_3)_2(aq)$$

What is the concentration (percent) of $MgSO_4$ in the original 0.4550 g solid mixture?

Solution

The plan for this calculation is similar to others used in stoichiometric calculations, the central step being the connection between the moles of $BaSO_4$ and $MgSO_4$ through their stoichiometric factor. Once the mass of $MgSO_4$ is computed, it may be used along with the mass of the sample mixture to calculate the requested percentage concentration.



The mass of $MgSO_4$ that would yield the provided precipitate mass is

$$0.6168 \text{ g } \cancel{BaSO_4} \times \frac{1 \text{ mol } \cancel{BaSO_4}}{233.43 \text{ g } \cancel{BaSO_4}} \times \frac{1 \text{ mol } \cancel{MgSO_4}}{1 \text{ mol } \cancel{BaSO_4}} \times \frac{120.37 \text{ g } MgSO_4}{1 \text{ mol } \cancel{MgSO_4}} = 0.3181 \text{ g } MgSO_4$$

The concentration of $MgSO_4$ in the sample mixture is then calculated to be

$$\text{percent } MgSO_4 = \frac{\text{mass } MgSO_4}{\text{mass sample}} \times 100\%$$

$$\frac{0.3181 \text{ g}}{0.4550 \text{ g}} \times 100\% = 69.91\%$$

? Exercise 4.3.2

What is the percent of chloride ion in a sample if 1.1324 g of the sample produces 1.0881 g of AgCl when treated with excess Ag^+?

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

Answer

23.76%

4.3.6: Summary

Chemical reactions are classified according to similar patterns of behavior. A large number of important reactions are included in three categories: precipitation, acid-base, and oxidation-reduction (redox). Precipitation reactions involve the formation of one or more insoluble products. Acid-base reactions involve the transfer of hydrogen ions between reactants. Redox reactions involve a change in oxidation number for one or more reactant elements. Writing balanced equations for some redox reactions that occur in aqueous solutions is simplified by using a systematic approach called the half-reaction method.

Glossary

insoluble
of relatively low solubility; dissolving only to a slight extent

precipitate
insoluble product that forms from reaction of soluble reactants

precipitation reaction
reaction that produces one or more insoluble products; when reactants are ionic compounds, sometimes called double-displacement or metathesis

salt
ionic compound that can be formed by the reaction of an acid with a base that contains a cation and an anion other than hydroxide or oxide

single-displacement reaction
(also, replacement) redox reaction involving the oxidation of an elemental substance by an ionic species

soluble
of relatively high solubility; dissolving to a relatively large extent

solubility
the extent to which a substance may be dissolved in water, or any solvent

analyte
chemical species of interest

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

quantitative analysis

the determination of the amount or concentration of a substance in a sample

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).
- Prof. Steven Farmer (Sonoma State University)

This page titled 4.3: Classifying Chemical Reactions - Precipitation Reactions is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

- **4.3: Classifying Chemical Reactions** is licensed CC BY 4.0.
- **4.6: Quantitative Chemical Analysis** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

4.4: Classifying Chemical Reactions - Acid Base Reactions

Learning Objectives

- Identify common acids and bases
- Identify when an acid-base reaction will occur
- Write a balanced chemical equation that describes what happens when a acid-base reaction occurs
- Solve stoichiometry problems with acid-base reactions

Humans interact with one another in various and complex ways, and we classify these interactions according to common patterns of behavior. When two humans exchange information, we say they are communicating. When they exchange blows with their fists or feet, we say they are fighting. Faced with a wide range of varied interactions between chemical substances, scientists have likewise found it convenient (or even necessary) to classify chemical interactions by identifying common patterns of reactivity. This module will provide an introduction to acid-base reactions, one of the most prevalent types of chemical reactions.

4.4.1: Acid Reactions

An acid-base reaction is one in which a hydrogen ion, H^+, is transferred from one chemical species to another. Such reactions are of central importance to numerous natural systems and manufacturing processes, ranging from the chemical transformations inside cells, lakes, and oceans; to the industrial-scale production of fertilizers, pharmaceuticals, and manufacturing materials.

For purposes of this brief introduction, we will only consider the acid-base reactions that take place in aqueous solutions. In this context, an acid is a substance that dissolves in water to yield hydronium ions, H_3O^+. As an example, consider the equation shown here for hydrochloric acid:

$$\mathrm{HCl}(aq) + \mathrm{H_2O}(aq) \rightarrow \mathrm{Cl^-}(aq) + \mathrm{H_3O^+}(aq) \tag{4.4.1}$$

The process represented by this equation shows hydrogen chloride is an acid. When dissolved in water, H^+ ions are transferred from HCl molecules to H_2O molecules to generate hydronium, H_3O^+, ions as shown in Figure 4.4.2.

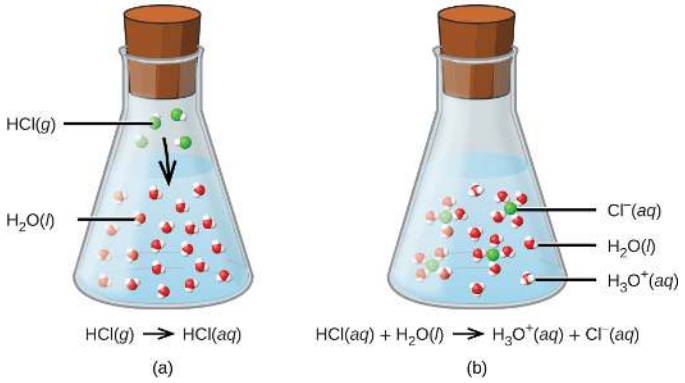


Figure 4.4.2: When hydrogen chloride gas dissolves in water, (a) it reacts as an acid, transferring protons to water molecules to yield (b) hydronium ions (and solvated chloride ions)

The nature of HCl is such that its reaction with water as just described is essentially 100% efficient: Virtually every HCl molecule that dissolves in water will undergo this reaction. Acids that completely react in this fashion are called strong acids, and HCl is one among just a handful of common acid compounds that are classified as strong (Table 4.4.1).

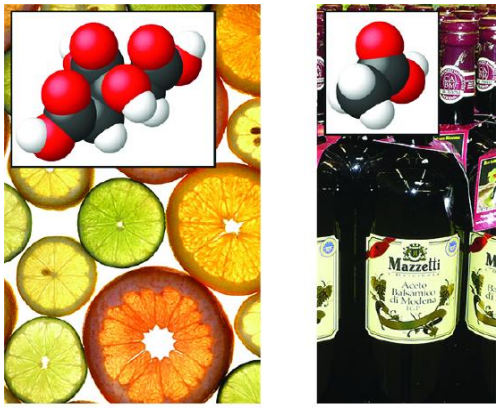
Table 4.4.2: Common Strong Acids

Compound Formula	Name in Aqueous Solution
HBr	hydrobromic acid
HCl	hydrochloric acid
HNO_3	nitric acid
H_2SO_4	sulfuric acid

A far greater number of compounds behave as weak acids and only partially react with water, leaving a large majority of dissolved molecules in their original form and generating a relatively small amount of hydronium ions. Weak acids are commonly encountered in nature. Examples include citric acid, the tangy taste of citrus fruits, formic acid, the stinging sensation of insect bites, and acetic acid, the main ingredient in vinegar. The reaction of acetic acid with water to produce acetate ions and hydronium ions is shown below. :

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{CH_3CO_2^-}(aq) + \mathrm{H_3O^+}(aq) \tag{4.4.2}$$

Notice the double arrow used to represent the equilibrium reaction where only some of the acetic acid molecules dissociate. When dissolved in water under typical conditions, only about 1% of acetic acid molecules are present in the ionized form, $\mathrm{CH_3CO_2^-}$. The double-arrow in the equation indicates that the reaction goes in both directions, which is why only some of the molecules are present in the ionized form. Other week acids are shown in Figure 4.4.3.



(a) (b)

Figure 4.4.3: (a) Fruits such as oranges, lemons, and grapefruit contain the weak acid citric acid. (b) Vinegars contain the weak acid acetic acid. (credit a: modification of work by Scott Bauer; credit b: modification of work by Brücke-Osteuropa/Wikimedia Commons)

4.4.2: Base Reactions

A base is a substance that will dissolve in water to yield hydroxide ions, OH^-. The most common bases are ionic compounds composed of alkali or alkaline earth metal cations (groups 1 and 2) combined with the hydroxide ion—for example, NaOH and $Ca(OH)_2$. When these compounds dissolve in water, hydroxide ions are released directly into the solution. For example, KOH and $Ba(OH)_2$ dissolve in water and dissociate completely to produce cations (K^+ and Ba^{2+}, respectively) and hydroxide ions, OH^-. These bases, along with other hydroxides that completely dissociate in water, are considered strong bases.

Consider as an example the dissolution of lye (sodium hydroxide) in water:

$$\mathrm{NaOH}(s) \rightarrow \mathrm{Na^+}(aq) + \mathrm{OH^-}(aq) \tag{4.4.3}$$

This equation confirms that sodium hydroxide is a base. When dissolved in water, NaOH dissociates to yield Na^+ and OH^- ions. This is also true for any other ionic compound containing hydroxide ions. Since the dissociation process is essentially complete when ionic compounds dissolve in water under typical conditions, NaOH and other ionic hydroxides are all classified as strong bases.

Unlike ionic hydroxides, some compounds produce hydroxide ions when dissolved by chemically reacting with water molecules. In all cases, these compounds react only partially and so are classified as weak bases. These types of compounds are also abundant in nature and important commodities in various technologies. For example, global production of the weak base ammonia is typically well over 100 million metric tons annually, being widely used as an agricultural fertilizer, a raw material for chemical synthesis of other compounds, and an active ingredient in household cleaners (Figure 4.4.4). When dissolved in water, ammonia reacts partially to yield hydroxide ions, as shown here:

$$\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq) \tag{4.4.4}$$

This is, by definition, an acid-base reaction, in this case involving the transfer of H^+ ions from water molecules to ammonia molecules. Under typical conditions, only about 1% of the dissolved ammonia is present as NH_4^+ ions.



(a) (b)

Figure 4.4.4: Ammonia is a weak base used in a variety of applications. (a) Pure ammonia is commonly applied as an agricultural fertilizer. (b) Dilute solutions of ammonia are effective household cleansers. (credit a: modification of work by National Resources Conservation Service; credit b: modification of work by pat00139)

4.4.3: Acid-Base Reactions

The chemical reactions described in which acids and bases dissolved in water produce hydronium and hydroxide ions, respectively, are, by definition, acid-base reactions. In these reactions, water serves as both a solvent *and* a reactant. A neutralization reaction is a specific type of acid-base reaction in which the reactants are an acid and a base, the products are often a salt and water, and neither reactant is the water itself:

$$\text{acid} + \text{base} \rightarrow \text{salt} + \text{water} \tag{4.4.5}$$

To illustrate a neutralization reaction, consider what happens when a typical antacid such as milk of magnesia (an aqueous suspension of solid $Mg(OH)_2$) is ingested to ease symptoms associated with excess stomach acid (HCl):

$$Mg(OH)_2(s) + 2\,HCl(aq) \rightarrow MgCl_2(aq) + 2\,H_2O(l). \tag{4.4.6}$$

Note that in addition to water, this reaction produces a salt, magnesium chloride.

Example 4.4.2: Writing Equations for Acid-Base Reactions

Write balanced chemical equations for the acid-base reactions described here:

a. the weak acid hydrogen hypochlorite reacts with water
b. a solution of barium hydroxide is neutralized with a solution of nitric acid

Solution

(a) The two reactants are provided, HOCl and H_2O. Since the substance is reported to be an acid, its reaction with water will involve the transfer of H^+ from HOCl to H_2O to generate hydronium ions, H_3O^+ and hypochlorite ions, OCl^-.

$$HOCl(aq) + H_2O(l) \rightleftharpoons OCl^-(aq) + H_3O^+(aq)$$

A double-arrow is appropriate in this equation because it indicates the HOCl is a weak acid that has not reacted completely.

(b) The two reactants are provided, $Ba(OH)_2$ and HNO_3. Since this is a neutralization reaction, the two products will be water and a salt composed of the cation of the ionic hydroxide (Ba^{2+}) and the anion generated when the acid transfers its hydrogen ion (NO_3^-).

$$Ba(OH)_2(aq) + 2\,HNO_3(aq) \rightarrow Ba(NO_3)_2(aq) + 2\,H_2O(l)$$

Exercise 4.4.21

Write the net ionic equation representing the neutralization of any strong acid with an ionic hydroxide. (Hint: Consider the ions produced when a strong acid is dissolved in water.)

Answer

$$H_3O^+(aq) + OH^-(aq) \rightarrow 2\,H_2O(l)$$

In the 18th century, the strength (actually the concentration) of vinegar samples was determined by noting the amount of potassium carbonate, K_2CO_3, which had to be added, a little at a time, before bubbling ceased. The greater the weight of potassium carbonate added to reach the point where the bubbling ended, the more concentrated the vinegar.

We now know that the effervescence that occurred during this process was due to reaction with acetic acid, CH_3CO_2H, the compound primarily responsible for the odor and taste of vinegar. Acetic acid reacts with potassium carbonate according to the following equation:

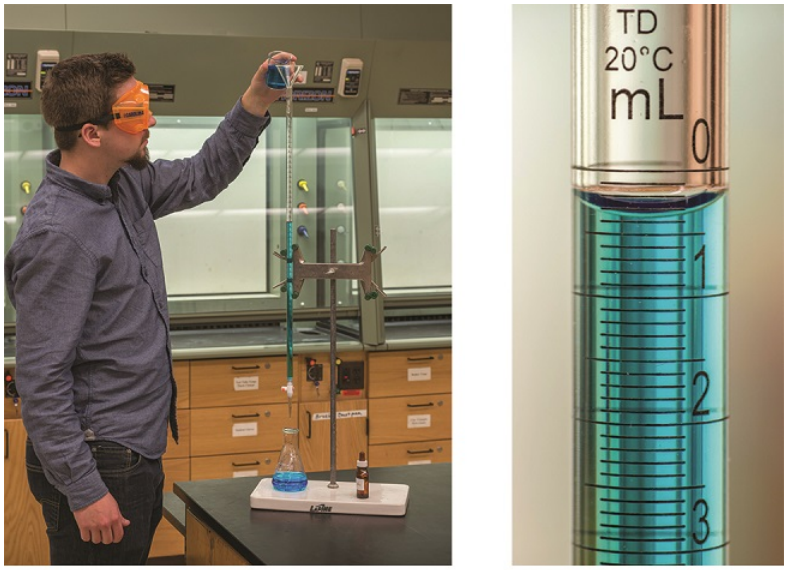
$$2\,\mathrm{CH_3CO_2H}(aq) + \mathrm{K_2CO_3}(s) \rightarrow 2\mathrm{KCH_3CO_3}(aq) + \mathrm{CO_2}(g) + \mathrm{H_2O}(l)$$

The bubbling was due to the production of CO_2.

The test of vinegar with potassium carbonate is one type of quantitative analysis—the determination of the amount or concentration of a substance in a sample. In the analysis of vinegar, the concentration of the solute (acetic acid) was determined from the amount of reactant that combined with the solute present in a known volume of the solution. In other types of chemical analyses, the amount of a substance present in a sample is determined by measuring the amount of product that results.

4.4.4: Titration

The described approach to measuring vinegar strength was an early version of the analytical technique known as titration analysis. A typical titration analysis involves the use of a buret (Figure 4.4.1) to make incremental additions of a solution containing a known concentration of some substance (the titrant) to a sample solution containing the substance whose concentration is to be measured (the analyte). The titrant and analyte undergo a chemical reaction of known stoichiometry, and so measuring the volume of titrant solution required for complete reaction with the analyte (the equivalence point of the titration) allows calculation of the analyte concentration. The equivalence point of a titration may be detected visually if a distinct change in the appearance of the sample solution accompanies the completion of the reaction. The halt of bubble formation in the classic vinegar analysis is one such example, though, more commonly, special dyes called indicators are added to the sample solutions to impart a change in color at or very near the equivalence point of the titration. Equivalence points may also be detected by measuring some solution property that changes in a predictable way during the course of the titration. Regardless of the approach taken to detect a titration's equivalence point, the volume of titrant actually measured is called the end point. Properly designed titration methods typically ensure that the difference between the equivalence and end points is negligible. Though any type of chemical reaction may serve as the basis for a titration analysis, precipitation and acid-base reactions are most common.



(a) (b)

Figure 4.4.1: (a) A student fills a buret in preparation for a titration analysis. (b) A typical buret permits volume measurements to the nearest 0.1 mL. (credit a: modification of work by Mark Blaser and Matt Evans; credit b: modification of work by Mark Blaser and Matt Evans)

Example 4.4.1: Titration Analysis

The end point in a titration of a 50.00-mL sample of aqueous HCl was reached by addition of 35.23 mL of 0.250 M NaOH titrant. The titration reaction is:

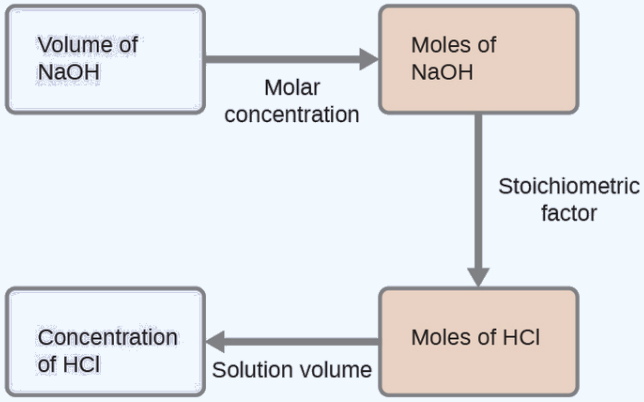
$$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \rightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l)$$

What is the molarity of the HCl?

Solution

As for all reaction stoichiometry calculations, the key issue is the relation between the molar amounts of the chemical species of interest as depicted in the balanced chemical equation. The approach outlined in previous modules of this chapter is followed, with additional considerations required, since the amounts of reactants provided and requested are expressed as solution concentrations.

For this exercise, the calculation will follow the following outlined steps:



The molar amount of HCl is calculated to be:

$$35.23\ \text{mL}\ \cancel{\text{NaOH}} \times \frac{1\ \cancel{\text{L}}}{1000\ \cancel{\text{mL}}} \times \frac{0.250\ \text{mol}\ \cancel{\text{NaOH}}}{1\ \cancel{\text{L}}} \times \frac{1\ \text{mol HCl}}{1\ \text{mol}\ \cancel{\text{NaOH}}} = 8.81 \times 10^{-3}\ \text{mol HCl}$$

Using the provided volume of HCl solution and the definition of molarity, the HCl concentration is:

$$M = \frac{\text{mol HCl}}{\text{L solution}}$$

$$M = \frac{8.81 \times 10^{-3}\ \text{mol HCl}}{50.00\ \text{mL} \times \frac{1\ \text{L}}{1000\ \text{mL}}}$$

$$M = 0.176\ M$$

Note: For these types of titration calculations, it is convenient to recognize that solution molarity is also equal to the number of *milli*moles of solute per *milli*liter of solution:

$$M = \frac{\text{mol solute}}{\text{L solution}} \times \frac{\frac{10^3\ \text{mmol}}{\text{mol}}}{\frac{10^3\ \text{mL}}{\text{L}}} = \frac{\text{mmol solute}}{\text{mL solution}}$$

Using this version of the molarity unit will shorten the calculation by eliminating two conversion factors:

$$\frac{35.23\ \text{mL NaOH} \times \frac{0.250\ \text{mmol NaOH}}{\text{mL NaOH}} \times \frac{1\ \text{mmol HCl}}{1\ \text{mmol NaOH}}}{50.00\ \text{mL solution}} = 0.176\ M\,\text{HCl}$$

? Exercise 4.4.1

A 20.00-mL sample of aqueous oxalic acid, $H_2C_2O_4$, was titrated with a 0.09113-*M* solution of potassium permanganate, $KMnO_4$.

$$2\,MnO_4^-(aq) + 5\,H_2C_2O_4(aq) + 6\,H^+(aq) \rightarrow 10\,CO_2(g) + 2\,Mn^{2+}(aq) + 8\,H_2O(l)$$

A volume of 23.24 mL was required to reach the end point. What is the oxalic acid molarity?

Answer

0.2648 *M*

4.4.5: Summary

Chemical reactions are classified according to similar patterns of behavior. A large number of important reactions are included in three categories: precipitation, acid-base, and oxidation-reduction (redox). Precipitation reactions involve the formation of one or more insoluble products. Acid-base reactions involve the transfer of hydrogen ions between reactants. Redox reactions involve a change in oxidation number for one or more reactant elements. Writing balanced equations for some redox reactions that occur in aqueous solutions is simplified by using a systematic approach called the half-reaction method.

Glossary

acid
substance that produces H_3O^+ when dissolved in water

acid-base reaction
reaction involving the transfer of a hydrogen ion between reactant species

base
substance that produces OH^- when dissolved in water

neutralization reaction
reaction between an acid and a base to produce salt and water

strong acid
acid that reacts completely when dissolved in water to yield hydronium ions

strong base
base that reacts completely when dissolved in water to yield hydroxide ions

weak acid
acid that reacts only to a slight extent when dissolved in water to yield hydronium ions

weak base
base that reacts only to a slight extent when dissolved in water to yield hydroxide ions

analyte
chemical species of interest

buret
device used for the precise delivery of variable liquid volumes, such as in a titration analysis

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*)

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

indicator
substance added to the sample in a titration analysis to permit visual detection of the end point

quantitative analysis

the determination of the amount or concentration of a substance in a sample

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

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 4.4: Classifying Chemical Reactions - Acid Base Reactions is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

- **4.3: Classifying Chemical Reactions** is licensed CC BY 4.0.
- **4.6: Quantitative Chemical Analysis** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

4.5: Classifying Chemical Reactions - Combustion Reactions

Learning Objectives

- Define combustion reactions
- Identify when a combustion reaction will occur
- Write a balanced chemical equation that describes what happens when a combustion reaction occurs
- Solve stoichometry problems with combustion reactions

Humans interact with one another in various and complex ways, and we classify these interactions according to common patterns of behavior. When two humans exchange information, we say they are communicating. When they exchange blows with their fists or feet, we say they are fighting. Faced with a wide range of varied interactions between chemical substances, scientists have likewise found it convenient (or even necessary) to classify chemical interactions by identifying common patterns of reactivity. This module will provide an introduction to combustion reactions, one of the most prevalent types of chemical reactions.

4.5.1: Combustion Reactions

Combustion reactions are another common class of reactions. These reactions provide the energy to drive your car, heat your home, and cook your food. Anytime something burns, it is a combustion reaction. These reactions are critical to our economy but they are also responsible for emitting 35 gigatons of CO_2 into the atmosphere in 2020. In a combustion reaction a fuel, like methane, reacts with oxygen to produce carbon dioxide and water. Almost all combustion reactions require additional oxygen, which comes from the atmosphere, with the reactants. In a combustion reaction all the carbon in the reactants is converted into carbon dioxide and all the hydrogen in the reactants is converted into water.

Example 4.5.1: Writing Equations for Combustion Reactions

Write balanced chemical equations for the combustion reaction described here:

a. the combustion of methane, CH_4
b. the combustion of ethane, C_2H_6

Solution

(a) In addition to methane, CH_4, the combustion reaction also requires oxygen from the atmosphere. The products of the combustion reaction will be H_2O and CO_2.

$$\mathrm{CH_4}(g) + 2\,\mathrm{O_2}(g) \rightarrow \mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(l)$$

(b) In addition to ethane, C_2H_6, the combustion reaction also requires oxygen from the atmosphere. The products of the combustion reaction will be H_2O and CO_2.

$$2\,\mathrm{C_2H_6}(g) + 7\,\mathrm{O_2}(g) \rightarrow 4\,\mathrm{CO_2}(g) + 6\,\mathrm{H_2O}(l)$$

Notice that balancing the reaction requires doubling the number of ethane molecules so that the coefficient for oxygen is a whole number.

Exercise 4.5.1

Write the balanced equation for the combustion of methanol, CH_3OH

Answer

$$2\,\mathrm{CH_3OH}(l) + 3\,\mathrm{O_2}(g) \rightarrow 2\,\mathrm{CO_2}(g) + 4\,\mathrm{H_2O}(l)$$

4.5.2: Combustion in Biological Systems

Similar reactions also occur in biological systems. The overall chemical reaction that occurs in aerobic respiration is basically the same as the combustion of glucose. In biological systems these reactions are broken down into small steps to control the release of energy. The overall reaction for the combustion of glucose is:

$$\mathrm{C_6H_{12}O_6}(s) + 6\ \mathrm{O_2}(g) \rightarrow 6\ \mathrm{CO_2}(g) + 6\ \mathrm{H_2O}(l)$$

4.5.3: Combustion Analysis

The elemental composition of hydrocarbons and related compounds may be determined via a gravimetric method known as combustion analysis. In a combustion analysis, a weighed sample of the compound is heated to a high temperature under a stream of oxygen gas, resulting in its complete combustion to yield gaseous products of known identities. The complete combustion of hydrocarbons, for example, will yield carbon dioxide and water as the only products. The gaseous combustion products are swept through separate, preweighed collection devices containing compounds that selectively absorb each product (Figure 4.5.1). The mass increase of each device corresponds to the mass of the absorbed product and may be used in an appropriate stoichiometric calculation to derive the mass of the relevant element.

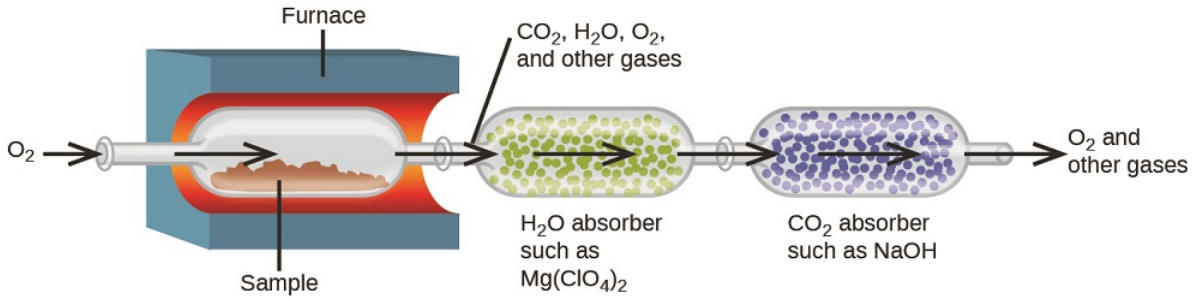


Figure 4.5.1: This schematic diagram illustrates the basic components of a combustion analysis device for determining the carbon and hydrogen content of a sample.

Example 4.5.2: Combustion Analysis

Polyethylene is a hydrocarbon polymer used to produce food-storage bags and many other flexible plastic items. A combustion analysis of a 0.00126-g sample of polyethylene yields 0.00394 g of CO_2 and 0.00161 g of H_2O. What is the empirical formula of polyethylene?

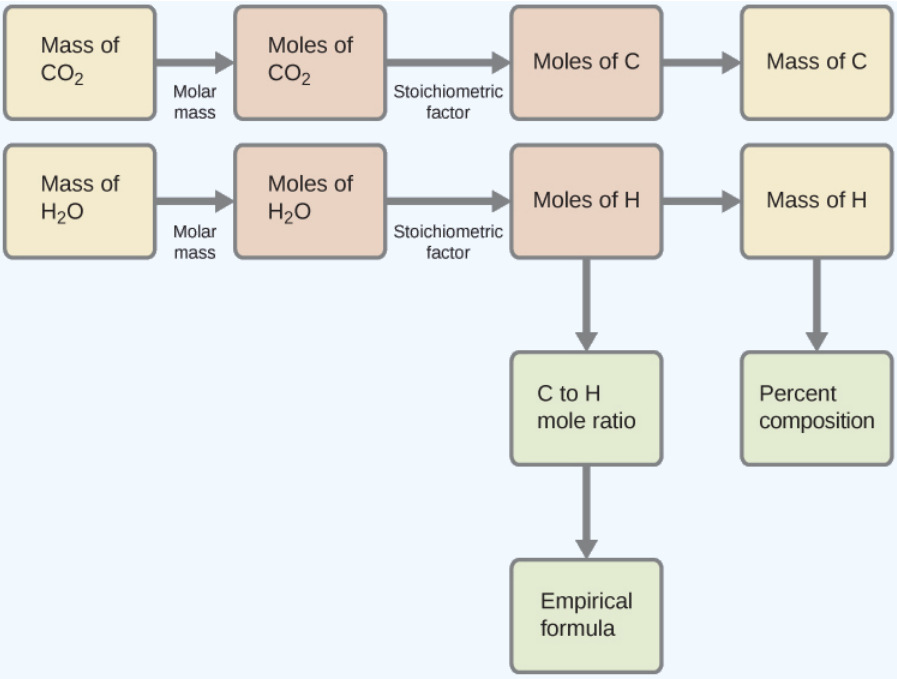
Solution

The primary assumption in this exercise is that all the carbon in the sample combusted is converted to carbon dioxide, and all the hydrogen in the sample is converted to water:

$$\mathrm{C_xH_y}(s) + \text{excess}\ \mathrm{O_2}(g) \rightarrow x\mathrm{CO_2}(g) + \frac{y}{2}\mathrm{H_2O}(g)$$

Note that a balanced equation is not necessary for the task at hand. To derive the empirical formula of the compound, only the subscripts *x* and *y* are needed.

First, calculate the molar amounts of carbon and hydrogen in the sample, using the provided masses of the carbon dioxide and water, respectively. With these molar amounts, the empirical formula for the compound may be written as described in the previous chapter of this text. An outline of this approach is given in the following flow chart:



$$\text{mol C} = 0.00394 \text{ g } CO_2 \times \frac{1 \text{ mol } CO_2}{44.01 \text{ g/mol}} \times \frac{1 \text{ mol C}}{1 \text{ mol } CO_2} = 8.95 \times 10^{-5} \text{ mol C}$$

$$\text{mol H} = 0.00161 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g/mol}} \times \frac{2 \text{ mol H}}{1 \text{ mol } H_2O} = 1.79 \times 10^{-4} \text{ mol H}$$

The empirical formula for the compound is then derived by identifying the smallest whole-number multiples for these molar amounts. The H-to-C molar ratio is

$$\frac{\text{mol H}}{\text{mol C}} = \frac{1.79 \times 10^{-4} \text{ mol H}}{8.95 \times 10^{-5} \text{ mol C}} = \frac{2 \text{ mol H}}{1 \text{ mol C}}$$

and the empirical formula for polyethylene is CH_2.

? Exercise 4.5.2

A 0.00215-g sample of polystyrene, a polymer composed of carbon and hydrogen, produced 0.00726 g of CO_2 and 0.00148 g of H_2O in a combustion analysis. What is the empirical formula for polystyrene?

Answer

CH

4.5.4: Summary

Chemical reactions are classified according to similar patterns of behavior. A large number of important reactions are included in three categories: precipitation, acid-base, and combustion. Precipitation reactions involve the formation of one or more insoluble products. Acid-base reactions involve the transfer of hydrogen ions between reactants.

Glossary

combustion analysis

gravimetric technique used to determine the elemental composition of a compound via the collection and weighing of its gaseous combustion products

combustion reaction

vigorous redox reaction producing significant amounts of energy in the form of heat and, sometimes, light

4.5.5: 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 4.5: Classifying Chemical Reactions - Combustion Reactions is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

- **4.3: Classifying Chemical Reactions** is licensed CC BY 4.0.
- **4.6: Quantitative Chemical Analysis** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

4.E: Stoichiometry of Chemical Reactions- Homework

4.E.1: For Chapter 4 you MUST Know

- Solubility rules for:
  - Always Soluble: lithium, sodium, potassium, ammonium, acetate, and nitrate
  - Usually Soluble with exceptions for silver (I) and lead (II)
    - chloride, bromide, iodide
    - sulfate with additional exceptions for calcium, strontium, and barium
  - Usually NOT soluble with exceptions for ammonium and alkali metals
    - carbonate
    - phosphate
    - hydroxides added exceptions for strontium, and barium

4.E.2: Turn in your answers for the following questions - show your work

1. Balance the following equations. Give the names of the reactants and the products. Given 10.0 grams of each reactant. How many grams of each product could be produced? What is the total mass of reactants and products when the reaction is complete?
   a. CH_4 (g) + O_2 (g) --> CO_2 (g) + H_2O (g)
   b. NaCl (aq) + $AgNO_3$ (aq) --> AgCl (s) + $NaNO_3$ (aq)
2. Solution Reaction
   a. 10.00 grams of solid potassium hydroxide is added to 250.0 mL of distilled water. Write a chemical equation that describes what happens. Calculate the moles of each product.
   b. 10.00 grams of pure hydrochloric acid is added to 250.0 mL of distilled water. Write a chemical equation that describes what happens. Calculate the moles of each product.
   c. The two solutions are mixed together.
      1. Write a chemical equation that describes what happens.
      2. Calculate the moles of each product.
      3. Calculate the molarity of each product.
3. Solution Reaction
   a. 5.00 grams of sodium chloride is diluted to 100.0 mL with distilled water. Write a chemical equation that describes what happens, calculate the concentration of each ion in solution, calculate the mass of any solid.
   b. 5.00 grams of silver (I) nitrate is diluted to 100.0 mL with distilled water. Write a chemical equation that describes what happens, calculate the concentration of each ion in solution, and calculate the mass of any solid.
   c. The two solutions above are mixed together.
      1. Write a chemical equation that describes what happens
      2. Calculate the moles of each ion in the final solution
      3. Calculate the mass of any solid product
      4. Calculate the molarity of each ion in the final solution

4.E.3: The Following Questions are for your practice - Do Not Turn In. They include answers so you can check your work

4.E.3.1: Writing and Balancing Chemical Equations

1. Write a balanced molecular equation describing each of the following chemical reactions.
   a. Solid calcium carbonate is heated and decomposes to solid calcium oxide and carbon dioxide gas.
   b. Gaseous butane, C_4H_{10}, reacts with diatomic oxygen gas to yield gaseous carbon dioxide and water vapor.

   Answer a

   $$\mathrm{CaCO_3}(s) \rightarrow \mathrm{CaO}(s) + \mathrm{CO_2}(g) \ ;$$

   Answer b

   $$2\,\mathrm{C_4H_{10}}(g) + 13\,\mathrm{O_2}(g) \rightarrow 8\,\mathrm{CO_2}(g) + 10\,\mathrm{H_2O}(g) \ ;$$

2. From the balanced molecular equations, write the complete ionic and net ionic equations for the following:

a. $K_2C_2O_4(aq) + Ba(OH)_2(aq) \rightarrow 2\,KOH(aq) + BaC_2O_2(s)$

answer

$$2\,K^+(aq) + C_2O_4^{2-}(aq) + Ba^{2+}(aq) + 2\,OH^-(aq) \rightarrow 2\,K^+(aq) + 2\,OH^-(aq) + BaC_2O_4(s) \quad \text{(complete)} \quad (4.E.1)$$

$$Ba^{2+}(aq) + C_2O_4^{2-}(aq) \rightarrow BaC_2O_4(s) \quad \text{(net)} \quad (4.E.2)$$

4.E.3.2: Classifying Chemical Reactions

Complete and balance the equations for the following acid-base neutralization reactions. If water is used as a solvent, write the reactants and products as aqueous ions. In some cases, there may be more than one correct answer, depending on the amounts of reactants used.

1. a. $Mg(OH)_2(s) + HClO_4(aq) \rightarrow$
   b. $SO_3(g) + H_2O(l) \rightarrow$ (assume an excess of water and that the product dissolves)

answer a

$Mg(OH)_2(s) + 2\,HClO_4(aq) \rightarrow Mg^{2+}(aq) + 2\,ClO_4^-(aq) + 2\,H_2O(l)$;

answer b

$SO_3(g) + 2\,H_2O(l) \rightarrow H_3O^+(aq) + HSO_4^-(aq)$, (a solution of H_2SO_4);

4.E.3.3: Reaction Stoichiometry

1. H_2 is produced by the reaction of 118.5 mL of a 0.8775-M solution of H_3PO_4 according to the following equation: $2\,Cr + 2\,H_3PO_4 \rightarrow 3\,H_2 + 2\,CrPO_4$.
   a. Outline the steps necessary to determine the number of moles and mass of H_2.

   Answer

   1. Convert mL to L
   2. Multiply L by the molarity to determine moles of H_3PO_4
   3. Convert moles of H_3PO_4 to moles of H_2
   4. Multiply moles of H_2 by the molar mass of H_2 to get the answer in grams

   b. Perform the calculations outlined.

   Answer

   1. $118.5\ mL \times \dfrac{1\ L}{1000\ mL} = 0.1185\ L$
   2. $0.1185\ L \times \dfrac{0.8775\ moles\ H_3PO_4}{1\ L} = 0.1040\ moles\ H_3PO_4$
   3. $0.1040\ moles\ H_3PO_4 \times \dfrac{3\ moles\ H_2}{2\ moles\ H_3PO_4} = 0.1560\ moles\ H_2$
   4. $0.1560\ moles\ H_2 \times \dfrac{2.02g}{1\ mole} = 0.3151g\ H_2$

2. Carborundum is silicon carbide, SiC, a very hard material used as an abrasive on sandpaper and in other applications. It is prepared by the reaction of pure sand, SiO_2, with carbon at high temperature. Carbon monoxide, CO, is the other product of this reaction. Write the balanced equation for the reaction, and calculate how much SiO_2 is required to produce 3.00 kg of SiC.

   Answer

   $SiO_2 + 3\,C \rightarrow SiC + 2\,CO$, 4.50 kg SiO_2

3. Urea, $CO(NH_2)_2$, is manufactured on a large scale for use in producing urea-formaldehyde plastics and as a fertilizer. What is the maximum mass of urea that can be manufactured from the CO_2 produced by combustion of 1.00×10^3 kg of carbon followed by the reaction?

$$CO_2(g) + 2\,NH_3(g) \rightarrow CO(NH_2)_2(s) + H_2O(l) \quad (4.E.3)$$

Answer

5.00×10^3 kg

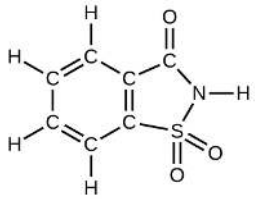
4.E.3.4: Reaction Yields

1. Freon-12, CCl_2F_2, is prepared from CCl_4 by reaction with HF. The other product of this reaction is HCl. Outline the steps needed to determine the percent yield of a reaction that produces 12.5 g of CCl_2F_2 from 32.9 g of CCl_4. Freon-12 has been banned and is no longer used as a refrigerant because it catalyzes the decomposition of ozone and has a very long lifetime in the atmosphere. Determine the percent yield.

Answer

$$\text{g } CCl_4 \rightarrow \text{mol } CCl_4 \rightarrow \text{mol } CCl_2F_2 \rightarrow \text{g } CCl_2F_2, \text{ percent yield} = 48.3\%$$

2. How many molecules of the sweetener saccharin can be prepared from 30 C atoms, 25 H atoms, 12 O atoms, 8 S atoms, and 14 N atoms?



Answer

Only four molecules can be made.

4.E.3.5: Quantitative Chemical Analysis

1. Titration of a 20.0-mL sample of acid rain required 1.7 mL of 0.0811 *M* NaOH to reach the end point. If we assume that the acidity of the rain is due to the presence of sulfuric acid, what was the concentration of sulfuric acid in this sample of rain?

Answer

3.4×10^{-3} *M* H_2SO_4

2. A 0.025-g sample of a compound composed of boron and hydrogen, with a molecular mass of ~28 amu, burns spontaneously when exposed to air, producing 0.063 g of B_2O_3. What are the empirical and molecular formulas of the compound.

Answer

The empirical formula is BH_3. The molecular formula is B_2H_6.

This page titled 4.E: Stoichiometry of Chemical Reactions- Homework is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

CHAPTER OVERVIEW

5: Electronic Structure and Periodic Properties

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

General Chemistry

The study of chemistry must at some point extend to the molecular level, for the physical and chemical properties of a substance are ultimately explained in terms of the structure and bonding of molecules. This module introduces some basic facts and principles that are needed for a discussion of organic molecules.

5.1: Light and Atomic Structure

5.2: Development of Quantum Theory

5.3: Electronic Structure of Atoms (Electron Configurations)

5.4: Periodic Variations in Element Properties

5.E: Electronic Structure and Periodic Properties- Homework

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 5: Electronic Structure and Periodic Properties is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

5.1: Light and Atomic Structure

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
- Describe the Bohr model of the hydrogen atom
- Use the Rydberg equation to calculate energies of light emitted or absorbed by hydrogen atoms

5.1.1: Light and Electromagnetic Energy

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 traveling 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 traveling 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.

5.1.1.1: 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 5.1.1, 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 sound is the loudness.

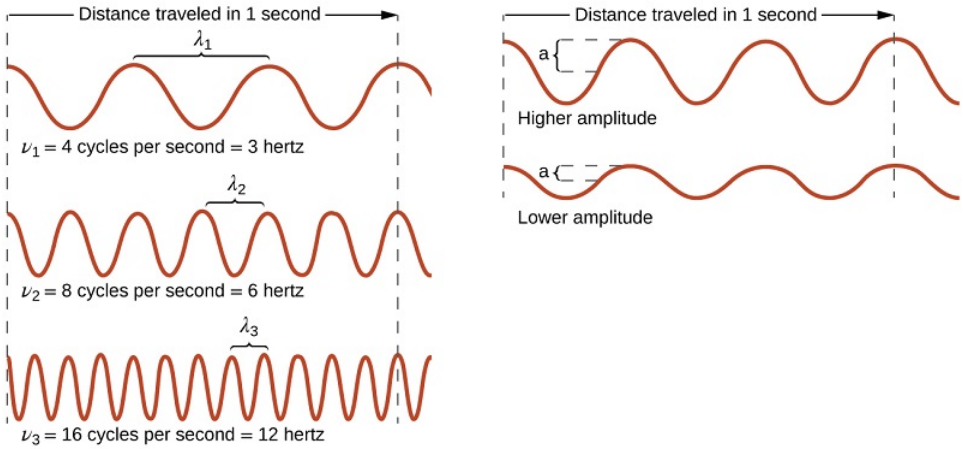


Figure 5.1.1: One-dimensional sinusoidal waves show the relationship among wavelength, frequency, and speed. The wave with the shortest wavelength has the highest frequency. Amplitude is one-half the height of the wave from peak to trough. (CC BY 4.0; OpenStax)

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:

$$c = 2.998 \times 10^8\ \mathrm{ms}^{-1} = \lambda\nu \tag{5.1.1}$$

Wavelength and frequency are inversely proportional: As the wavelength increases, the frequency decreases. The inverse proportionality is illustrated in Figure 5.1.2. 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).

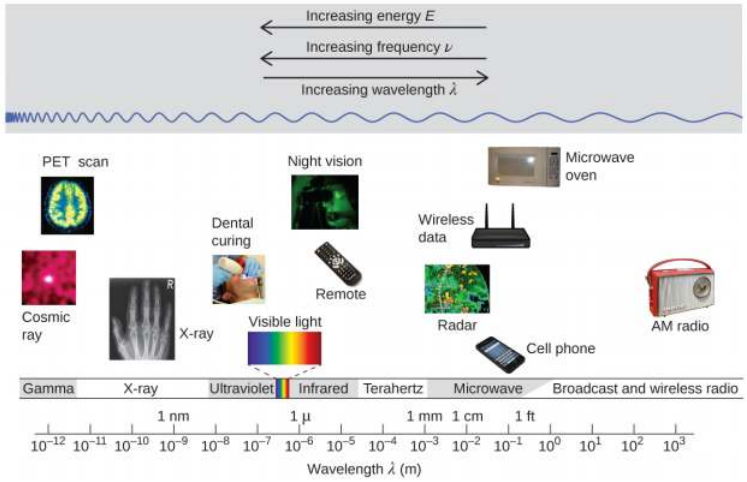


Figure 5.1.2: Portions of the electromagnetic spectrum are shown in order of decreasing frequency and increasing wavelength. Examples of some applications for various wavelengths include positron emission tomography (PET) scans, X-ray imaging, remote controls, wireless Internet, cellular telephones, 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 5.1.1: 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 5.1.1 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 5.1.1

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

One particularly characteristic phenomenon of waves results when two or more waves come into contact: They interfere with each other. Figure 5.1.3 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 5.1.3 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.

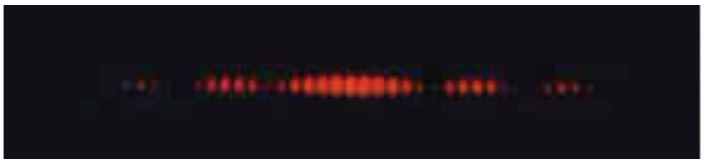


Figure 5.1.3: Interference fringe patterns are shown for light passing through two closely spaced, narrow slits. The spacing of the fringes depends on the wavelength, with the fringes being more closely spaced for the shorter-wavelength blue light. (credit: PASCO)

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 traveling 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 5.1.4 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 5.1.4. 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.

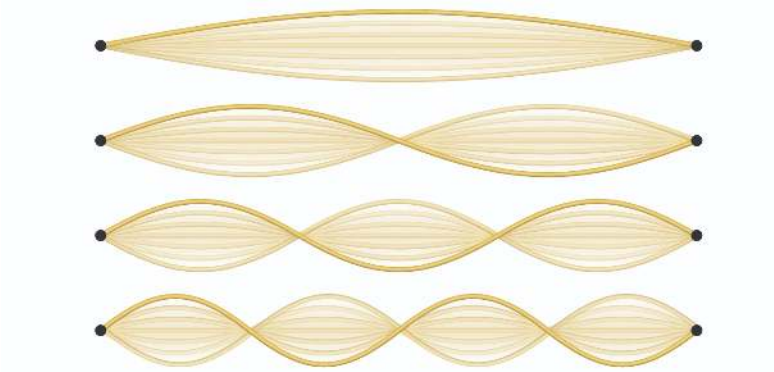


Figure 5.1.4: A vibrating string shows some one-dimensional standing waves. Since the two end points of the string are held fixed, only waves having an integer number of half-wavelengths can form. The points on the string between the end points that are not moving are called the nodes.

An example of two-dimensional standing waves is shown in Figure 5.1.5 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. 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 5.1.5 shows two radial nodes, while the image in the lower right shows the vibrational pattern associated with three radial nodes and two angular nodes.

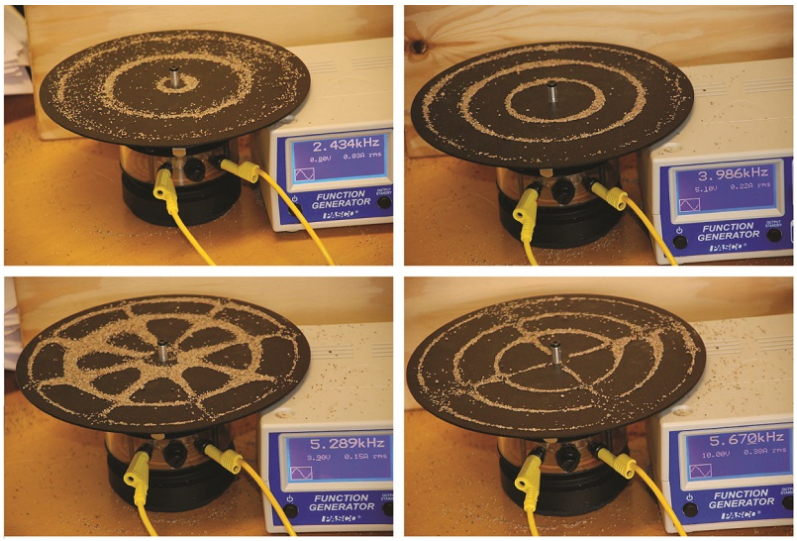


Figure 5.1.5: *Two-dimensional standing waves can be visualized on a vibrating surface. The surface has been sprinkled with a powder that collects near the nodal lines. There are two types of nodes visible: radial nodes (circles) and angular nodes (radii). For a more animated video, check this link out.*

5.1.1.2: The Photoelectric Effect

The next paradox in the classical theory to be resolved concerned the photoelectric effect (Figure 5.1.6). 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 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 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, not amplitude. 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. This shows the brightness or intensity of light depends on the number of photos, not the amplitude of the wave.

According to Planck's formula where E is the energy of a single photon, h is planks constant (6.62607015 x 10^{-34} J sec) and ν is the frequency.

$$E = \mathrm{h}\nu \tag{5.1.2}$$

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.

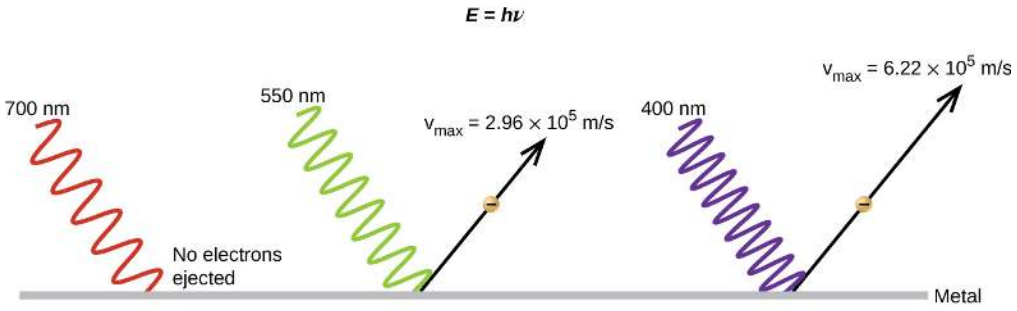


Figure 5.1.6: Photons with low frequencies do not have enough energy to cause electrons to be ejected via the photoelectric effect. For any frequency of light above the threshold frequency, the kinetic energy of an ejected electron will increase linearly with the energy of the incoming photon.

Example 5.1.2: 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.

$$\begin{aligned} E &= \frac{hc}{\lambda} \\ &= \frac{(6.626 \times 10^{-34}\ \mathrm{J\ \cancel{s}})(2.998 \times 10^{8}\ \mathrm{m\ \cancel{s}^{-1}})}{(640\ \mathrm{\cancel{nm}})\left(\frac{1\ \mathrm{m}}{10^{9}\ \mathrm{\cancel{nm}}}\right)} \\ &= 3.10 \times 10^{-19}\ \mathrm{J} \end{aligned}$$

? Exercise 5.1.2

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

5.1.1.3: 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. 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.

In contrast to continuous spectra, light can also occur as discrete or line spectra having very narrow line widths interspersed throughout the spectral regions. 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 5.1.7). Each element displays its own characteristic set of lines, as do molecules, although their spectra are generally much more complicated.



Figure 5.1.7: 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 5.1.8.

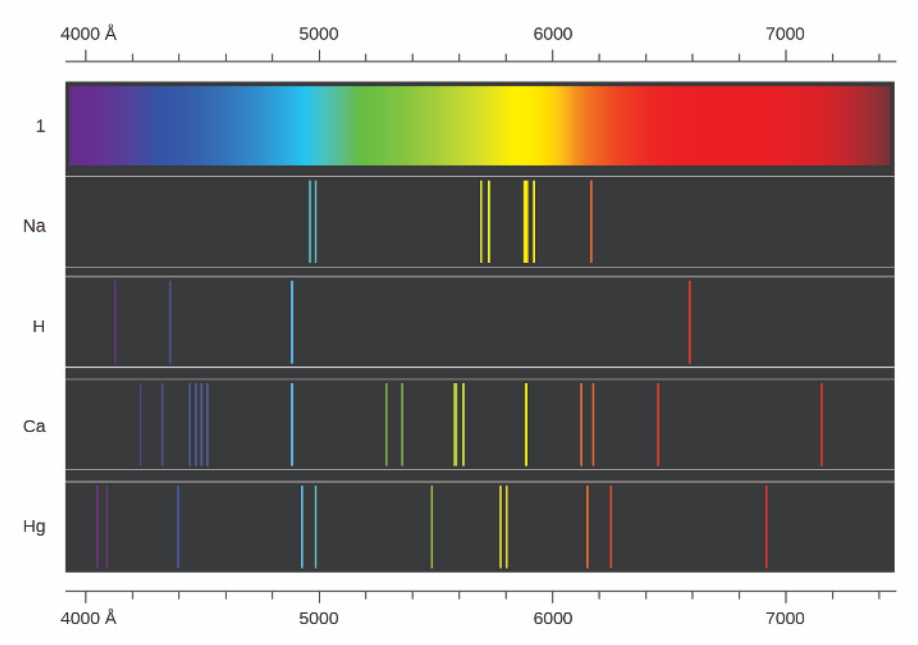


Figure 5.1.8: Line spectra of select gas. Compare the two types of emission spectra: continuous spectrum of white light (top) and the line spectra of the light from excited sodium, hydrogen, calcium, and mercury atoms.

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:

$$\frac{1}{\lambda} = k\left(\frac{1}{4} - \frac{1}{n^2}\right),\ n = 3,\ 4,\ 5,\ 6 \tag{5.1.3}$$

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 ($1.097 \times 10^7\ \text{m}^{-1}$).

$$\frac{1}{\lambda} = R_\infty\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{5.1.4}$$

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.

5.1.2: Atomic Structure

Following the work of Ernest Rutherford and his colleagues in the early twentieth century, the picture of atoms consisting of tiny dense nuclei surrounded by lighter and even tinier electrons continually moving about the nucleus was well established. This picture was called the planetary model, since it pictured the atom as a miniature “solar system” with the electrons orbiting the nucleus like planets orbiting the sun. The simplest atom is hydrogen, consisting of a single proton as the nucleus about which a single electron moves. This classical mechanics description of the atom is incomplete, however, since an electron moving in an elliptical orbit would be accelerating (by changing direction) and, according to classical electromagnetism, it should continuously emit electromagnetic radiation. This loss in orbital energy should result in the electron’s orbit getting continually smaller until it spirals into the nucleus, implying that atoms are inherently unstable.

In 1913, Niels Bohr attempted to resolve the atomic paradox by ignoring classical electromagnetism’s prediction that the orbiting electron in hydrogen would continuously emit light. Instead, he incorporated into the classical mechanics description of the atom

Planck's ideas of quantization and Einstein's finding that light consists of photons whose energy is proportional to their frequency. Bohr assumed that the electron orbiting the nucleus would not normally emit any radiation (the stationary state hypothesis), but it would emit or absorb a photon if it moved to a different orbit. This model leads directly to the Rydberg equation discussed in section 7.1. In this equation, h is Planck's constant (6.62607015 x 10^{-34} J sec), with $n = 1, 2, 3, \ldots$, k is a constant comprising fundamental constants such as the electron mass and charge, k has a value of $2.179 \times 10^{-18}\ J$.

$$\frac{1}{\lambda} = \frac{k}{hc}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{5.1.5}$$

The lowest few energy levels are shown in Figure 5.1.9. One of the fundamental laws of physics is that matter is most stable with the lowest possible energy. Thus, the electron in a hydrogen atom usually moves in the $n = 1$ orbit, the orbit in which it has the lowest energy. When the electron is in this lowest energy orbit, the atom is said to be in its ground state. If the atom receives energy from an outside source, it is possible for the electron to move to an orbit with a higher n value and the atom is now in an excited state with a higher energy. When an electron transitions from an excited state (higher energy orbit) to the ground state, the difference in energy is emitted as a photon. Similarly, if a photon is absorbed by an atom, the energy of the photon moves an electron from a lower energy orbit up to a more excited one.

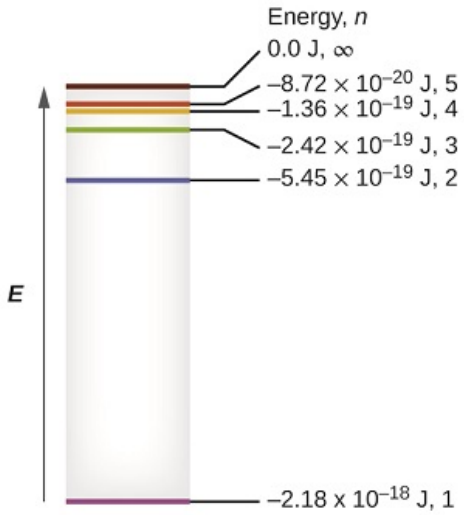


Figure 5.1.9: Quantum numbers and energy levels in a hydrogen atom. The more negative the calculated value, the lower the energy.

We can relate the energy of electrons in atoms to what we learned previously about energy. The law of conservation of energy says that we can neither create nor destroy energy. Thus, if a certain amount of external energy is required to excite an electron from one energy level to another, that same amount of energy will be liberated when the electron returns to its initial state (Figure 5.1.10). In effect, an atom can "store" energy by using it to promote an electron to a state with a higher energy and release it when the electron returns to a lower state. The energy can be released as one quantum of energy, as the electron returns to its ground state (say, from $n = 5$ to $n = 1$), or it can be released as two or more smaller quanta as the electron falls to an intermediate state, then to the ground state (say, from $n = 5$ to $n = 4$, emitting one quantum, then to $n = 1$, emitting a second quantum).

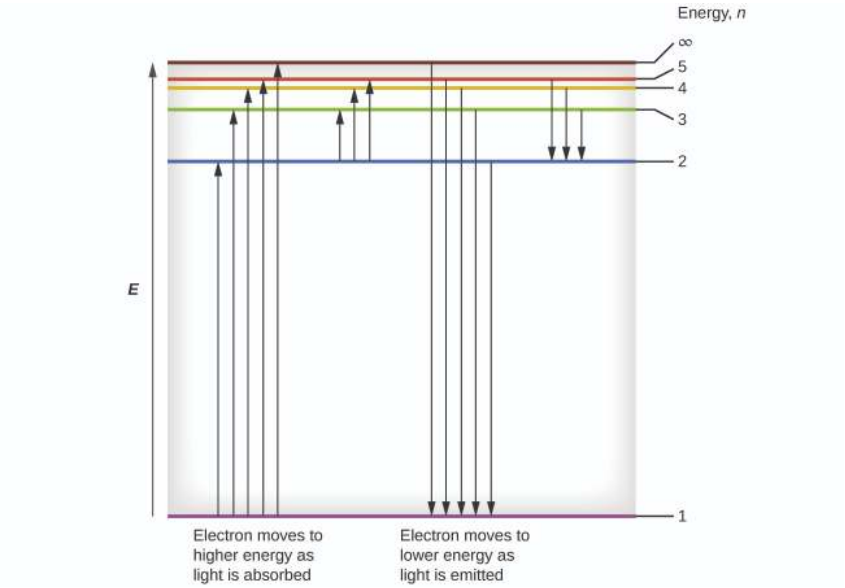


Figure 5.1.10: The horizontal lines show the relative energy of orbits in the Bohr model of the hydrogen atom, and the vertical arrows depict the energy of photons absorbed (left) or emitted (right) as electrons move between these orbits.

With three extremely puzzling paradoxes now solved (blackbody radiation, the photoelectric effect, and the hydrogen atom), and all involving Planck's constant in a fundamental manner, it became clear to most physicists at that time that the classical theories that worked so well in the macroscopic world were fundamentally flawed and could not be extended down into the microscopic domain of atoms and molecules. Unfortunately, despite Bohr's remarkable achievement in deriving a theoretical expression for the Rydberg constant, he was unable to extend his theory to the next simplest atom, He, which only has two electrons. Bohr's model was severely flawed, since it was still based on the classical mechanics notion of precise orbits, a concept that was later found to be untenable in the microscopic domain, when a proper model of quantum mechanics was developed to supersede classical mechanics.

Example 5.1.3: Calculating Electron Transitions in a One–electron System

What is the energy (in joules) and the wavelength (in meters) of the line in the spectrum of hydrogen that represents the movement of an electron from Bohr orbit with n = 4 to the orbit with n = 6? In what part of the electromagnetic spectrum do we find this radiation?

Solution

In this case, the electron starts out with $n = 4$, so $n_1 = 4$. It comes to rest in the $n = 6$ orbit, so $n_2 = 6$. The difference in energy between the two states is given by this expression:

$$\Delta E = E_1 - E_2 = 2.179 \times 10^{-18} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{5.1.6}$$

$$\Delta E = 2.179 \times 10^{-18} \left(\frac{1}{4^2} - \frac{1}{6^2} \right) \ J \tag{5.1.7}$$

$$\Delta E = 2.179 \times 10^{-18} \left(\frac{1}{16} - \frac{1}{36} \right) \ J \tag{5.1.8}$$

$$\Delta E = 7.566 \times 10^{-20} \ J \tag{5.1.9}$$

This energy difference is *positive*, indicating a photon enters the system (is absorbed) to excite the electron from the n = 4 orbit up to the $n = 6$ orbit. The wavelength of a photon with this energy is found by the expression $E = hc\lambda$. Rearrangement gives:

$$\lambda = \frac{hc}{E} \tag{5.1.10}$$

From the figure of electromagnetic radiation, we can see that this wavelength is found in the infrared portion of the electromagnetic spectrum.

? Exercise 5.1.3

What is the wavelength in meters and the energy in Joules of the photon produced when an electron falls from the $n = 5$ to the $n = 3$ level in a H atom.

Answer

$6.837 \times 10^{-7}\ m$ and $2.90 \times 10^{-19}\ J$

Bohr's model of the hydrogen atom provides insight into the behavior of matter at the microscopic level, but it is does not account for electron–electron interactions in atoms with more than one electron. It does introduce several important features of all models used to describe the distribution of electrons in an atom. These features include the following:

- The energies of electrons (energy levels) in an atom are quantized, described by quantum numbers: integer numbers having only specific allowed value and used to characterize the arrangement of electrons in an atom.
- An electron's energy increases with increasing distance from the nucleus.
- The discrete energies (lines) in the spectra of the elements result from quantized electronic energies.

Of these features, the most important is the postulate of quantized energy levels for an electron in an atom. As a consequence, the model laid the foundation for the quantum mechanical model of the atom. Bohr won a Nobel Prize in Physics for his contributions to our understanding of the structure of atoms and how that is related to line spectra emissions.

5.1.3: Summary

Light and other forms of electromagnetic radiation move through a vacuum with a constant speed, c, of 2.998×10^8 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 $E = \dfrac{hc}{\lambda}$), 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.

Bohr incorporated Planck's and Einstein's quantization ideas into a model of the hydrogen atom that resolved the paradox of atom stability and discrete spectra. The Bohr model of the hydrogen atom explains the connection between the quantization of photons and the quantized emission from atoms. Bohr described the hydrogen atom in terms of an electron moving in a circular orbit about a nucleus. He postulated that the electron was restricted to certain orbits characterized by discrete energies. Transitions between these allowed orbits result in the absorption or emission of photons. When an electron moves from a higher-energy orbit to a more stable one, energy is emitted in the form of a photon. To move an electron from a stable orbit to a more excited one, a photon of

energy must be absorbed. Using the Bohr model, we can calculate the energy of an electron and the radius of its orbit in any one-electron system.

Key Equations

- $c = \lambda\nu$, where c = 2.99792458 x 10^8 m/s
- $E = h\nu = \frac{hc}{\lambda}$, where h = 6.626 × 10^{-34} J s
- $\frac{1}{\lambda} = R_\infty \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$, where R_∞ = 1.097 x 10^7 m^{-1}

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

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.

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

excited state
state having an energy greater than the ground-state energy

frequency (ν)
number of wave cycles (peaks or troughs) that pass a specified point in space per unit time

ground state
state in which the electrons in an atom, ion, or molecule have the lowest energy possible

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

quantum number

integer number having only specific allowed values and used to characterize the arrangement of electrons in an atom

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)

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).

- 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 5.1: Light and Atomic Structure is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

- **6.1: Electromagnetic Energy** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.
- **6.2: The Bohr Model** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

5.2: Development of Quantum Theory

Learning Objectives

- Extend the concept of wave–particle duality that was observed in electromagnetic radiation to matter as well
- Understand the general idea of the quantum mechanical description of electrons in an atom, and that it uses the notion of three-dimensional wave functions, or orbitals, that define the distribution of probability to find an electron in a particular part of space
- List and describe traits of the four quantum numbers that form the basis for completely specifying the state of an electron in an atom

Bohr's model explained the experimental data for the hydrogen atom and was widely accepted, but it also raised many questions. Why did electrons orbit at only fixed distances defined by a single quantum number n = 1, 2, 3, and so on, but never in between? Why did the model work so well describing hydrogen and one-electron ions, but could not correctly predict the emission spectrum for helium or any larger atoms? To answer these questions, scientists needed to completely revise the way they thought about matter.

5.2.1: Behavior in the Microscopic World

We know how matter behaves in the macroscopic world—objects that are large enough to be seen by the naked eye follow the rules of classical physics. A billiard ball moving on a table will behave like a particle: It will continue in a straight line unless it collides with another ball or the table cushion, or is acted on by some other force (such as friction). The ball has a well-defined position and velocity (or a well-defined momentum, $p = mv$, defined by mass m and velocity v) at any given moment. In other words, the ball is moving in a classical trajectory. This is the typical behavior of a classical object.

When waves interact with each other, they show interference patterns that are not displayed by macroscopic particles such as the billiard ball. For example, interacting waves on the surface of water can produce interference patters similar to those shown on Figure 5.2.1. This is a case of wave behavior on the macroscopic scale, and it is clear that particles and waves are very different phenomena in the macroscopic realm.

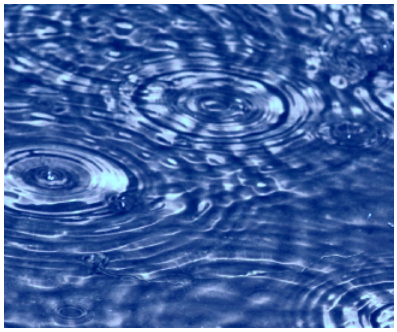


Figure 5.2.1: An interference pattern on the water surface is formed by interacting waves. The waves are caused by reflection of water from the rocks. (credit: modification of work by Sukanto Debnath)

As technological improvements allowed scientists to probe the microscopic world in greater detail, it became increasingly clear by the 1920s that very small pieces of matter follow a different set of rules from those we observe for large objects. The unquestionable separation of waves and particles was no longer the case for the microscopic world.

5.2.2: deBroglie Wavelength

One of the first people to pay attention to the special behavior of the microscopic world was Louis de Broglie. He asked the question: If electromagnetic radiation can have particle-like character, can electrons and other submicroscopic particles exhibit wavelike character? In his 1925 doctoral dissertation, de Broglie extended the wave–particle duality of light that Einstein used to resolve the photoelectric-effect paradox to material particles. He predicted that a particle with mass *m* and velocity *v* (that is, with linear momentum *p*) should also exhibit the behavior of a wave with a wavelength value λ, given by this expression in which *h* is the familiar Planck's constant

$$\lambda = \frac{h}{mv} = \frac{h}{p} \tag{5.2.1}$$

This is called the *de Broglie wavelength*. Unlike the other values of λ discussed in this chapter, the de Broglie wavelength is a characteristic of particles and other bodies, not electromagnetic radiation (note that this equation involves velocity symbolized by an italic "v" [*v*, m/s], not the greek symbol nu for frequency [ν, Hz]. Although these two symbols are identical, they mean very different things). Where Bohr had postulated the electron as being a particle orbiting the nucleus in quantized orbits, de Broglie argued that Bohr's assumption of quantization can be explained if the electron is considered not as a particle, but rather as a circular standing wave such that only an integer number of wavelengths could fit exactly within the orbit (Figure 5.2.2).

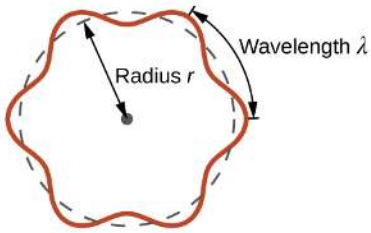


Figure 5.2.1: If an electron is viewed as a wave circling around the nucleus, an integer number of wavelengths must fit into the orbit for this standing wave behavior to be possible.

For a circular orbit of radius r, the circumference is 2πr, and so de Broglie's condition is:

$$2\pi r = n\lambda \tag{5.2.2}$$

with $n = 1, 2, 3, \ldots$

Since the de Broglie expression relates the wavelength to the momentum and, hence, velocity this expression can be rearranged to give Bohr's formula for the quantization of the angular momentum:

$$L = \frac{nh}{2\pi} = n\hbar \tag{5.2.3}$$

Classical angular momentum L for a circular motion is equal to the product of the radius of the circle and the momentum of the moving particle p.

$$L = rp = rmv \quad \text{(for a circular motion)} \tag{5.2.4}$$

Shortly after de Broglie proposed the wave nature of matter, two scientists at Bell Laboratories, C. J. Davisson and L. H. Germer, demonstrated experimentally that electrons can exhibit wavelike behavior by showing an interference pattern for electrons traveling through a regular atomic pattern in a crystal. The regularly spaced atomic layers served as slits, as used in other interference experiments. Since the spacing between the layers serving as slits needs to be similar in size to the wavelength of the tested wave for an interference pattern to form, Davisson and Germer used a crystalline nickel target for their "slits," since the spacing of the atoms within the lattice was approximately the same as the de Broglie wavelengths of the electrons that they used. Figure 5.2.3 shows an interference pattern.

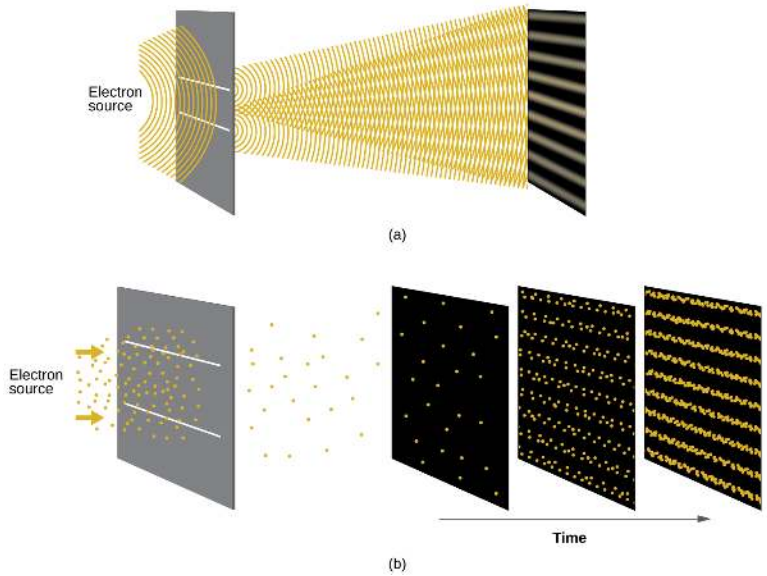


Figure 5.2.3: (a) The interference pattern for electrons passing through very closely spaced slits demonstrates that quantum particles such as electrons can exhibit wavelike behavior. (b) The experimental results illustrated here demonstrate the wave–particle duality in electrons. The electrons pass through very closely spaced slits, forming an interference pattern, with increasing numbers of electrons being recorded from the left image to the right. With only a few electrons recorded, it is clear that the electrons arrive as individual localized "particles," but in a seemingly random pattern. As more electrons arrive, a wavelike interference pattern begins to emerge. Note that the probability of the final electron location is still governed by the wave-type distribution, even for a single electron, but it can be observed more easily if many electron collisions have been recorded.

Video 5.2.1 discusses this same experiment of the wave–particle duality of matter can be seen by observing what happens if electron collisions are recorded over a long period of time. Initially, when only a few electrons have been recorded, they show clear particle-like behavior, having arrived in small localized packets that appear to be random. As more and more electrons arrived and were recorded, a clear interference pattern that is the hallmark of wavelike behavior emerged. Thus, it appears that while electrons are small localized particles, their motion does not follow the equations of motion implied by classical mechanics, but instead it is governed by some type of a wave equation that governs a probability distribution even for a single electron's motion. Thus the wave–particle duality first observed with photons is actually a fundamental behavior intrinsic to all quantum particles.



Video 5.2.1: View the Dr. Quantum – Double Slit Experiment cartoon for an easy-to-understand description of wave–particle duality and the associated experiments.

Example 5.2.1: Calculating the Wavelength of a Particle

If an electron travels at a velocity of 1.000×10^{7} m s^{-1} and has a mass of 9.109×10^{-31} kg, what is its wavelength?

Solution

We can use de Broglie's equation to solve this problem, since 1 J = 1 kg m^2/s^2.

$$\begin{aligned}\lambda &= \frac{h}{mv} \\ &= \frac{6.626 \times 10^{-34}\text{Js}}{(9.109 \times 10^{-31}\text{ kg})(1.000 \times 10^{7}\text{ m/s})} \\ &= 7.274 \times 10^{-11}\text{ m}\end{aligned}$$

This is a small value, but it is significantly larger than the size of an electron in the classical (particle) view. This size is the same order of magnitude as the size of an atom. This means that electron wavelike behavior is going to be noticeable in an atom.

? Exercise 5.2.1

Calculate the wavelength of a softball with a mass of 0.100 kg traveling at a velocity of 35 m s^{-1}, assuming that it can be modeled as a single particle.

Answer

1.9×10^{-34} m.

We never think of a thrown softball having a wavelength, since this wavelength is so small it is impossible for our senses or any known instrument to detect (strictly speaking, the wavelength of a real baseball would correspond to the wavelengths of its constituent atoms and molecules, which, while much larger than this value, would still be microscopically tiny). The de Broglie wavelength is only appreciable for matter that has a very small mass and/or a very high velocity.

5.2.3: Heisenberg's Uncertainty Principle

Werner Heisenberg considered the limits of how accurately we can measure properties of an electron or other microscopic particles. He determined that there is a fundamental limit to how accurately one can measure both a particle's position and its momentum simultaneously. The more accurately we measure the momentum of a particle, the less accurately we can determine its position at that time, and vice versa. This is summed up in what we now call the Heisenberg uncertainty principle: *It is fundamentally impossible to determine simultaneously and exactly both the momentum and the position of a particle*. This allows us to calculate the limit to how precisely we can know both the simultaneous position of an object and its momentum.

It should be noted that Heisenberg's uncertainty principle is not just limited to uncertainties in position and momentum, but it also links other dynamical variables. For example, when an atom absorbs a photon and makes a transition from one energy state to another, the uncertainty in the energy and the uncertainty in the time required for the transition are similarly related, as $\Delta E\,\Delta t \geq \frac{\hbar}{2}$.

Heisenberg's principle imposes ultimate limits on what is knowable in science. The uncertainty principle can be shown to be a consequence of wave–particle duality, which lies at the heart of what distinguishes modern quantum theory from classical mechanics. Recall that the equations of motion obtained from classical mechanics are trajectories where, at any given instant in time, both the position and the momentum of a particle can be determined exactly. Heisenberg's uncertainty principle implies that such a view is untenable in the microscopic domain and that there are fundamental limitations governing the motion of quantum particles. This does not mean that microscopic particles do not move in trajectories, it is just that measurements of trajectories are limited in their precision. In the realm of quantum mechanics, measurements introduce changes into the system that is being observed.

5.2.4: The Quantum–Mechanical Model of an Atom

Shortly after de Broglie published his ideas that the electron in a hydrogen atom could be better thought of as being a circular standing wave instead of a particle moving in quantized circular orbits, as Bohr had suggested, Erwin Schrödinger extended de Broglie's work by incorporating the de Broglie relation into a wave equation, deriving what is today known as the Schrödinger

equation. When Schrödinger applied his equation to hydrogen-like atoms, he was able to reproduce Bohr's expression for the energy and, thus, the Rydberg formula governing hydrogen spectra, and he did so without having to invoke Bohr's assumptions of stationary states and quantized orbits, angular momenta, and energies; quantization in Schrödinger's theory was a natural consequence of the underlying mathematics of the wave equation. Like de Broglie, Schrödinger initially viewed the electron in hydrogen as being a physical wave instead of a particle, but where de Broglie thought of the electron in terms of circular stationary waves, Schrödinger properly thought in terms of three-dimensional stationary waves, or wavefunctions, represented by the Greek letter psi, ψ. A few years later, Max Born proposed an interpretation of the wavefunction ψ that is still accepted today: Electrons are still particles, and so the waves represented by ψ are not physical waves but, instead, are complex probability amplitudes. The square of the magnitude of a wavefunction $|\psi|^2$ describes the probability of the quantum particle being present near a certain location in space. This means that wavefunctions can be used to determine the distribution of the electron's density with respect to the nucleus in an atom.

Schrödinger's work, as well as that of Heisenberg and many other scientists following in their footsteps, is generally referred to as quantum mechanics. Video 5.2.2 describes an interesting paradox that Schrödinger used to explain how observation or measurement changes a system at the quatum mechanical level.



Video 5.2.2: You may also have heard of Schrödinger because of his famous thought experiment. This story explains the concepts of superposition and entanglement as related to a cat in a box with poison (https://www.youtube.com/watch?v=IOYy...eature=youtube).

5.2.5: Understanding Quantum Theory of Electrons in Atoms

The goal of this section is to understand the electron orbitals (location of electrons in atoms), their different energies, and other properties. The use of quantum theory provides the best understanding to these topics. This knowledge is critical to understanding chemical bonding.

Electrons in atoms can exist only on discrete energy levels. The energy of an electron in an atom is quantized, it can only have certain specific values. It can change between these values but is never between these values.

The energy levels, or orbitals, are labeled with quantum numbers. The principal quantum number is *n*, where $n = 1, 2, 3, \ldots$. Generally speaking, the energy of an electron in an atom is greater for greater values of *n*. The principal quantum number defines the location of the energy level. It is essentially the same concept as the *n* in the Bohr atom description. Another name for the principal quantum number is the shell number. The shells of an atom can be thought of concentric circles radiating out from the nucleus. The electrons that belong to a specific shell are most likely to be found within the corresponding circular area. The further we proceed from the nucleus, the higher the shell number, and so the higher the energy level (Figure 5.2.4). The positively charged protons in the nucleus stabilize the electronic orbitals by electrostatic attraction between the positive charges of the protons and the negative charges of the electrons. So the further away the electron is from the nucleus, the greater the energy it has.

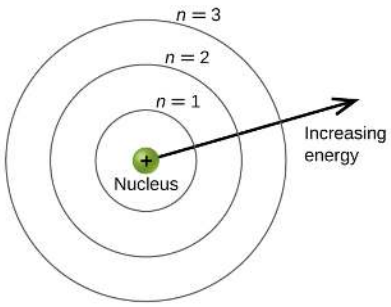


Figure 5.2.4: Different shells are numbered by principal quantum numbers.

The next quantum number is *l*, the angular momentum quantum number. It is an integer that defines the shape of the orbital, and takes on the values, $l = 0, 1, 2, \ldots, n - 1$. An orbital with $n = 1$ can have only one value of *l*, $l = 0$, but when $n = 2$ this permits $l = 0$ and $l = 1$, and so on. The principal quantum number defines the general size and energy of the orbital. The *l* value specifies the shape of the orbital. Orbitals with $l = 0$ are called *s* orbitals (or the *s* subshells). The value $l = 1$ corresponds to the *p* orbitals. For a given *n*, *p* orbitals constitute a *p* subshell (e.g., 3*p* if $n = 3$). The orbitals with $l = 2$ are called the *d* orbitals, followed by the *f* orbitals for $l = 3$.

Together the *n* and *l* quantum numbers describe the energy and shape of an orbital. A close look at the shape of the orbitals shows there are certain distances from the nucleus at which the probability density of finding an electron located at a particular orbital is zero. This is a node like the ones described for standing waves in section 7.1. The value of the wavefunction ψ is zero at this distance for this orbital. Such a value of radius *r* is called a radial node. The number of radial nodes in an orbital is $n - l - 1$. Figure 5.2.5 shows cross sections of the 1s, 2s, and 3s orbitals ($n = 1$, 2, and 3; while $l = 0$) and the probability graph showing the probability as a function of radial distance from the nucleus of the atom. These graphs show there are $1 - 0 - 1 = 0$ places where the density is zero (nodes) for 1*s* ($n = 1$), $2 - 0 - 1 = 1$ node for 2*s*, and $3 - 0 - 1 = 2$ nodes for the 3*s* orbitals.

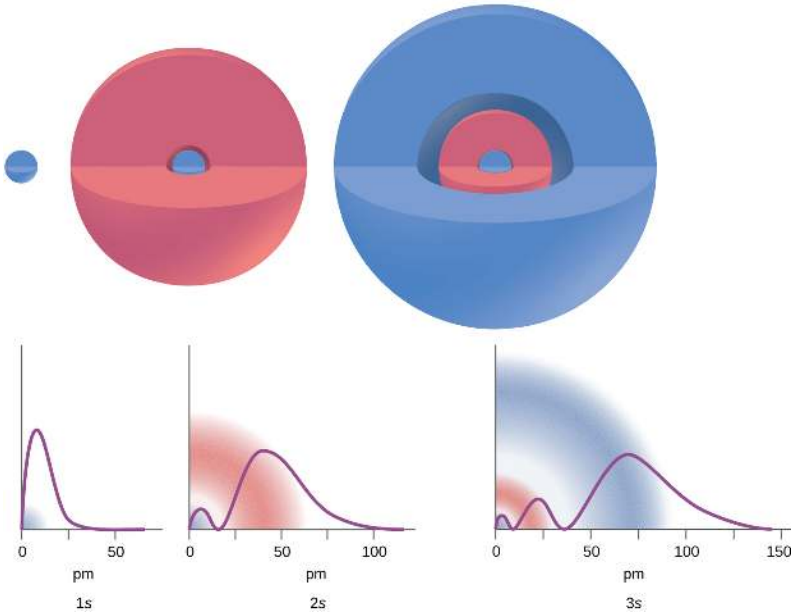


Figure 5.2.5: The graphs show the probability (y axis) of finding an electron for the 1s, 2s, 3s orbitals as a function of distance from the nucleus.

Figure 5.2.6 shows the shapes of all the possible orbitals for $l = 0$, 1, 2, and 3. The *s* subshell electron density distribution is spherical and the *p* subshell has a dumbbell shape. The *d* and *f* orbitals are more complex. These shapes represent the three-dimensional regions within which the electron is likely to be found. Notice that for the s orbital when $l = 0$ there is only one possible orientation, a sphere does not have a top or bottom. However when $l = 1$, 2, or 3 there are different possible orientations. These orientations are represented by the third quantum number m_l , the magnetic quantum number. For an *s* orbital, $l = 0$, and the only value of m_l is zero. For *p* orbitals, $l = 1$, and m_l can be equal to –1, 0, or +1. Generally speaking, m_l can be equal to $-l$, $-(l - 1)$,

…, –1, 0, +1, …, (l – 1), l. The total number of possible orbitals with the same value of l (a subshell) is $2l + 1$. Thus, there is one *s*-orbital for $m_l = 0$, there are three *p*-orbitals for $m_l = 1$, five *d*-orbitals for $m_l = 2$, seven *f*-orbitals for $m_l = 3$, and so forth.

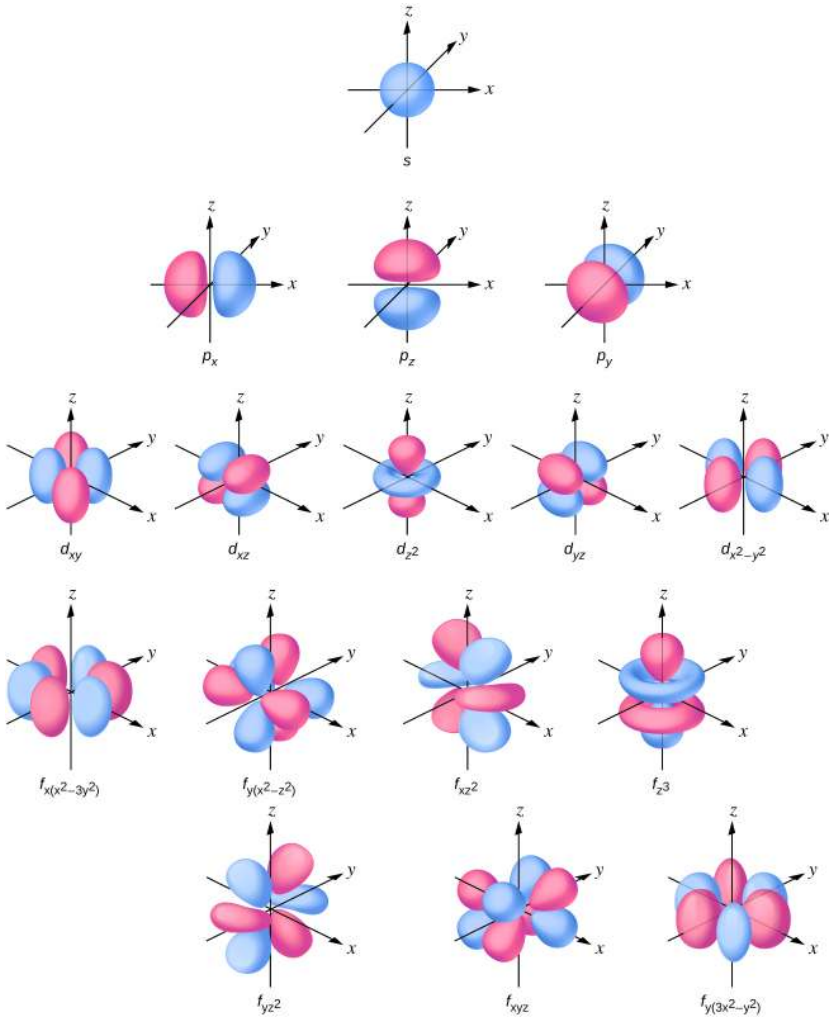


Figure 5.2.6: Shapes of s, p, d, and f orbitals.

The principal quantum number defines the general value of the electronic energy. The angular momentum quantum number determines the shape of the orbital. And the magnetic quantum number specifies orientation of the orbital in space. This is sumarized in the Energy level diagram shown in Figure 5.2.7. The number before the orbital name (such as 2*s*, 3*p*, and so forth) stands for the principal quantum number, *n*. The letter in the orbital name defines the subshell with a specific angular momentum quantum number $l = 0$ for *s* orbitals, 1 for *p* orbitals, 2 for *d* orbitals. Finally, there are more than one possible orbitals for $l \geq 1$, each corresponding to a specific value of m_l. In the case of a hydrogen atom or a one-electron ion (such as He^+, Li^{2+}, and so on), energies of all the orbitals with the same *n* are the same. This is called a degeneracy, and the energy levels for the same principal quantum number, *n*, are called degenerate energy levels. However, in atoms with more than one electron, this degeneracy is eliminated by the electron–electron interactions, and orbitals that belong to different subshells have different energies. Orbitals within the same subshell (for example *ns*, *np*, *nd*, *nf*, such as 2*p*, 3*s*) are still degenerate and have the same energy.

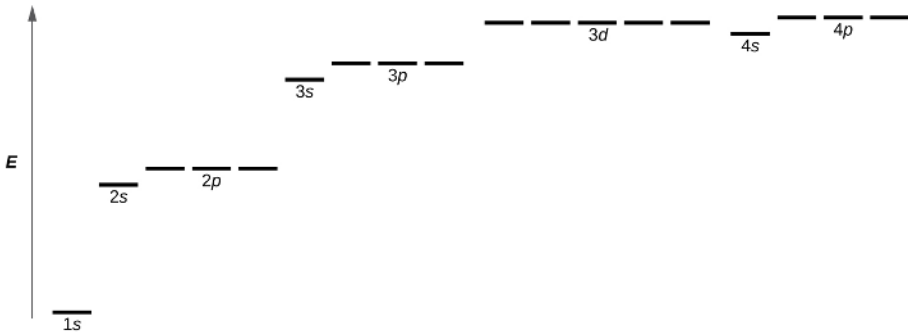


Figure 5.2.7: *The chart shows the energies of electron orbitals in a multi-electron atom.*

These 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.

5.2.6: The Pauli Exclusion Principle

While the three quantum numbers discussed in the previous section work well for describing electron orbitals, some experiments showed that they were not sufficient to explain all observed results. It was demonstrated in the 1920s that when hydrogen-line spectra are examined at extremely high resolution, some lines are actually not single peaks but, rather, pairs of closely spaced lines. This is the so-called fine structure of the spectrum, and it implies that there are additional small differences in energies of electrons even when they are located in the same orbital. These observations led Samuel Goudsmit and George Uhlenbeck to propose that electrons have a fourth quantum number. They called this the spin quantum number, or m_s. Any electron, regardless of the atomic orbital it is located in, can only have one of two values for the spin quantum number, $m_s = -\frac{1}{2}$ or $m_s = \frac{1}{2}$ as shown in Figure 5.2.8.

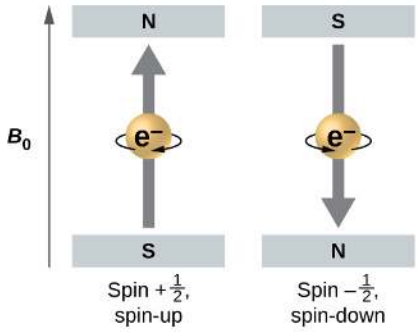


Figure 5.2.8: Electrons with spin values *(±1/2) in an external magnetic field.*

An electron in an atom is completely described by four quantum numbers: *n*, *l*, m_l, and m_s. The first three quantum numbers define the orbital and the fourth quantum number describes the intrinsic electron property called spin. An Austrian physicist Wolfgang Pauli formulated a general principle that gives the last piece of information that we need to understand the general behavior of electrons in atoms. The Pauli exclusion principle can be formulated as follows: No two electrons in the same atom can have exactly the same set of all the four quantum numbers. What this means is that electrons can share the same orbital (the same set of the quantum numbers *n*, *l*, and m_l), but only if their spin quantum numbers m_s have different values. Since the spin quantum number can only have two values $\left(\pm\frac{1}{2}\right)$, no more than two electrons can occupy the same orbital (and if two electrons are located in the same orbital, they must have opposite spins). Therefore, any atomic orbital can be populated by only zero, one, or two electrons. The properties and meaning of the quantum numbers of electrons in atoms are briefly summarized in Table 5.2.1.

Table 5.2.1: *Quantum Numbers, Their Properties, and Significance*

Name	Symbol	Allowed values	Physical meaning
principal quantum number	n	1, 2, 3, 4, ….	shell, the general region for the value of energy for an electron on the orbital
angular momentum or azimuthal quantum number	l	$0 \le l \le n-1$	subshell, the shape of the orbital
magnetic quantum number	m_l	$-l \le m_l \le l$	orientation of the orbital
spin quantum number	m_s	$+\frac{1}{2}, -\frac{1}{2}$	direction of the intrinsic quantum "spinning" of the electron

Example 5.2.2: Working with Shells and Subshells

Indicate the number of subshells, the number of orbitals in each subshell, and the values of l and m_l for the orbitals in the $n = 4$ shell of an atom.

Solution

For $n = 4$, l can have values of 0, 1, 2, and 3. Thus, *s*, *p*, *d*, and *f* subshells are found in the $n = 4$ shell of an atom. For $l = 0$ (the *s* subshell), m_l can only be 0. Thus, there is only one 4*s* orbital. For $l = 1$ (*p*-type orbitals), m can have values of –1, 0, +1, so we find three 4*p* orbitals. For $l = 2$ (*d*-type orbitals), m_l can have values of –2, –1, 0, +1, +2, so we have five 4*d* orbitals. When $l = 3$ (*f*-type orbitals), m_l can have values of –3, –2, –1, 0, +1, +2, +3, and we can have seven 4*f* orbitals. Thus, we find a total of 16 orbitals in the $n = 4$ shell of an atom.

Exercise 5.2.2

Identify the subshell in which electrons with the following quantum numbers are found:

a. $n = 3$, $l = 1$;
b. $n = 5$, $l = 3$;
c. $n = 2$, $l = 0$.

Answer a

3*p*

Answer b

5*f*

Answer c

2s

Example 5.2.3: Maximum Number of Electrons

Calculate the maximum number of electrons that can occupy a shell with (a) $n = 2$ and (b) $n = 5$. Note you are only looking at the orbitals with the specified n value, not those at lower energies.

Solution

(a) When $n = 2$, there are four orbitals (a single 2*s* orbital, and three orbitals labeled 2*p*). These four orbitals can contain eight electrons.

(b) When $n = 5$, there are five subshells of orbitals that we need to sum:

$$\begin{array}{r} 1 \text{ orbital labeled } 5s \\ 3 \text{ orbitals labeled } 5p \\ 5 \text{ orbitals labeled } 5d \\ 7 \text{ orbitals labeled } 5f \\ +9 \text{ orbitals labeled } 5g \\ \hline 25 \text{ orbitals total} \end{array}$$

Again, each orbital hods two electorns, so 50 electrons can fit in this shell

Exercise 5.2.3

If a shell contains a maximum of 32 electrons, what is the principal quantum number, *n*?

Answer

n = 4

Example 5.2.4: Working with Quantum Numbers

Complete the following table for atomic orbitals:

Orbital	*n*	*l*	m_l degeneracy	Radial nodes (no.)
4*f*				
	4	1		
	7		7	3
5*d*				

Solution

The table can be completed using the following rules:

- The orbital designation is *nl*, where *l* = 0, 1, 2, 3, 4, 5, … is mapped to the letter sequence s, *p*, *d*, *f*, *g*, *h*, …,
- The m_l degeneracy is the number of orbitals within an *l* subshell, and so is 2*l* + 1 (there is one *s* orbital, three *p* orbitals, five *d* orbitals, seven *f* orbitals, and so forth).
- The number of radial nodes is equal to *n* – *l* – 1.

Orbital	***n***	***l***	**m_l degeneracy**	**Radial nodes (no.)**
4*f*	4	3	7	0
4*p*	4	1	3	2
7*f*	7	3	7	3
5*d*	5	2	5	2

Exercise 5.2.4

How many orbitals have *l* = 2 and *n* = 3?

Answer

The five degenerate 3*d* orbitals

5.2.7: Summary

Macroscopic objects act as particles. Microscopic objects (such as electrons) have properties of both a particle and a wave. Their exact trajectories cannot be determined. The quantum mechanical model of atoms describes the three-dimensional position of the electron in a *probabilistic* manner according to a mathematical function called a wavefunction, often denoted as ψ. Atomic wavefunctions are also called orbitals. The squared magnitude of the wavefunction describes the distribution of the probability of finding the electron in a particular region in space. Therefore, atomic orbitals describe the areas in an atom where electrons are most likely to be found.

An atomic orbital is characterized by three quantum numbers. The principal quantum number, n, can be any positive integer. The general region for value of energy of the orbital and the average distance of an electron from the nucleus are related to n. Orbitals having the same value of n are said to be in the same shell. The angular momentum quantum number, l, can have any integer value from 0 to $n – 1$. This quantum number describes the shape or type of the orbital. Orbitals with the same principal quantum number and the same l value belong to the same subshell. The magnetic quantum number, m_l, with $2l + 1$ values ranging from $–l$ to $+l$, describes the orientation of the orbital in space. In addition, each electron has a spin quantum number, m_s, that can be equal to $\pm\frac{1}{2}$. No two electrons in the same atom can have the same set of values for all the four quantum numbers.

Glossary

angular momentum quantum number (l)
quantum number distinguishing the different shapes of orbitals; it is also a measure of the orbital angular momentum

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

***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

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

***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

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

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

***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

Pauli exclusion principle

specifies that no two electrons in an atom can have the same value for all four quantum numbers

principal quantum number (*n*)

quantum number specifying the shell an electron occupies in an atom

quantum mechanics

field of study that includes quantization of energy, wave-particle duality, and the Heisenberg uncertainty principle to describe matter

***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

shell

set of orbitals with the same principal quantum number, *n*

spin quantum number (m_s)

number specifying the electron spin direction, either $+\frac{1}{2}$ or $-\frac{1}{2}$

subshell

set of orbitals in an atom with the same values of *n* and *l*

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

---

This page titled 5.2: Development of Quantum Theory is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

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

5.3: 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.

5.3.1: 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 5.3.1 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.

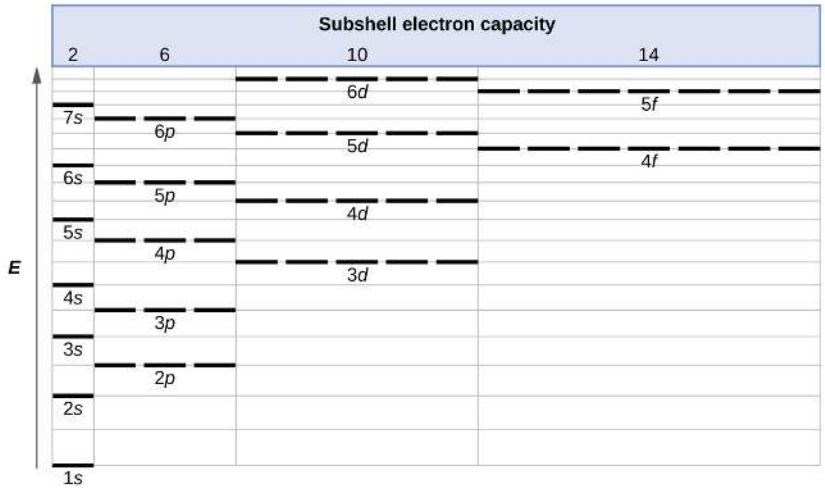


Figure 5.3.1: Generalized energy-level diagram for atomic orbitals in an atom with two or more electrons (not to scale).

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.

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 5.3.2):

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 $n = 3$.

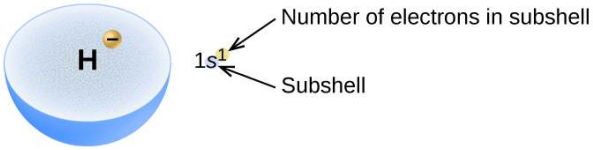


Figure 5.3.2: The diagram of an electron configuration specifies the subshell (n and l value, with letter symbol) and superscript number of electrons.

5.3.2: 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 5.3.3), 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 5.3.3 illustrates the traditional way to remember the filling order for atomic orbitals.

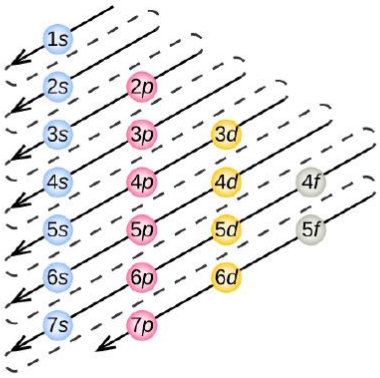


Figure 5.3.3: The arrow leads through each subshell in the appropriate filling order for electron configurations. This chart is straightforward to construct. Simply make a column for all the s orbitals with each n shell on a separate row. Repeat for p, d, and f. Be sure to only include orbitals allowed 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 5.3.4 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.

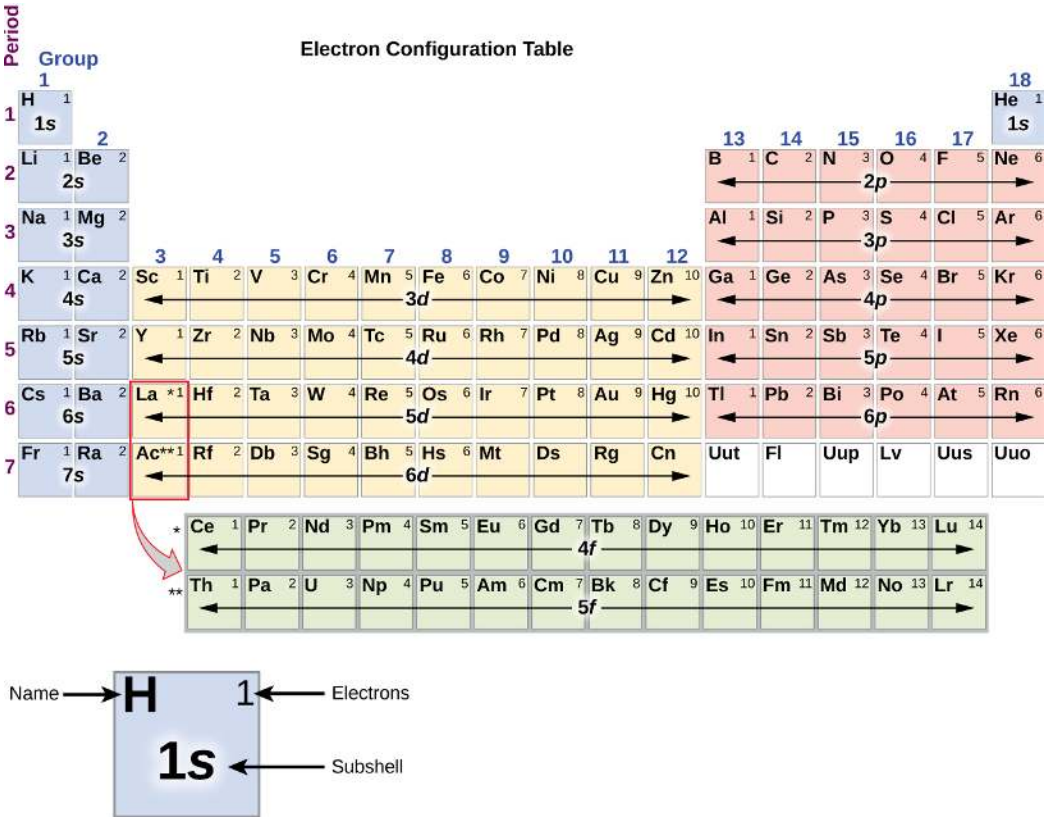
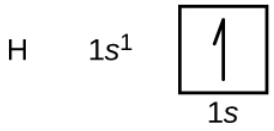
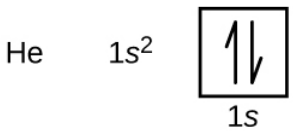


Figure 5.3.4: This periodic table shows the electron configuration for each subshell. By "building up" from hydrogen, this table can be used to determine the electron configuration for any atom on the periodic table.

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 5.3.3 or 5.3.4, 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:

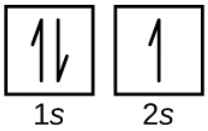


Following hydrogen is the noble gas helium, which has an atomic number of 2. The helium atom contains two protons and two electrons. The first electron has the same four quantum numbers as the hydrogen atom electron (n = 1, l = 0, m_l = 0, $m_s = +\frac{1}{2}$). The second electron also goes into the 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:

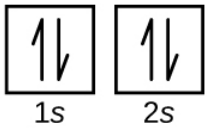


The n = 1 shell is completely filled in a helium atom.

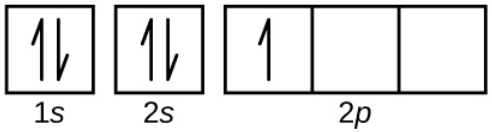
The next atom is the alkali metal lithium with an atomic number of 3. The first two electrons in lithium fill the 1*s* orbital and have the same sets of four quantum numbers as the two electrons in helium. The remaining electron must occupy the orbital of next lowest energy, the 2*s* orbital (Figure 5.3.3 or 5.3.4). Thus, the electron configuration and orbital diagram of lithium are:

Li $1s^2 2s^1$ 

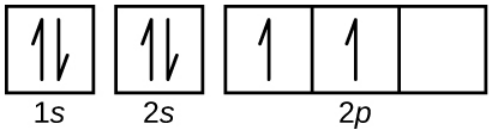
An atom of the alkaline earth metal beryllium, with an atomic number of 4, contains four protons in the nucleus and four electrons surrounding the nucleus. The fourth electron fills the remaining space in the 2*s* orbital.

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:

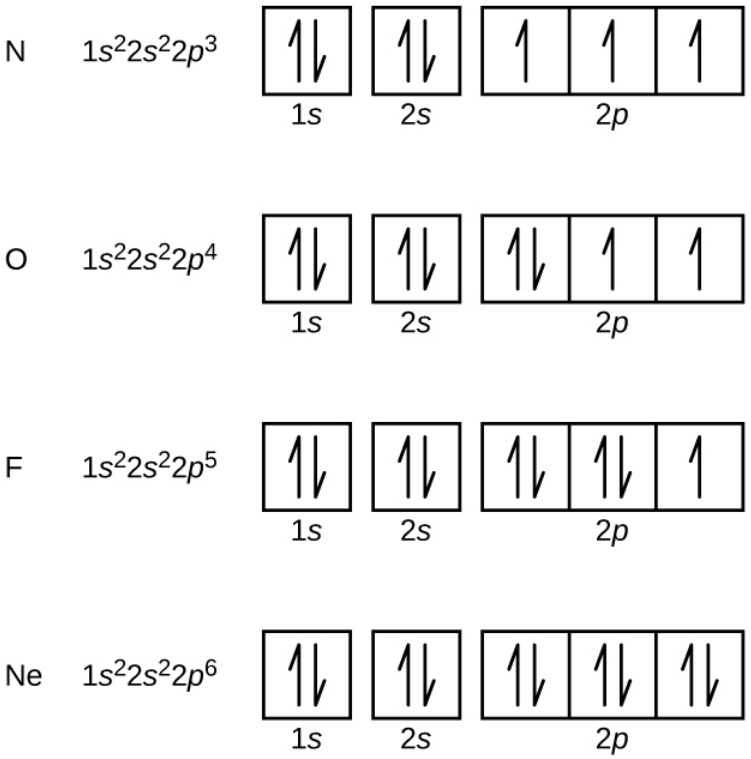


Figure 5.3.5: Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] 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 5.3.5). 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]$3s^1$ in Figure 5.3.6.

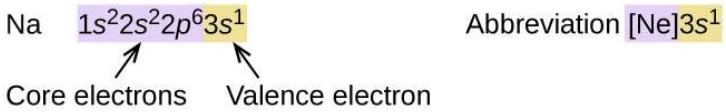


Figure 5.3.6: A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

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 5.3.7 shows the lowest energy, or ground-state, electron configuration for these elements as well as that for atoms of each of the known elements.

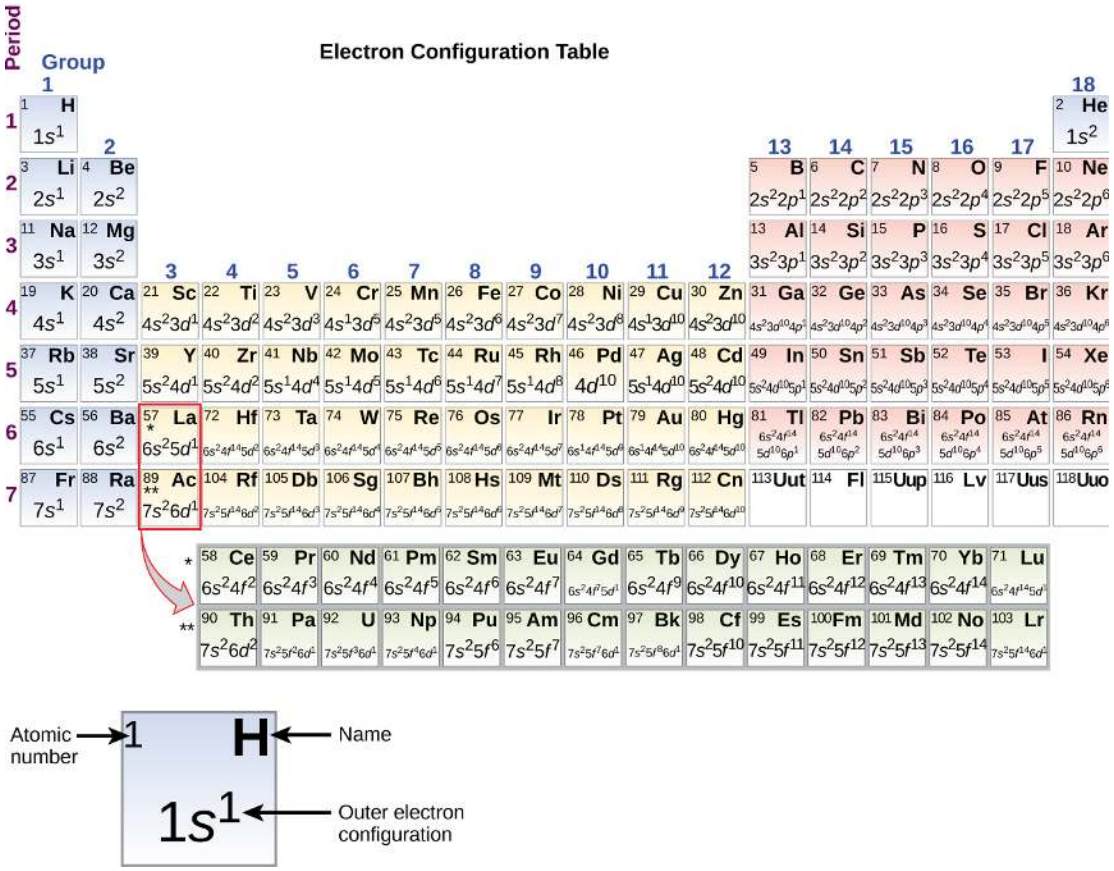


Figure 5.3.7: This version of the periodic table shows the outer-shell electron configuration of each element. Note that down each group, the configuration is often similar.

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 5.3.1 or 5.3.3). 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.

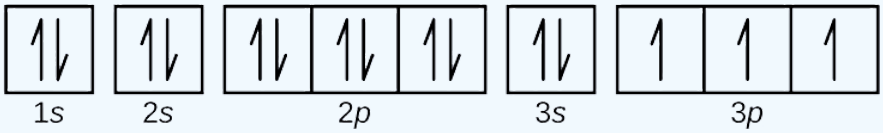
Example 5.3.1: Quantum Numbers and Electron Configurations

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 5.3.1

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. Figure 5.3.7, however, shows there are exceptions to the order of filling of orbitals that are shown in Figure 5.3.1 or 5.3.3. 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.

5.3.3: 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 5.3.6), 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 5.3.6, 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 5.3.6 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 5.3.6. 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 (colored yellow in Figure 5.3.7).
3. **Inner transition elements** are metallic elements in which the last electron added occupies an *f* orbital. They are shown in green in Figure 5.3.6. 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.

5.3.4: 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 5.3.2: 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 5.3.2

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 5.3: Electronic Structure of Atoms (Electron Configurations) is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

- **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.

5.4: Periodic Variations in Element Properties

Learning Objectives

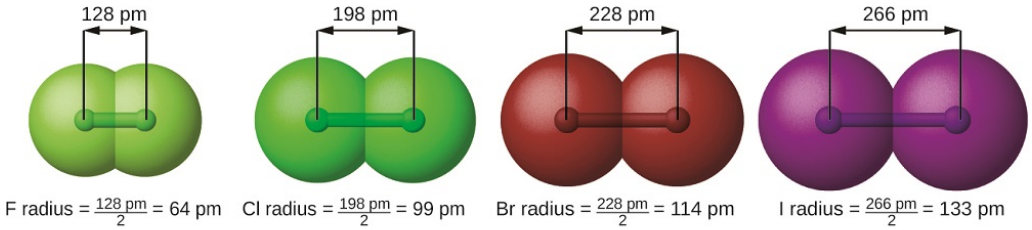
- Describe and explain the observed trends in atomic size, ionization energy, and electron affinity of the elements

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.

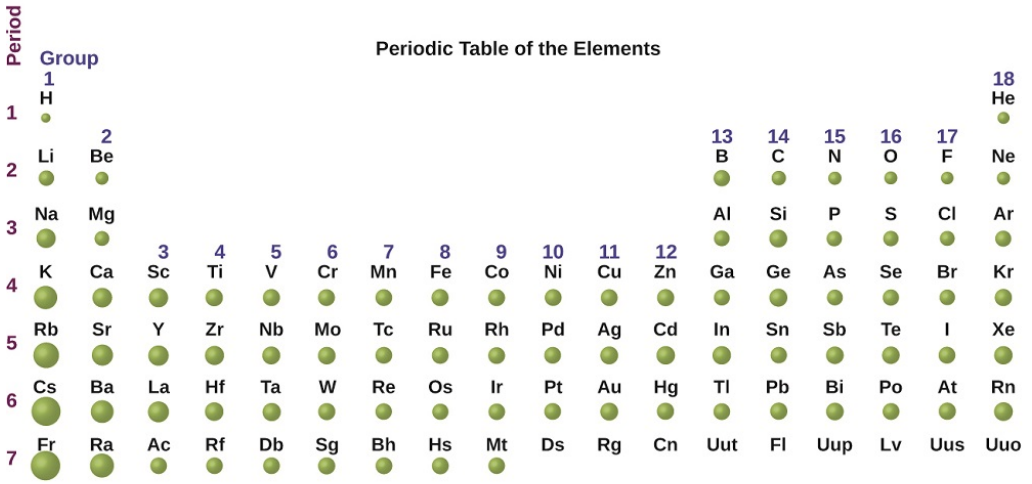
As we go across a period from left to right, we add a proton to the nucleus and an electron to the valence shell with each successive element. As we go down the elements in a group, the number of electrons in the valence shell remains constant, but the principal quantum number increases by one each time. 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.

5.4.1: 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 5.4.1), 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 5.4.1: (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 are shown to scale. 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 5.4.1 and Figure 5.4.1. The trends for the entire periodic table can be seen in Figure 5.4.2.

Table 5.4.1: 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 5.4.2, 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.

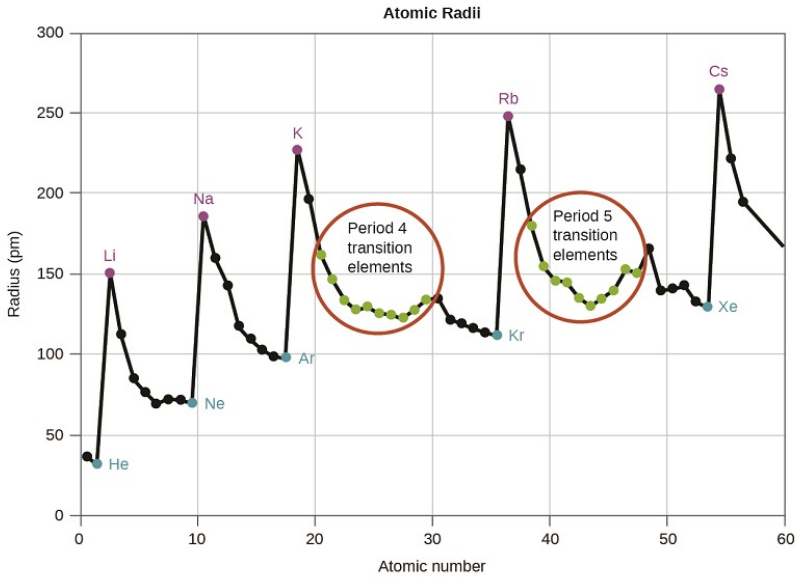


Figure 5.4.2: Within each period, the trend in atomic radius decreases as Z increases; for example, from K to Kr. Within each group (e.g., the alkali metals shown in purple), the trend is that atomic radius increases as Z increases.

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 5.4.1: 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 5.4.1

Give an example of an atom whose size is smaller than fluorine.

Answer

Ne or He

5.4.2: 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 5.4.3). 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 5.4.3: 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 5.4.3). 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.

5.4.3: 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:

$$\mathrm{X}(g) \longrightarrow \mathrm{X}^{+}(g) + \mathrm{e}^{-} \quad \mathrm{IE}_1$$

The energy required to remove the second most loosely bound electron is called the second ionization energy (IE_2).

$$\mathrm{X}^{+}(g) \longrightarrow \mathrm{X}^{2+}(g) + \mathrm{e}^{-} \quad \mathrm{IE}_2$$

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.

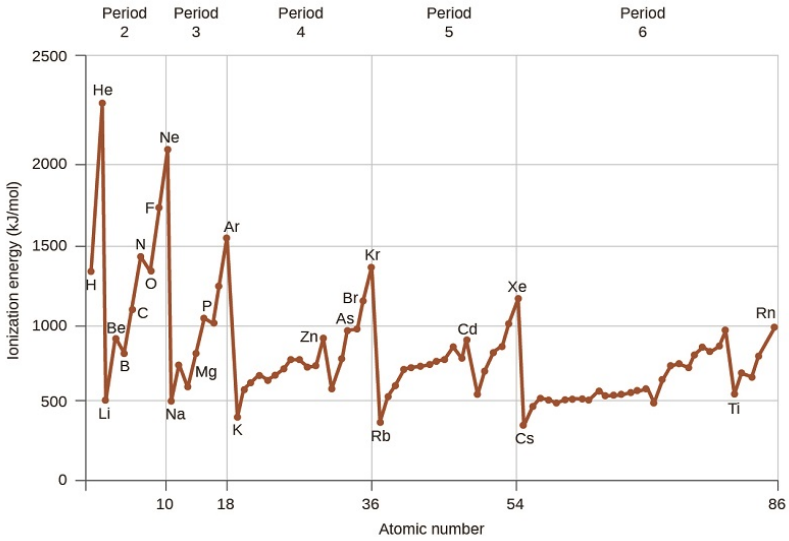


Figure 5.4.4: The first ionization energy of the elements in the first five periods are plotted against their atomic number.

Figure 5.4.4 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 ($[\mathrm{He}]2s^2$) is an *s* electron, whereas the electron removed during the ionization of boron ($[\mathrm{He}]2s^2 2p^1$) 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. These same values are shown in periodic table form in Figure 5.4.5.

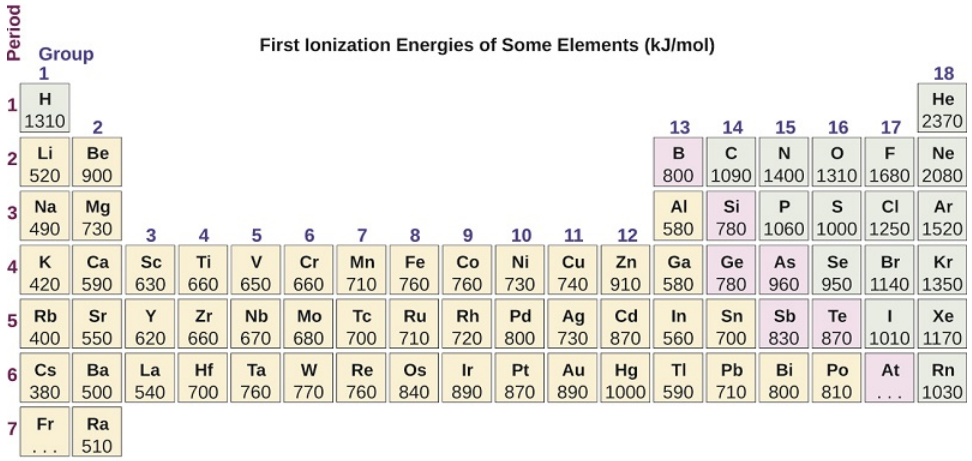
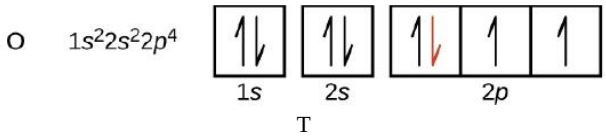


Figure 5.4.5: This version of the periodic table shows the first ionization energy of (IE: $_1$), in kJ/mol, of selected elements. The trends for first ionization energies across periods and down groups are shown in this version of the periodic table.

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 5.4.4.



T

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 5.4.2, 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 5.4.2: 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 5.4.2: 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

$$\mathrm{Al} \quad (\mathrm{Al}^{2+} \longrightarrow \mathrm{Al}^{3+} + \mathrm{e}^-)$$

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 5.4.2

Which has the lowest value for IE_1: O, Po, Pb, or Ba?

Answer

Ba

5.4.4: 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).

$$\mathrm{X}(g) + \mathrm{e}^- \longrightarrow \mathrm{X}^-(g) \quad \mathrm{EA}_1$$

This process can be either endothermic or exothermic, depending on the element. The EA of some of the elements is given in Figure 5.4.6. 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.

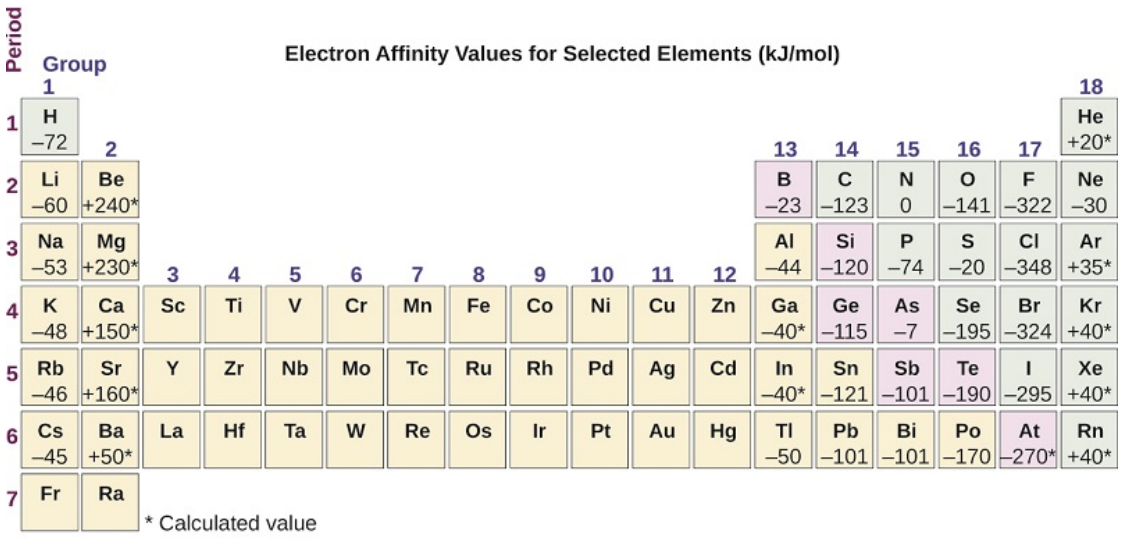


Figure 5.4.6: This version of the periodic table displays the electron affinity values (in kJ/mol) for selected elements.:

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.

5.4.5: 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 5.4: Periodic Variations in Element Properties is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

- **6.5: Periodic Variations in Element Properties** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

5.E: Electronic Structure and Periodic Properties- Homework

5.E.1: Turn in your answers for the following questions - show your work

1. Write the electron configuration (ie: $1s^2$, $2s^1$), orbital energy diagram, and orbital box diagram for,
   a. H, and Na
   b. Be and Ca
   c. C and Ge
   d. Cl^{1-} and K^{1+}
2. Chlorophyll b absorbs light at a wavelength of 625 nm, what is the frequency (Hz) and energy (J) for a photon of light at this wavelength?

5.E.2: The Following Questions are for your practice - Do Not Turn In. They include answers so you can check your work

5.E.2.1: Electromagnetic Energy

1. An FM radio station found at 103.1 on the FM dial broadcasts at a frequency of $1.031 \times 10^8\ s^{-1}$ (103.1 MHz). What is the wavelength of these radio waves in meters?

   answer

$$\lambda = \frac{c}{\nu}$$

$$\lambda = \frac{2.998 \times 10^8\ \frac{m}{s}}{1.031 \times 10^8\ \frac{1}{s}} = 2.908\ m$$

2. 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

$$E = \frac{hc}{\lambda}$$

$$E = \frac{(2.998 \times 10^8 \frac{m}{s})\ (6.6262 \times 10^{-34} Js)}{4.358 \times 10^{-7} m}$$

$$= 4.56 \times 10^{-19} J$$

5.E.2.2: The Bohr Model

1. 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

5.E.2.3: Development of Quantum Theory

1. Describe the properties of an electron associated with each of the following four quantum numbers: *n*, *l*, m_l, and m_s.

   answer

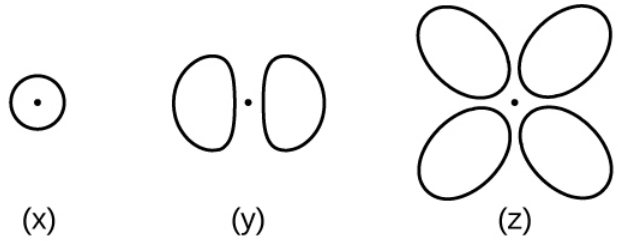
   n determines the general range for the value of energy and the probable distances that the electron can be from the nucleus. *l* determines the shape of the orbital. m_l determines the orientation of the orbitals of the same *l* value with respect to one another. m_s determines the spin of an electron.

2. 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*

3. 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)?
   b. How many orbitals of type (x) are found in a shell with $n = 2$? How many of type (y)?
   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 $n = 2$.
   d. What are the possible l and m_l values for an orbital of type (x)? Of type (y)?

answer

(a) x. 2, y. 2 ;(b) x. 1, y. 3 (c) x. 4 0 0 $\frac{1}{2}$, y. 2 1 0 $\frac{1}{2}$; (d) x. $l = 0$, $m_l = 0$, y. $l = 1$, $m_l = –1$, 0, or +1

4. 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	$+\frac{1}{2}$
4	1	+1	$+\frac{1}{2}$
4	1	−1	$-\frac{1}{2}$

5.E.2.4: Periodic Variations in Element Properties

1. Using complete subshell notation ($1s^2 2s^2 2p^6$, and so forth), predict the electron configuration of each of the following atoms:
   a. C
   b. P

answer

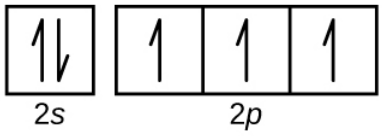
a.) $1s^2 2s^2 2p^2$

b.) $1s^2 2s^2 2p^6 3s^2 3p^3$

2. Use an orbital box diagram to describe the electron configuration of the valence shell of each of the following atoms:

   a. N

answer



3. 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-}

4. Based on their positions in the periodic table, predict which has the smallest atomic radius: Mg, Sr, Si, Cl, I.

answer

Rb < Li < N < F

5. 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

$Si^{4+} < Al^{3+} < Ca^{2+} < K^+$

This page titled 5.E: Electronic Structure and Periodic Properties- Homework is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

CHAPTER OVERVIEW

6: Chemical Bonding and Molecular Geometry

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

General Chemistry

A chemical bond is an attraction between atoms that allows the formation of chemical substances that contain two or more atoms. The bond is caused by the electrostatic force of attraction between opposite charges, either between electrons and nuclei, or as the result of a dipole attraction. All bonds can be explained by quantum theory, but, in practice, simplification rules allow chemists to predict the strength, directionality, and polarity of bonds. The octet rule and VSEPR theory are two examples. More sophisticated theories are valence bond theory which includes orbital hybridization and resonance, and the linear combination of atomic orbitals molecular orbital method. Electrostatics are used to describe bond polarities and the effects they have on chemical substances.

6.1: Ionic and Covalent Bonding

6.2: Lewis Symbols and Structures

6.3: Formal Charge and Resonance

6.4: Molecular Structure and Polarity

6.5: Intermolecular Forces

6.E: Chemical Bonding and Molecular Geometry- Homework

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 6: Chemical Bonding and Molecular Geometry is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

6.1: Ionic and Covalent Bonding

6.1.1: Introduction

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
- Describe the formation of covalent bonds
- Define electronegativity and assess the polarity of covalent bonds

It has long been known that pure carbon occurs in different forms (allotropes) including graphite and diamonds. But it was not until 1985 that a new form of carbon was recognized: buckminsterfullerene, commonly known as a "buckyball" and is shown in Figure 6.1.1. This molecule was named after the architect and inventor R. Buckminster Fuller (1895–1983), whose signature architectural design was the geodesic dome, characterized by a lattice shell structure supporting a spherical surface. Experimental evidence revealed the formula, C_{60}, and then scientists determined how 60 carbon atoms could form one symmetric, stable molecule. They were guided by bonding theory—the topic of this chapter—which explains how individual atoms connect to form more complex structures.



Figure 6.1.1: Nicknamed "buckyballs," buckminsterfullerene molecules (C_{60}) contain only carbon atoms. Here they are shown in a ball-and-stick model (left). These molecules have single and double carbon-carbon bonds arranged to form a geometric framework of hexagons and pentagons, similar to the pattern on a soccer ball (center). This unconventional molecular structure is named after architect R. Buckminster Fuller, whose innovative designs combined simple geometric shapes to create large, strong structures such as this weather radar dome near Tucson, Arizona (right). (credit middle: modification of work by "Petey21"/Wikimedia Commons; credit right: modification of work by Bill Morrow).

6.1.2: Ionic Bonding

As you have learned, ions are atoms or molecules bearing an electrical charge. A cation is a positive ion that forms when a neutral atom loses one or more electrons from its valence shell. An an anion is a negative ion that forms when a neutral atom gains one or more electrons in its valence shell. The opposite charges of a cation and an anion cause an attraction that forms an ionic bond.

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 charged ions have very different physical and chemical properties. Figure 6.1.2 shows sodium metal, a soft, silvery-white metal that burns vigorously in air and reacts explosively with water, which is made of of sodium atoms. It also shows chlorine gas, a yellow-green gas that is extremely corrosive to most metals and very poisonous to animals and plants, which is made up of chlorine *atoms* combined into molecules of chlorine or Cl_2. Sodium metal reacts vigerously with chlorine gas to form sodium chloride, a white crystalline compound called table salt. Sodium chloride contains sodium *cations* and chloride *anions* and

has properties entirely different from sodium metal and chlorine gas. Sodium chloride is essential to life and dissolves in water while sodium atoms react vigorously with water and chlorine gas is poisonous.



Figure 6.1.2: (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)

6.1.2.1: 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.

Since 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 × +3) + (3 × –2) = 0].

It is important to note that the formula for an ionic compound does *not* represent the physical arrangement of its ions. Sodium chloride (NaCl) is not a molecule with one sodium atom connected to one chlorine atom. Instead each sodium ion is attracted to several chloride ions in different directions. This results in the ions arranging themselves into a tightly bound, three-dimensional structure called a lattice. The structure of this lattice depends upon the size and charge if the ions. Figure 6.1.3 shows the arragement for sodium chloride, which is a regular arrangement of equal numbers of Na^+ cations and Cl^- anions.

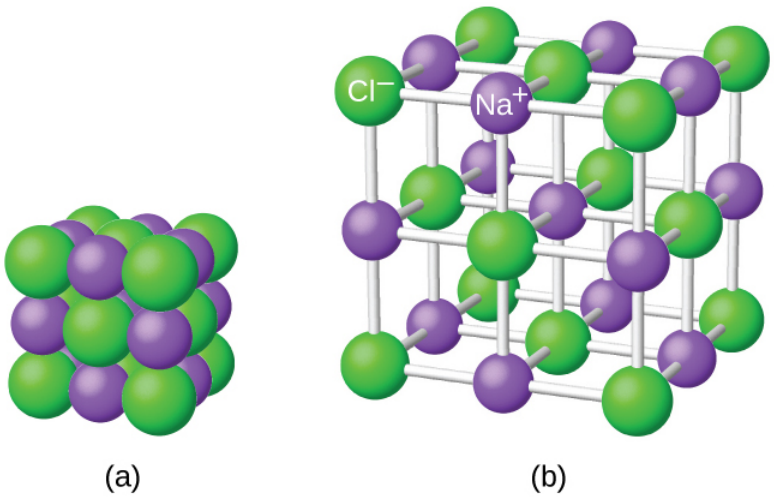


Figure 6.1.3: The atoms in sodium chloride (common table salt) are arranged to (a) maximize opposite charges interacting. The smaller spheres represent sodium ions, the larger ones represent chloride ions. In the expanded view (b), the geometry can be seen more clearly. Note that each ion is "bonded" to all of the surrounding ions—six in this case.

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:

$$\mathrm{NaCl}(s) \longrightarrow \mathrm{Na}^+(g) + \mathrm{Cl}^-(g) \quad \Delta H = 769\ \mathrm{kJ}$$

6.1.2.2: 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 $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$. 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 $1s^2 2s^2 2p^6 3s^2 3p^6$. The Ca^{2+} ion is therefore isoelectronic with the noble gas Ar.

Example 6.1.1: Determining the Electronic Structures of Cations

Potassium is required in our diet. Write the electron configuration for a potassium ion.

Solution

First, write the electron configuration for the neutral atom:

- K: $[Ar]4s^1$

Next, remove electrons from the highest energy orbital. Potassium is a member of group 1, so it should have a charge of 1+, and thus loses one electron from its *s* orbital. This gives the following electron configuration for the ion:

- K^{2+}: [Ar]

Exercise 6.1.1

Magnesium is also required in our diet. Write the electron configurations of the ion.

Answer

Mg^{2+}: [Ne]

6.1.2.3: 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 6.1.2: 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 6.1.2

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-}: $[Ne]3s^2 3p^6$

6.1.3: 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 shares an electron with the other hydrogen atom. This sharing of electrons forms a covalent bond.

Compounds that contain covalent bonds exhibit different physical properties than ionic compounds. In ionic compounds all the ions are strongly bound to each other in the lattice structure. With covalent bonds, the atoms are held together in distinct molecules. The attraction between these atoms is strong but the attraction between atoms in different molecules is much weaker because the molecules have a neutral charge. This is why molecular compounds often have lower melting and boiling points than ionic compounds. Many covalent compounds are liquids or gases at room temperature and as solids they are usually softer than ionic solids. Ionic compounds are good conductors of electricity when dissolved in water but most covalent compounds are poor conductors of electricity in any state since the molecules do not have an overall charge.

6.1.3.1: 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 6.1.4 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 where these opposing forces balance and the molecule has the lowest potential energy.

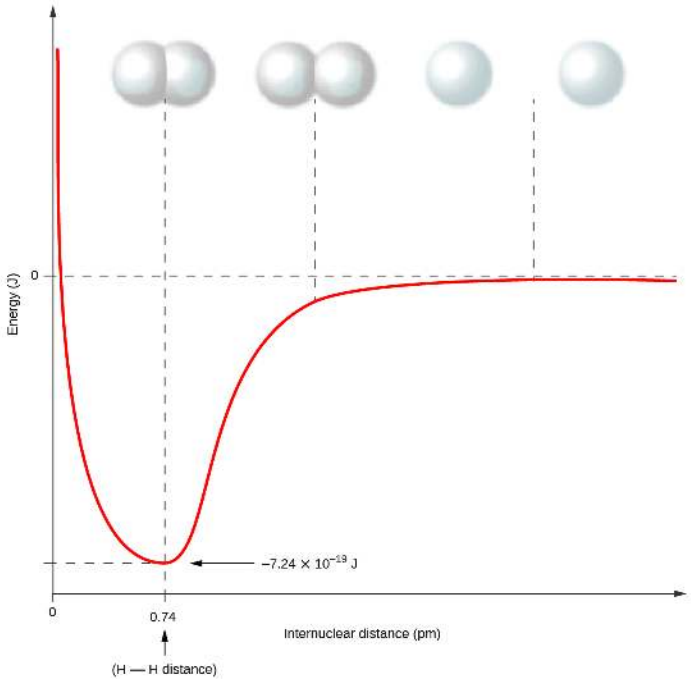


Figure 6.1.4*: The potential energy of two separate hydrogen atoms (right) decreases as they approach each other, and the single electrons on each atom are shared to form a covalent bond. The bond length is the internuclear distance at which the lowest potential energy is achieved.*

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:

$$2\,\mathrm{H}(g) \longrightarrow \mathrm{H_2}(g) \quad \Delta H = -436\ \mathrm{kJ}$$

6.1.3.2: 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 6.1.5 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 6.1.4, which shows the even distribution of electrons in the H_2 nonpolar bond.

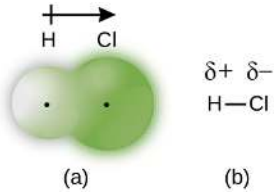


Figure 6.1.5: (a) The distribution of electron density in the HCl molecule is uneven. The electron density is greater around the chlorine nucleus. The small, black dots indicate the location of the hydrogen and chlorine nuclei in the molecule. (b) Symbols δ+ and δ– indicate the polarity of the H–Cl bond.

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 6.1.5*b*.

6.1.3.3: 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 6.1.6 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.)

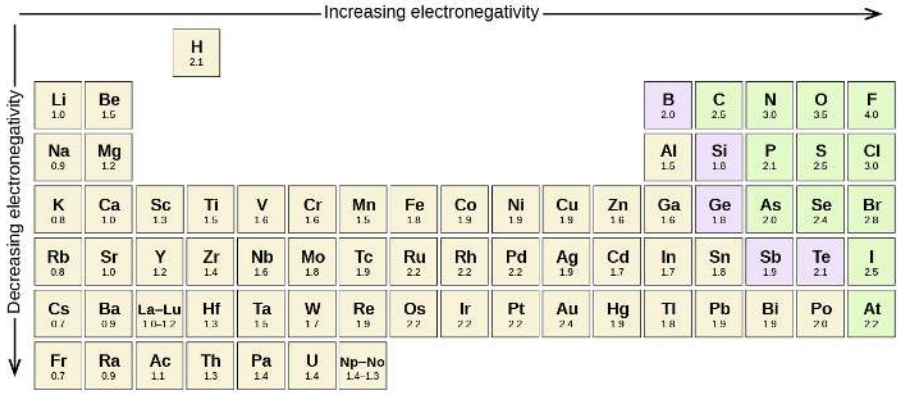


Figure 6.1.6: The electronegativity values derived by Pauling follow predictable periodic trends with the higher electronegativities toward the upper right of the periodic table.

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 fight against the nuclear arms race between East and West. 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.

6.1.3.4: Electronegativity versus Electron Affinity

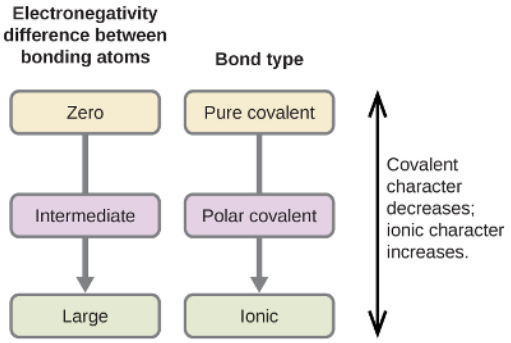
We must be careful not to confuse electronegativity and electron affinity. The electron affinity of an element is a measurable physical quantity, namely, the energy released or absorbed when an isolated gas-phase atom acquires an electron, measured in kJ/mol. Electronegativity, on the other hand, describes 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.

6.1.3.5: 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).

The simplist 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. This idea is refined in Figure 6.1.7, which shows a rough approximation of the electronegativity differences associated with

covalent, polar covalent, and ionic bonds. This table is a general guide but there are 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.



Bond Type	Electronegativity Difference
pure covalent	< 0.4
polar covalent	between 0.4 and 1.8
ionic	> 1.8

Figure 6.1.7: As the electronegativity difference increases between two atoms, the bond becomes more 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. Bonding in potassium nitrate is both ionic, from the electrostatic attraction between the ions K^+ and NO_3^-, and covalent, from the bonding between nitrogen and the oxygen atoms in NO_3^-.

Example 6.1.3: 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 6.1.1 shows these bonds in order of increasing polarity.

Table 6.1.1: Bond Polarity and Electronegativity Difference

Bond	ΔEN	Polarity
C–H	0.4	$\overset{\delta-}{C}-\overset{\delta+}{H}$
S–H	0.4	$\overset{\delta-}{S}-\overset{\delta+}{H}$
C–N	0.5	$\overset{\delta+}{C}-\overset{\delta-}{N}$
N–H	0.9	$\overset{\delta-}{N}-\overset{\delta+}{H}$
C–O	1.0	$\overset{\delta+}{C}-\overset{\delta-}{O}$
O–H	1.4	$\overset{\delta-}{O}-\overset{\delta+}{H}$

Exercise 6.1.3

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 6.1.3, arrange the bonds in order of increasing polarity and designate the positive and negative atoms using the symbols δ+ and δ–.

Answer

Answer to Exercise 7.2.1

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.

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

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 6.1: Ionic and Covalent Bonding is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

- **7.1: Prelude to Chemical Bonding and Molecular Geometry** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.
- **7.2: Ionic Bonding** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.
- **7.3: Covalent Bonding** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

6.2: 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.

6.2.1: 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 as shown in Figure 6.2.1 for a calcium atom:

Figure 6.2.1: Lewis Dot symbol for calcium atom

Figure 6.2.2 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 6.2.2: 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 6.2.3 demonstrates the use of Lewis symbols to show the transfer of electrons during the formation of ionic compounds.

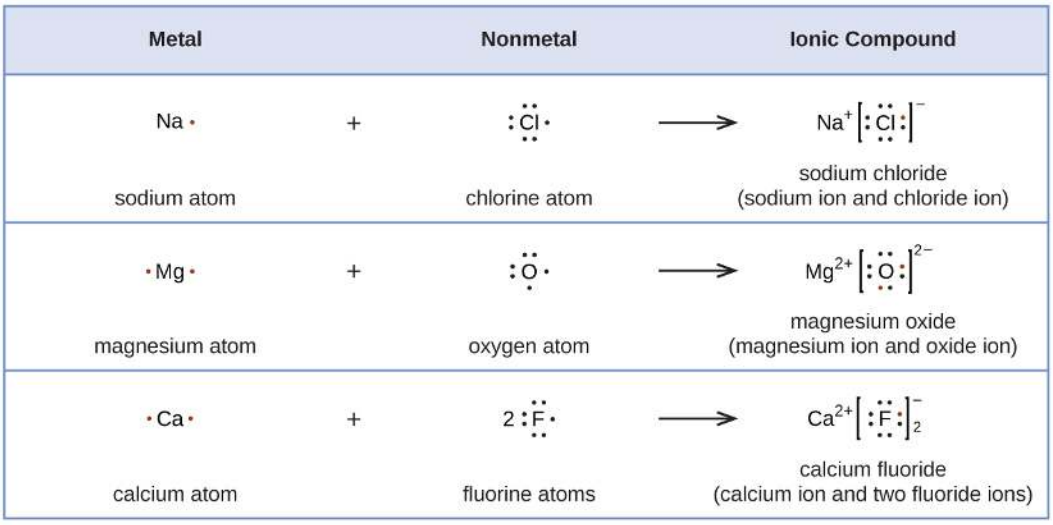
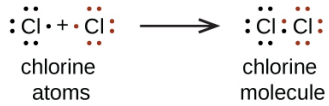


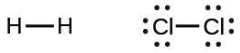
Figure 6.2.3: Cations are formed when atoms lose electrons, represented by fewer Lewis dots, whereas anions are formed by atoms gaining electrons. The total number of electrons does not change.

6.2.2: 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:

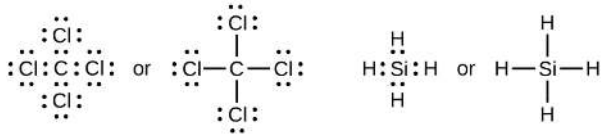


In the Lewis model, a single shared pair of electrons is a single bond. Each Cl atom interacts with eight valence electrons total: the six in the lone pairs and the two in the single bond.

6.2.3: The Octet

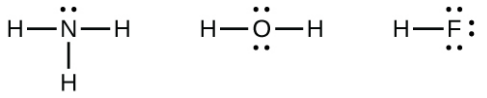
The other halogen molecules (F_2, Br_2, I_2, and At_2) form bonds like those in the chlorine molecule: one single bond between atoms and three lone pairs of electrons per atom. This allows each halogen atom to have a noble gas electron configuration. The tendency of main group atoms to form enough bonds 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 useful for 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).



Since hydrogen only needs two electrons to fill its valence shell, it is an exception to the octet rule and only forms one bond.

Continuing across the periodic table, 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, nitrogen forms three covalent bonds with one lone pair - as shown below for NH_3 (ammonia). Elements in group 16 have 6 valence electrons, so oxygen forms two bonds and has two lone pairs - as shown for H_2O. And finally elements in group 17 have 7 valence electrons, so HF forms one bond and the fluorine has three lone pairs.

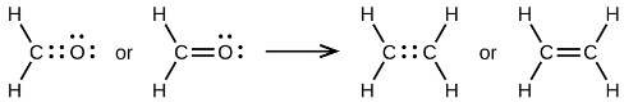


ammonia Water hydrogen fluoride

The octet rule has many exceptions in addition to hydrogen. Elements in the third row of the periodic table can exceed the octet rule and form more bonds than predicted by the octet rule.

6.2.4: 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

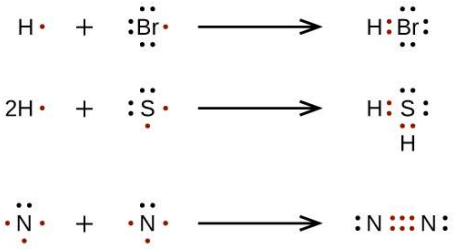
A triple bond forms when three electron pairs are shared by a pair of atoms, as in carbon monoxide (CO) and the cyanide ion (CN^-):



carbon monoxide cyanide ion

6.2.5: Writing Lewis Structures with an Octet

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:

$$\begin{aligned} &SiH_4 && (6.2.1)\\ &\text{Si: } 4 \text{ valence electrons/atom} \times 1 \text{ atom} = 4 && (6.2.2)\\ +&\text{H: } 1 \text{ valence electron/atom} \times 4 \text{ atoms} = 4 && (6.2.3)\\ &= 8 \text{ valence electrons} && (6.2.4)\end{aligned}$$

   - 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):

$$\begin{aligned} &CHO_2^-\\ &\text{C: } 4 \text{ valence electrons/atom} \times 1 \text{ atom} = 4\\ &\text{H: } 1 \text{ valence electron/atom} \times 1 \text{ atom} = 1\\ &\text{O: } 6 \text{ valence electrons/atom} \times 2 \text{ atoms} = 12\\ +&\quad 1 \text{ additional electron} = 1\\ &= 18 \text{ valence electrons}\end{aligned}$$

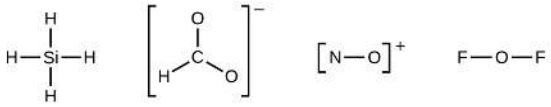
   - For a *positive ion*, such as NO^+, we add the number of valence electrons on the atoms in the ion and then subtract the number of positive charges on the ion (one electron is lost for each single positive charge) from the total number of valence electrons:

$$\begin{aligned} &NO^+\\ &\text{N: } 5 \text{ valence electrons/atom} \times 1 \text{ atom} = 5\\ &\text{O: } 6 \text{ valence electron/atom} \times 1 \text{ atom} = 6\\ +&-1 \text{ electron (positive charge)} = -1\\ &= 10 \text{ valence electrons}\end{aligned}$$

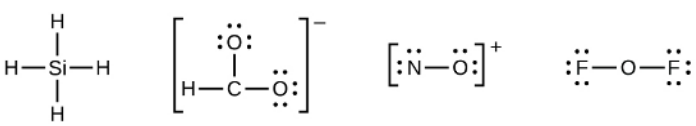
   - Since OF_2 is a neutral molecule, we simply add the number of valence electrons:

$$\begin{aligned} &OF_2\\ &\text{O: } 6 \text{ valence electrons/atom} \times 1 \text{ atom} = 6\\ +&\text{F: } 7 \text{ valence electrons/atom} \times 2 \text{ atoms} = 14\\ &= 20 \text{ valence electrons}\end{aligned}$$

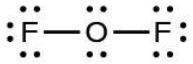
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond. (Note that we denote ions with brackets around the structure, indicating the charge outside the brackets:)



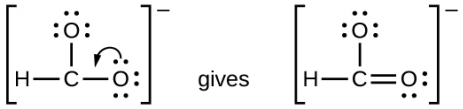
3. When several arrangements of atoms are possible, as for CHO_2^-, the less electronegative elements are more likely to be central atoms. In CHO_2^-, the less electronegative carbon atom occupies the central position with the oxygen and hydrogen atoms surrounding it. Other examples include P in $POCl_3$, S in SO_2, and Cl in ClO_4^-. Hydrogen only makes one bond so it can not be a central atom and since it is very electronegative fluorine also not 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; each of the oxygen atoms in CHO_2^- can take three lone pairs to complete their octet; NO^+ does not have enough electrons to complete the octets for N and O; OF_2 has enough electrons to complete the octets for the fluorine atoms.:



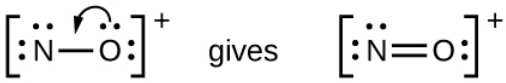
5. Place all remaining electrons on the central atom.
   - For SiH_4, CHO_2^-, and NO^+, there are no remaining electrons; we already placed all of the electrons determined in Step 1.
   - For OF_2, we had 16 electrons remaining in Step 3, and we placed 12, leaving 4 to be placed on the central atom:



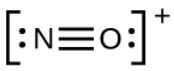
6. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.
   - SiH_4: Si already has an octet, so nothing needs to be done.
   - CHO_2^-: We have distributed the valence electrons as lone pairs on the oxygen atoms, but the carbon atom lacks an octet so one lone pair is moved to create a double bond:



- 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 from the oxygen atom to form a double bond:



- This completes the octet for nitrogen, but not for oxygen. Moving one of the nitrogen lone pairs to create a triple bond complets the octet for oxygen to give a final structure:



- In OF_2, each atom has an octet as drawn, so nothing changes.

Example 6.2.1: Writing Lewis Structures

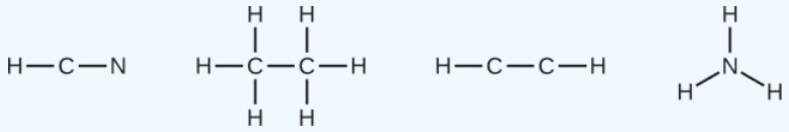
NASA's Cassini-Huygens mission detected a large cloud of hydrogen cyanide (HCN) on Titan, one of Saturn's moons. Titan also contains ethane (H_3CCH_3), acetylene (HCCH), and ammonia (NH_3). What are the Lewis structures of these molecules?

Solution

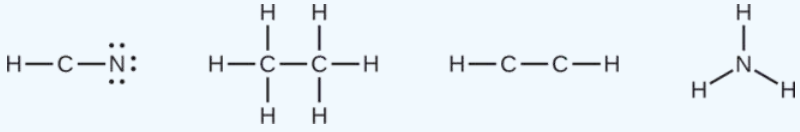
Calculate the number of valence electrons.

- 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:



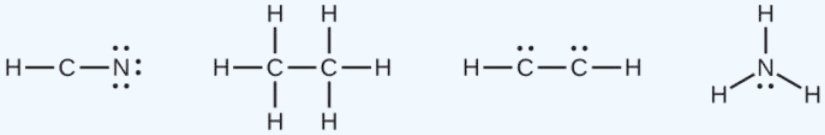
Where needed, distribute electrons to the terminal atoms:



- 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

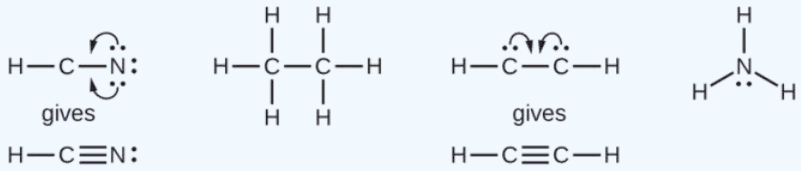
Where needed, place remaining electrons on the central atom:



- 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 6.2.1

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



6.2.6: Beyond the Octet

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.

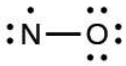
6.2.6.1: Odd-electron Molecules

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.

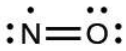
To draw the Lewis structure for an odd-electron molecule like NO, we follow the same five steps we would for other molecules, but with a few minor changes:

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:

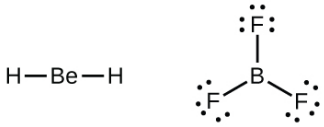


4. *Place all remaining electrons on the central atom.* Since there are no remaining electrons, this step does not apply.
5. *Rearrange the electrons to make multiple bonds with the central atom in order to obtain octets wherever possible.* We know that an odd-electron molecule cannot have an octet for 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:)

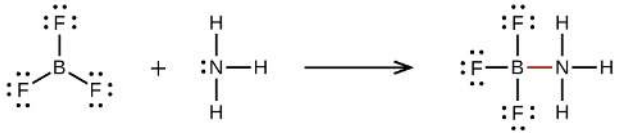


6.2.6.2: Electron-deficient Molecules

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:



6.2.6.3: 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 6.2.5 shows the Lewis structures for two hypervalent molecules, PCl_5 and SF_6.

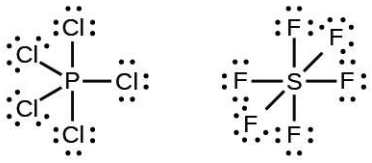
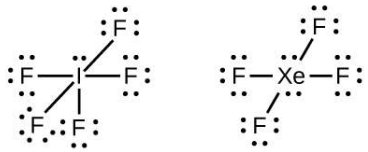


Table **6.2.5***: In PCl_5, the central atom phosphorus shares five pairs of electrons. In SF_6, sulfur shares six pairs of electrons.*

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 6.2.2: 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

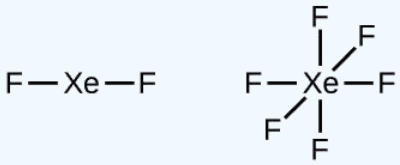
We can draw the Lewis structure of any covalent molecule by following the six steps discussed earlier. In this case, we can condense the last few steps, since not all of them apply.

Step 1: Calculate the number of valence electrons:

$$XeF_2: 8 + (2 \times 7) = 22$$

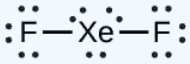
$$XeF_6: 8 + (6 \times 7) = 50$$

***Step 2: Draw a skeleton joining the atoms by single bonds.* Xenon will be the central atom because fluorine cannot be a central atom:**

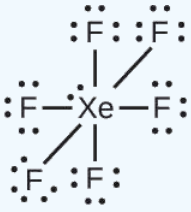


Step 3: Distribute the remaining electrons.

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:



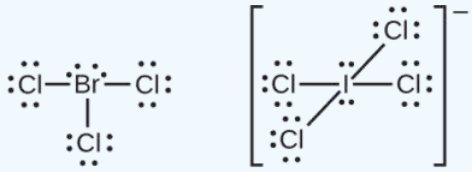
XeF_6: We place three lone pairs of electrons around each F atom, accounting for 36 electrons. Two electrons remain, and this lone pair is placed on the Xe atom:



Exercise 6.2.2: 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

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 6.2: Lewis Symbols and Structures is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

- **7.4: Lewis Symbols and Structures** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

6.3: Formal Charge 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
- 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

6.3.1: Formal Charge

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.

6.3.1.1: 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 of an atom as follows:

$$\text{formal charge} = \#\text{ valence shell electrons (free atom)} - \#\text{ lone pair electrons} - \#\text{ bonds}$$

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 equal to the charge of the molecule or ion.

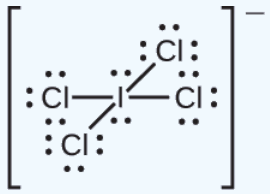
We must remember that the formal charge calculated for an atom is not the *actual* charge of the atom in the molecule. Formal charge is only a useful bookkeeping procedure; it does not indicate the presence of actual charges.

Example 6.3.1: Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the ion $\mathrm{ICl_4^-}$.

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 6.3.1

Calculate the formal charge for each atom in the carbon monoxide molecule:



Answer

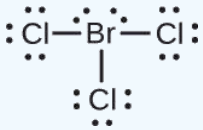
C −1, O +1

Example 6.3.2: 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

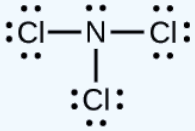
All atoms in $BrCl_3$ have a formal charge of zero, and the sum of the formal charges totals zero, as it must in a neutral molecule.

Exercise 6.3.2

Determine the formal charge for each atom in NCl_3.

Answer

N: 0; all three Cl atoms: 0



6.3.1.2: Using Formal Charge to Predict Molecular Structure

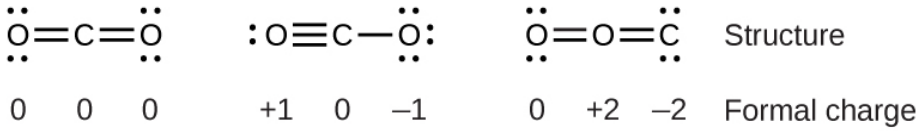
The arrangement of atoms in a molecule or ion is called its molecular structure. In many cases, following the steps for writing Lewis structures may lead to more than one possible molecular structure—different multiple bond and lone-pair electron placements or different arrangements of atoms, for instance. 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.

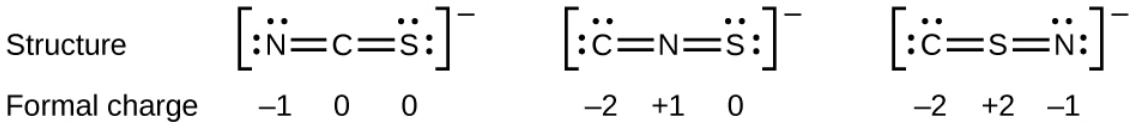
3. Lewis structures are preferable when adjacent formal charges are zero or of the opposite sign.
4. When we must choose among several Lewis structures with similar distributions of formal charges, the structure with the negative formal charges on the more electronegative atoms is preferable.

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:



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). The other two structures both have formal charges on two of the atoms.

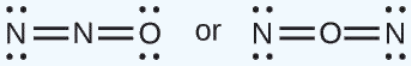
As another example, the thiocyanate ion, an ion formed from a carbon atom, a nitrogen atom, and a sulfur atom, could have three different molecular structures: CNS^-, NCS^-, or CSN^-. The formal charges present in each of these molecular structures can help us pick the most likely arrangement of atoms. Possible Lewis structures and the formal charges for each of the three possible structures for the thiocyanate ion are shown here:



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 6.3.3: Using Formal Charge to Determine Molecular Structure

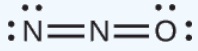
Nitrous oxide, N_2O, commonly known as laughing gas, is used as an anesthetic in minor surgeries, such as the routine extraction of wisdom teeth. Which is the likely structure for nitrous oxide?



Solution Determining formal charge yields the following:



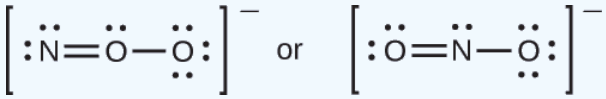
The structure with a terminal oxygen atom best satisfies the criteria for the most stable distribution of formal charge:



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 6.3.3

Which is the most likely molecular structure for the nitrite (NO_2^-) ion?



Answer

ONO^-

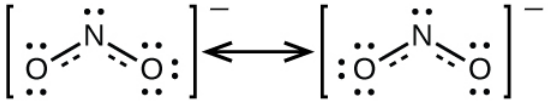
6.3.2: Resonance

You may have noticed that the nitrite anion in Example $6.3.3$ 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:



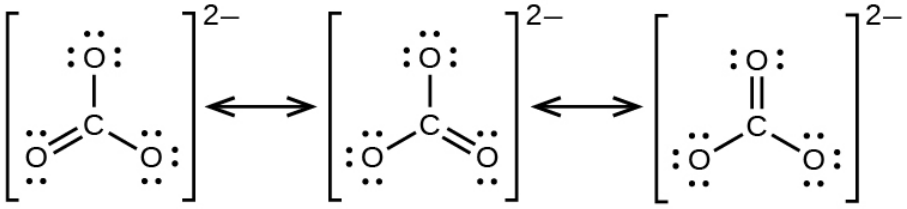
If nitrite ions do indeed contain a single and a double bond, we would expect for the two bond lengths to be different. A double bond between two atoms is shorter (and stronger) than a single bond between the same two atoms. Experiments show, however, that both N–O bonds in NO_2^- have the same strength 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:



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:



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.

6.3.3: Bond Length

Table $6.3.2$ shows average bond lengths for some common covalent bonds with carbon, nitrogen, and oxygen.

Table $6.3.2$: Bond Length (pm)

	C	N	O
C	154 (C-C) 134 (C=C) 120 (C≡C)	143 (C-N) 138 (C=N) 116 (C≡N)	143 (C-O) 123(C=O) 113(C≡O)

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).

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.

6.3.3.1: Key Equations

- Bond energy for a diatomic molecule: $\mathrm{XY}(g) \longrightarrow \mathrm{X}(g) + \mathrm{Y}(g) \quad \mathrm{D_{X–Y}} = \Delta H^\circ$
- Enthalpy change: $\Delta H = \Sigma \mathrm{D_{bonds\ broken}} - \Sigma \mathrm{D_{bonds\ formed}}$
- Lattice energy for a solid MX: $\mathrm{MX}(s) \longrightarrow \mathrm{M}^{n+}(g) + \mathrm{X}^{n-}(g) \quad \Delta H_{\mathrm{lattice}}$
- Lattice energy for an ionic crystal: $\Delta H_{\mathrm{lattice}} = \dfrac{\mathrm{C}(\mathrm{Z}^+)(\mathrm{Z}^-)}{\mathrm{R_o}}$
- $\text{formal charge} = \#\text{ valence shell electrons (free atom)} - \#\text{ one pair electrons} - \dfrac{1}{2}\ \#\text{ bonding electrons}$

Glossary

bond energy

(also, bond dissociation energy) energy required to break a covalent bond in a gaseous substance.

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)

lattice energy ($\Delta H_{\text{lattice}}$)

energy required to separate one mole of an ionic solid into its component gaseous ions

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

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 6.3: Formal Charge and Resonance is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

- **7.5: Formal Charges and Resonance** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.
- **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.

https://chem.libretexts.org/@go/page/432485

6.4: 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 6.4.1). A bond angle is the angle between two adjacent bonds. A bond length is the distance between the nuclei of two bonded atoms. Bond distances are measured in Ångstroms (1 Å = 10^{-10} m) or picometers (1 pm = 10^{-12} m, 100 pm = 1 Å).

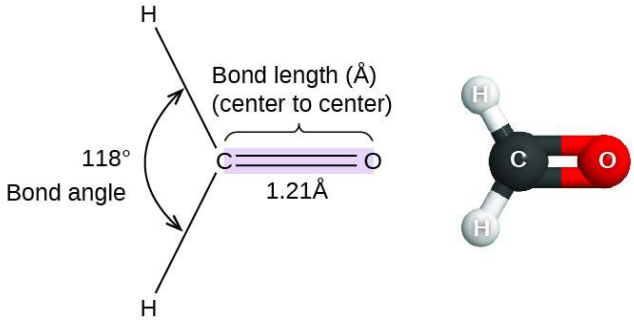


Figure 6.4.1: Bond distances (lengths) and angles are shown for the formaldehyde molecule, H_2CO.

6.4.1: VSEPR Theory

Valence shell electron-pair repulsion theory (VSEPR theory) is used to predict the structure around a central atom of a molecule based on the number of bonds and lone electron pairs in the Lewis structure. The VSEPR model assumes that electron pairs in the valence shell of a central atom arrange to minimize repulsions by maximizing the distance between these electron pairs. 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 the arrangement of atoms in a molecule. We should understand, however, that the theory is a first approximation and that fully understanding the structure of a molecule is much more complex.

A gaseous BeF_2 molecule is a simple example to introduce VSEPR. The Lewis structure of BeF_2 (Figure 6.4.2) shows two electron pairs around the central beryllium atom. There are two bonds and no lone pairs of electrons on this beryllium atom so according to VSEPR the bonds should be as far apart as possible. The electron density from the bonds repel and this repulsion is minimized when the bonds are on opposite sides of the central atom so the bond angle is 180° (Figure 6.4.2).

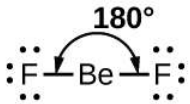


Figure 6.4.2: The BeF_2 molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the Be atom.

Figure 6.4.3 illustrates electron-pair geometries for different structures 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. The spatial relationship, diagrams for the structure, names for the structures, and bond angles are all shown in this figure.

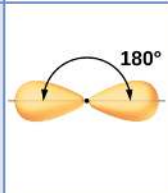
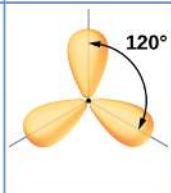
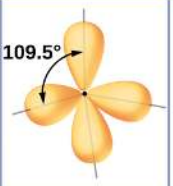
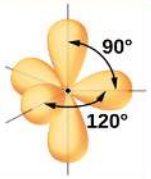
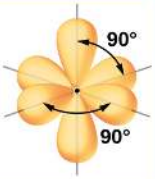
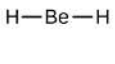
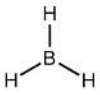
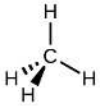
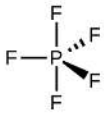
Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions 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 6.4.3: The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs).

6.4.2: 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 6.4.3 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 are the same as the molecular structures when there are no lone electron pairs around the central atom. When a central atom has lone pair electrons the molecular structure is different from the electron-pair geometry.

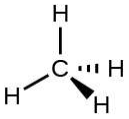


Figure 6.4.4: The molecular structure of the methane molecule, CH_4, is shown with a tetrahedral arrangement of the hydrogen atoms. VSEPR structures like this one are often drawn using the wedge and dash notation, in which solid lines represent bonds in the plane of the page, solid wedges represent bonds 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 6.4.4). 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 6.4.5). Since the electron-pair geometry and the molecular structure are different for ammonia we need two different names for these geometries.

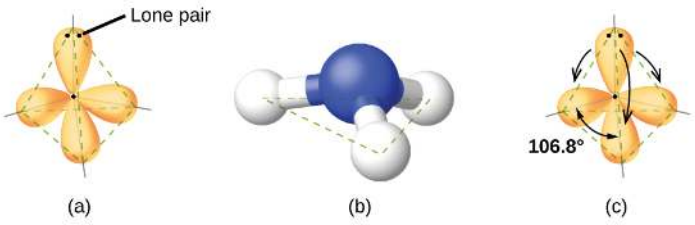


Figure 6.4.5: (a) The electron-pair geometry for the ammonia molecule is tetrahedral with one lone pair and three single bonds. (b) The trigonal pyramidal molecular structure is determined from the electron-pair geometry. (c) The actual bond angles deviate slightly from the idealized angles because the 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°.

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 6.4.5) 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. There are slight deviations from the ideal because lone pairs occupy larger regions of space than bonding electrons so the H–N–H bond angle in NH_3 is slightly smaller than the 109.5° angle tetrahedron. (Figure 6.4.6) summarizes the possible elecvtron-pair geometries and the corresponding molecular structures for up to six electron pairs.

Number of electron pairs	Electron pair geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	180° Linear				
3	120° Trigonal planar	<120° Bent or angular			
4	109° Tetrahedral	<109° Trigonal pyramid	<<109° Bent or angular		
5	90°, 120° Trigonal bipyramid	<90°, <120° Sawhorse or seesaw	<90° T-shape	180° Linear	
6	90° Octahedral	<90° Square pyramid	90° Square planar	<90° T-shape	180° Linear

Figure 6.4.6: 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.

Please note that because the lone pair-bonding pair repulsion is greater than the bonding pair-bonding pair repulsion the bond angles for real molecules will differ slightly from those shown in Figure 6.4.6. The ideal molecular structures are predicted based on the electron-pair geometries.

Small distortions from these ideal angles are shown for ammonia in Figure 6.4.5. The distortions result from differences in repulsion between various regions of electron density. VSEPR theory predicts the magnitude of these distortions by establishing an order of repulsions and an order of the space occupied by different types 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

Different types of electron pairs also need different amounts of space. 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

Taken together the amount of repulsion and the amount of space can help determine the location of the lone pair electrons in the molecular structure and the amount that expected bond angles are distorted in actual molecules. Consider formaldehyde, H_2CO shown in Figure 6.4.1. This molecule has three regions of high electron density, two single bonds and one double bond. The basic geometry is trigonal planar with predicted 120° bond angles. However, the double bond takes up more space and pushes the single bonds further away so the angle between the single bonds is slightly smaller (118°) than expected.

According to VSEPR theory, the terminal atom locations (Xs in Figure 6.4.7) 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 and all the positions are equivilent. For trigonal bipyramidal electron-pair geometries, however, there are two distinct X positions (Figure 6.4.7a): 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.

The molecule ClF_3 is an example of a compound with trigonal bipyramid electron-pair geometry and two sets of lone pair electrons. Figure 6.4.7 shows the three possible arrangements for the three C-F bonds in the ClF_3 molecule. The most stable structure is with the lone pairs in equatorial locations so they have the most space. This gives ClF_3 a T-shaped molecular structure as shown in Figure 6.4.7b.

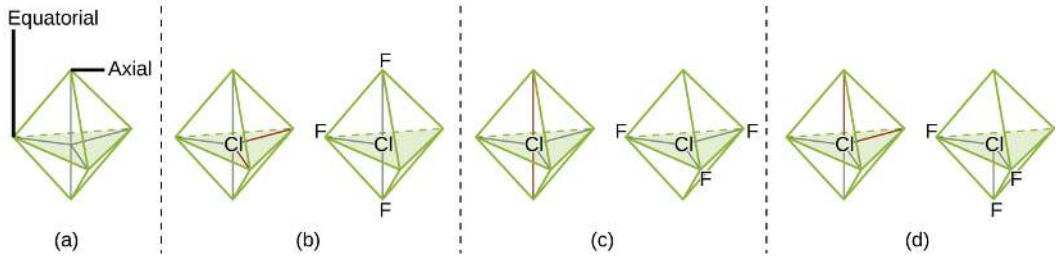


Figure 6.4.7: (a) In a trigonal bipyramid, the two axial positions are located directly across from one another, whereas the three equatorial positions are located in a triangular arrangement. (b–d) The two lone pairs (red lines) in ClF_3 have several possible arrangements, but the T-shaped molecular structure (b) is the one actually observed, consistent with the larger lone pairs both occupying equatorial positions.

Similarly for compounds with octahedral electron-pair geometry, when a central atom has lone electron pairs there are several different possible molecular structures. With two lone pairs they orient on opposite sides of the octahedron (180° apart), giving a square planar molecular structure that minimizes lone pair-lone pair repulsions. With three lone pairs they orient to give a T shaped molecule and with four lone pairs they orient to give a linear molecule. All these options are summarized in Figure 6.4.6.

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 6.4.7, first column).
4. Use the number of lone pairs to determine the molecular structure (Figure 6.4.7). 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.

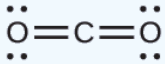
Example 6.4.1: Predicting Electron-pair Geometry and Molecular Structure

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

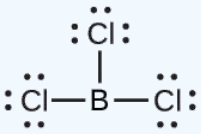
Solution

(a) We write the Lewis structure of CO_2 as:

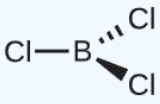


This shows us two regions of high electron density around the carbon atom—each double bond counts as one region, and there are no lone pairs on the carbon atom. Using VSEPR theory, we predict that the two regions of electron density arrange themselves on opposite sides of the central atom with a bond 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 6.4.1

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 6.4.2: 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:

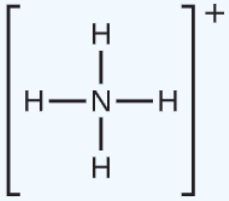


Figure 6.4.7).

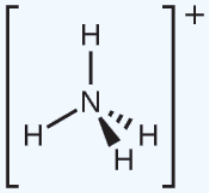


Figure 6.4.8: *The ammonium ion displays a tetrahedral electron-pair geometry as well as a tetrahedral molecular structure.*

Exercise 6.4.2

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 6.4.3: 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:

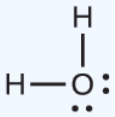


Figure 6.4.9. Thus, the electron-pair geometry is tetrahedral and the molecular structure is bent with an angle slightly less than 109.5°. In fact, the bond angle is 104.5°.

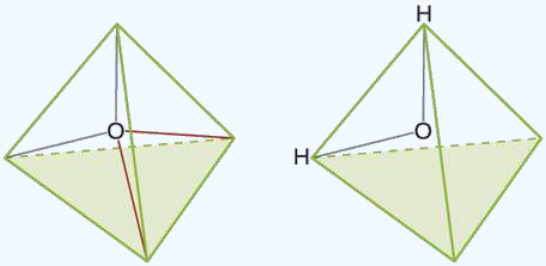


Figure 6.4.9: (a) H_2O has four regions of electron density around the central atom, so it has a tetrahedral electron-pair geometry. (b) Two of the electron regions are lone pairs, so the molecular structure is bent.

Exercise 6.4.3

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 6.4.4: 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:

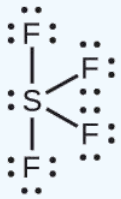


Figure 6.4.10).

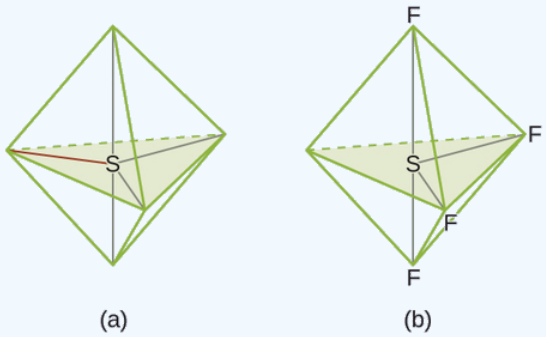


Figure 6.4.10: (a) SF_4 has a trigonal bipyramidal arrangement of the five regions of electron density. (b) One of the regions is a lone pair, which results in a seesaw-shaped molecular structure.

Exercise 6.4.4

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 6.4.4: 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:

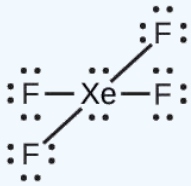


Figure 6.4.11: The five atoms are all in the same plane and have a square planar molecular structure.

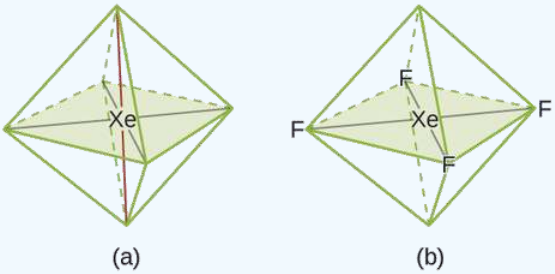


Figure 6.4.11: (a) XeF_4 adopts an octahedral arrangement with two lone pairs (red lines) and four bonds in the electron-pair geometry. (b) The molecular structure is square planar with the lone pairs directly across from one another.

Exercise 6.4.4

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

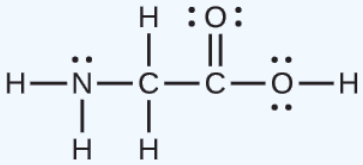
electron pair geometry: trigonal bipyramidal; molecular structure: linear

6.4.3: Molecular Structure for Multicenter Molecules

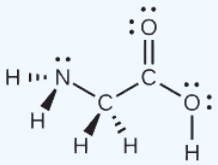
When a molecule or polyatomic ion has only one central atom, the molecular structure completely describes the shape of the molecule. Larger molecules do not have a single central atom, but are connected by a chain of interior atoms that each possess a "local" geometry. The way these local structures 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 6.4.5: 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:

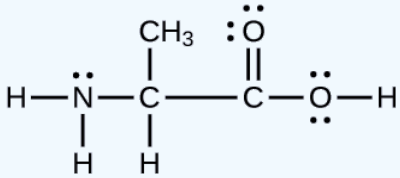
- nitrogen—four regions of electron density; tetrahedral
- carbon ($\underline{C}H_2$)—four regions of electron density; tetrahedral
- carbon ($\underline{C}O_2$)—three regions of electron density; trigonal planar
- oxygen ($\underline{O}H$)—four regions of electron density; tetrahedral

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 6.4.5

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 (CH)—tetrahedral; carbon (CH_3)—tetrahedral; carbon (CO_2)—trigonal planar; oxygen (OH)—tetrahedral; local structures: nitrogen—trigonal pyramidal; carbon (CH)—tetrahedral; carbon (CH_3)—tetrahedral; carbon (CO_2)—trigonal planar; oxygen (OH)—bent (109°)

Example 6.4.6: 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 6.4.6

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.

6.4.4: 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. This bond moment can be represented as a vector, a quantity having both direction and magnitude (Figure 6.4.12). 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.

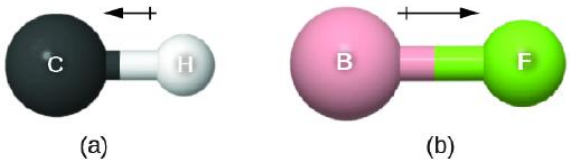


Figure 6.4.12: (a) There is a small difference in electronegativity between C and H, represented as a short vector. (b) The electronegativity difference between B and F is much larger, so the vector representing the bond moment is much longer.

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 6.4.13*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 6.4.13*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).

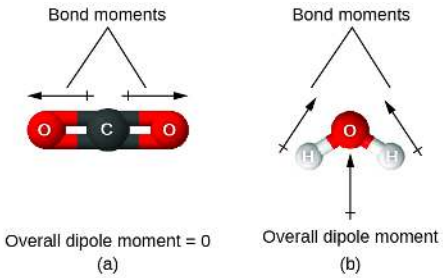
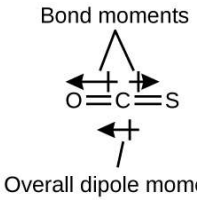


Figure 6.4.13: The overall dipole moment of a molecule depends on the individual bond dipole moments and how they are arranged. (a) Each CO bond has a bond dipole moment, but they point in opposite directions so that the net CO_2 molecule is nonpolar. (b) In contrast, water is polar because the OH bond 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:

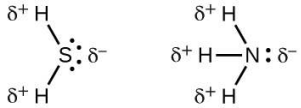


The C–O bond is considerably polar. Although C and S have very similar electronegativity values, S is slightly more electronegative than C, and so the C-S bond is just slightly polar. Because oxygen is more electronegative than sulfur, the oxygen end of the molecule is the negative end.

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:



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.

6.4.5: 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 6.4.14). 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.

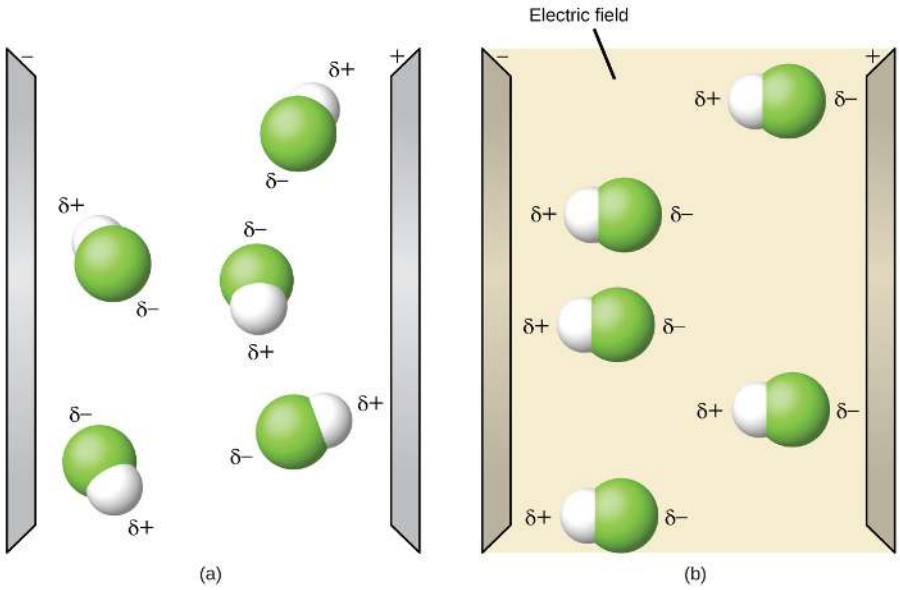


Figure 6.4.14: (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction.

Example 6.4.7: 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 6.4.14

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 6.4.7

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 6.4: Molecular Structure and Polarity is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

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

6.5: Intermolecular Forces

Learning Objectives

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

- 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 6.5.1 illustrates how changes in physical state may be induced by changing the temperature, hence, the average KE, of a given substance.

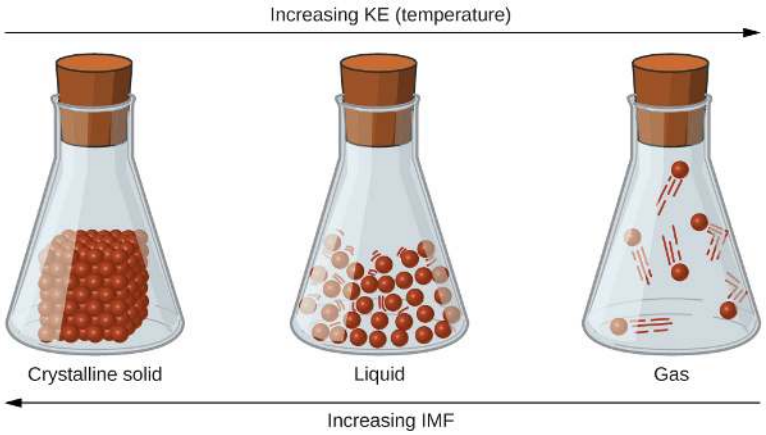


Figure 6.5.1: Transitions between solid, liquid, and gaseous states of a substance occur when conditions of temperature or pressure favor the associated changes in intermolecular forces. (Note: The space between particles in the gas phase is much greater than shown.)

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 6.5.2.



Figure 6.5.2: 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 6.5.3.



Figure 6.5.3: 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.

Link to Learning

Access this interactive simulation on states of matter, phase transitions, and intermolecular forces. This simulation is useful for visualizing concepts introduced throughout this chapter.

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 6.5.4: 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.

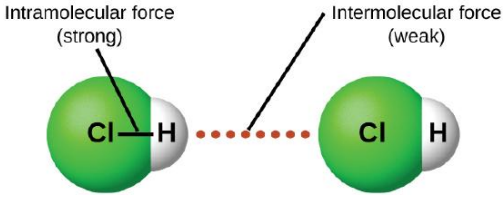


Figure 6.5.4: *Intra*molecular forces keep a molecule intact. *Inter*molecular forces hold multiple molecules together and determine many of a substance's properties.

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.

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 6.5.5.

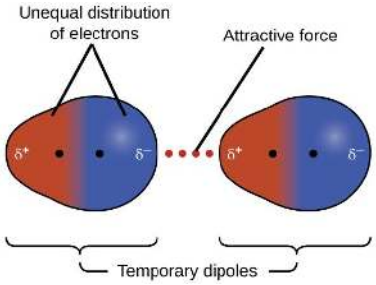


Figure 6.5.5: Dispersion forces result from the formation of temporary dipoles, as illustrated here for two nonpolar diatomic molecules.

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 6.5.1.

Table 6.5.1: 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.

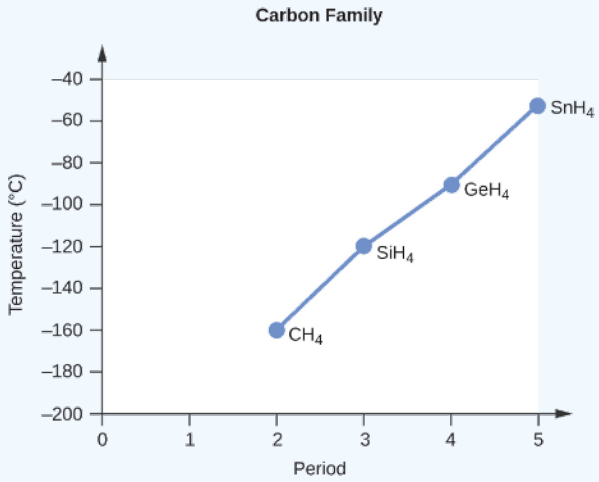
Example 6.5.1: London Forces and Their Effects

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 element shows this prediction to be correct:



Exercise 6.5.1

Order the following hydrocarbons from lowest to highest boiling point: C_2H_6, C_3H_8, and C_4H_{10}.

Answer

$C_2H_6 < C_3H_8 < C_4H_{10}$. 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 6.5.6) 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.

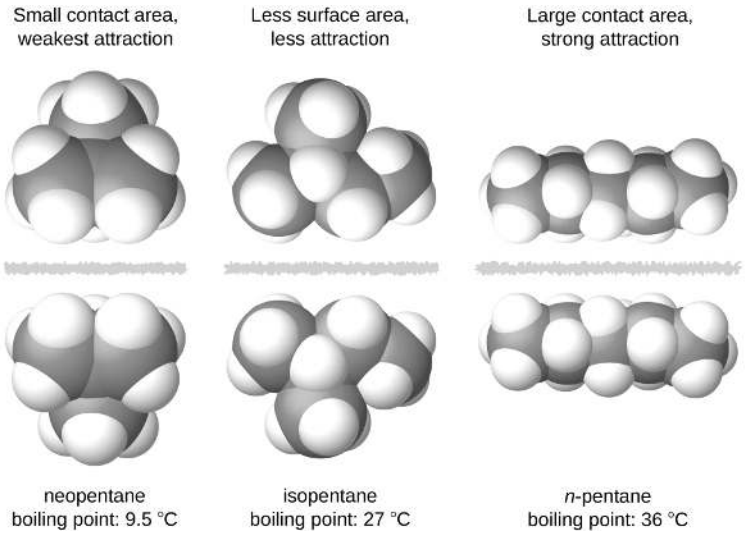


Figure 6.5.6: The strength of the dispersion forces increases with the contact area between molecules, as demonstrated by the boiling points of these pentane isomers.

Chemistry in Everyday Life: 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.

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 6.5.7, 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. Later research led by Alyssa Stark at University of Akron showed that geckos can maintain their hold on hydrophobic surfaces (similar to the leaves in their habitats) equally well whether the surfaces were wet or dry. Stark's experiment used a ribbon to gently pull the geckos until they slipped, so that the researchers could determine the geckos' ability to hold various surfaces under wet and dry conditions. Further investigations may eventually lead to the development of better adhesives and other applications.

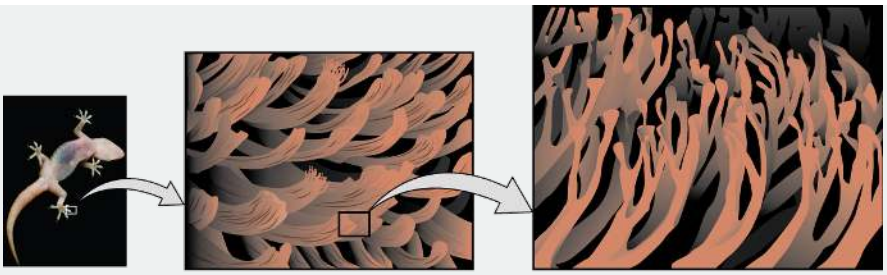


Figure 6.5.7: Geckos' toes contain large numbers of tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko's millions of spatulae. By changing how the spatulae contact the surface, geckos can turn their stickiness "on" and "off." (credit photo: modification of work by "JC*+A!"/Flickr)

Link to Learning

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.

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 6.5.8.

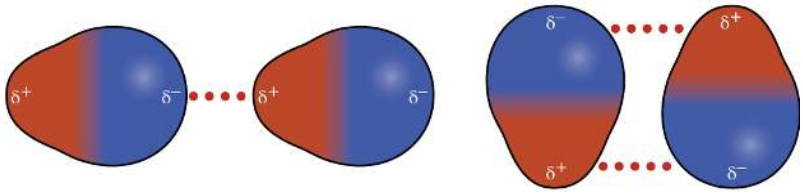


Figure 6.5.8: This image shows two arrangements of polar molecules, such as HCl, that allow an attraction between the partial negative end of one molecule and the partial positive end of another.

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 6.5.2: 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.

Exercise 6.5.2

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.

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 6.5.9 illustrates hydrogen bonding between water molecules.

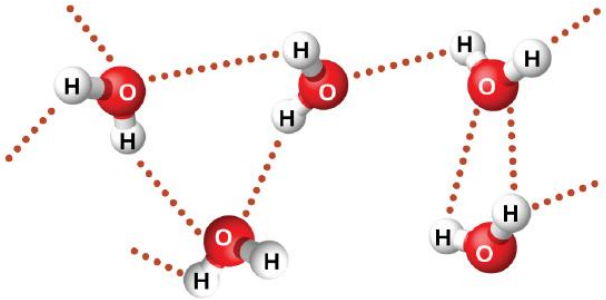


Figure 6.5.9: Water molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.

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 6.5.10. 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.

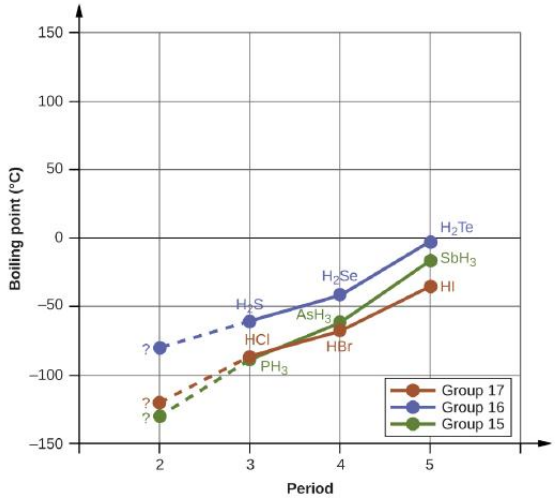


Figure 6.5.10: For the group 15, 16, and 17 hydrides, the boiling points for each class of compounds increase with increasing molecular mass for elements in periods 3, 4, and 5.

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 6.5.11. The stark contrast between our naïve predictions and reality provides compelling evidence for the strength of hydrogen bonding.

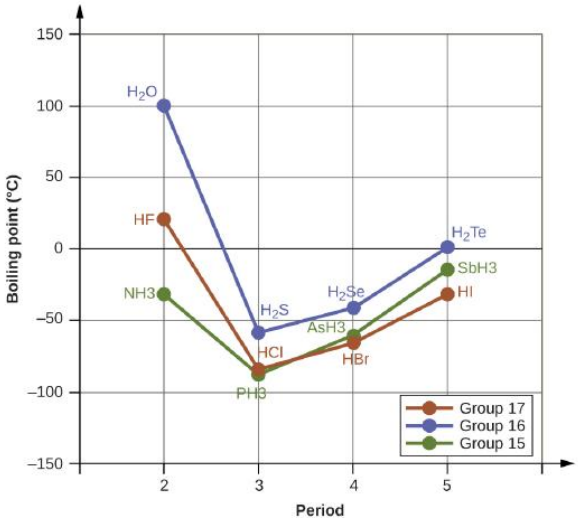


Figure 6.5.11: In comparison to periods 3−5, the binary hydrides of period 2 elements in groups 17, 16 and 15 (F, O and N, respectively) exhibit anomalously high boiling points due to hydrogen bonding.

Example 6.5.3: 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.

https://chem.libretexts.org/@go/page/476915

Exercise 6.5.3

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.

How Sciences Interconnect: 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 6.5.12

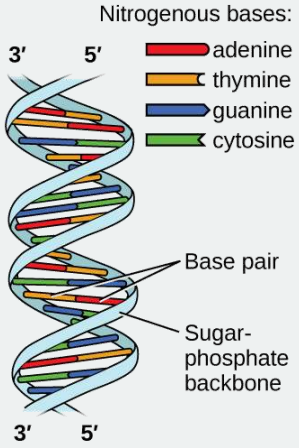


Figure 6.5.12: Two separate DNA molecules form a double-stranded helix in which the molecules are held together via hydrogen bonding. (credit: modification of work by Jerome Walker, Dennis Myts)

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 6.5.13

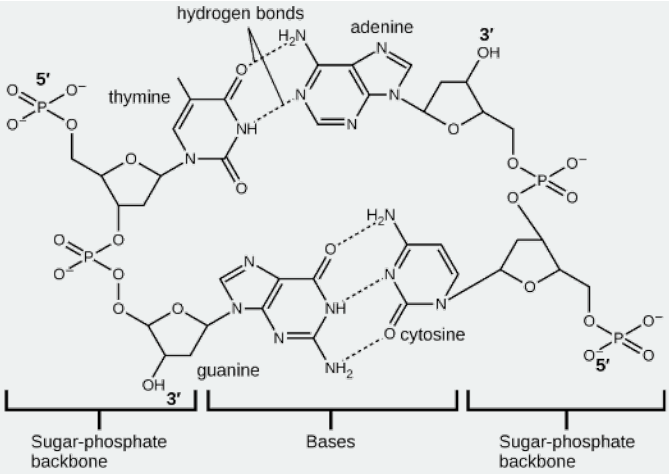


Figure 6.5.13: The geometries of the base molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called “complementary base pairs.”

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.

This page titled 6.5: 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.

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

6.E: Chemical Bonding and Molecular Geometry- Homework

6.E.1: Turn in your answers for the following questions - show your work

Draw Lewis dot structures, determine the molecular shape, electronic geometry, bond length, determine the bond energy, determine the bond polarity, and determine the formal charge for each atom.

a. a. H_2
b. b. CH_4
c. c. NH_3
d. d. H_2O
e. e. HBr
f. f. PCl_5
g. g. CO_2
h. h. BF_3
i. i. CF_2Cl_2
j. j. C_4H_8 (3 different structures)

6.E.2: The Following Questions are for your practice - Do Not Turn In. They include answers so you can check your work

6.E.2.1: Ionic Bonding

1. Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:
   a. Mg
   b. Al
   c. O
   d. Cl

   answer

   Mg^{2+}; Al^{3+}; O^{2-}; Cl^{-}

6.E.2.2: Covalent Bonding

1. Predict which of the following compounds are ionic and which are covalent, based on the location of their constituent atoms in the periodic table:
   a. Cl_2CO
   b. MnO
   c. NCl_3
   d. $CoBr_2$

   answer

   ionic: (b), (d); covalent: (a), (c)

2. From its position in the periodic table, determine which atom in each pair is more electronegative:
   1. Br or Cl
   2. N or O

   answer

   Cl; O

3. Identify the more polar bond in each of the following pairs of bonds:
   1. HF or HCl
   2. NO or CO

answer

HF; CO

6.E.2.3: Lewis Symbols and Structures

1. Write the Lewis symbols for each of the following ions:
   a. As^{3-}
   b. I^-

answer

eight electrons:



eight electrons:



2. 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
   2. Al_2O_3

answer

(a)



;

(b)

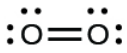


;

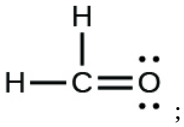
3. Write Lewis structures for the following:
   a. O_2
   b. H_2CO
   c. AsF_3

answer

(a)

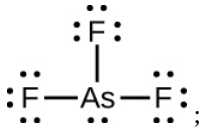


(b)



;

(c)

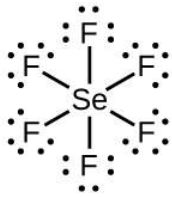


;

4. Write Lewis structures for the following:
    1. SeF_6
    2. XeF_4
    3. $SeCl_3^+$

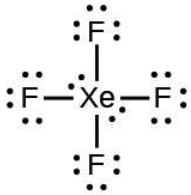
answer

SeF_6:



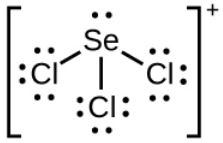
;

XeF_4:



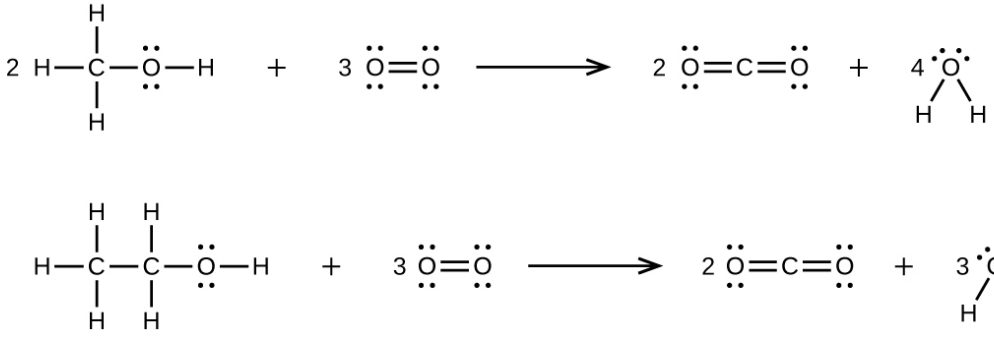
;

$SeCl_3^+$:



5. 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.

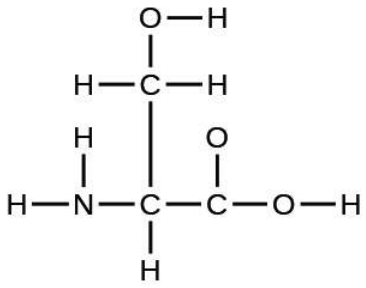
answer



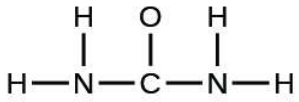
https://chem.libretexts.org/@go/page/432487

6. 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:

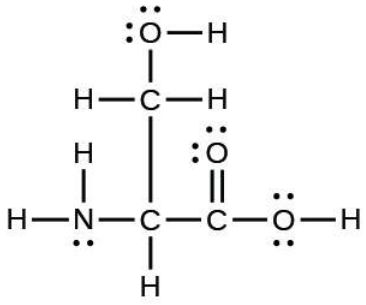


   urea:



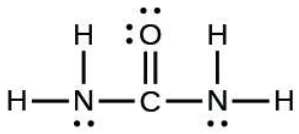
answer

(a)



;

(b)



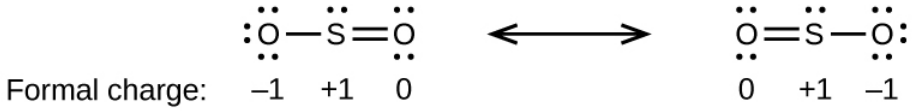
;

6.E.2.4: Formal Charges and Resonance

1. Draw all possible resonance structures for each of these compounds. Determine the formal charge on each atom in each of the resonance structures:
   1. SO_2
   2. NO_2^-

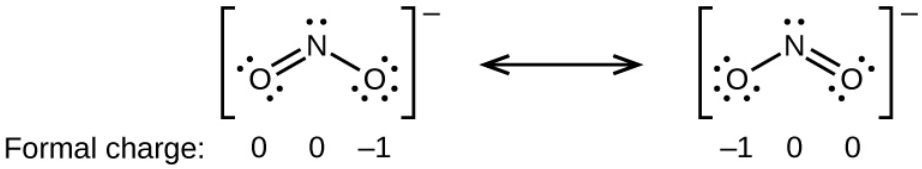
answer

(a)



;

(b)



6.E.2.5: Strengths of Ionic and Covalent Bonds

1. Using the table of bond energies determine the approximate enthalpy change for each of the following reactions:
    1. $\mathrm{H_2}(g) + \mathrm{Br_2}(g) \longrightarrow 2\ \mathrm{HBr}(g)$

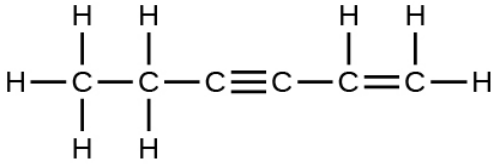
answer

1. −114 kJ;

2. Complete the following Lewis structure by adding bonds (not atoms), and then indicate the longest bond:



answer

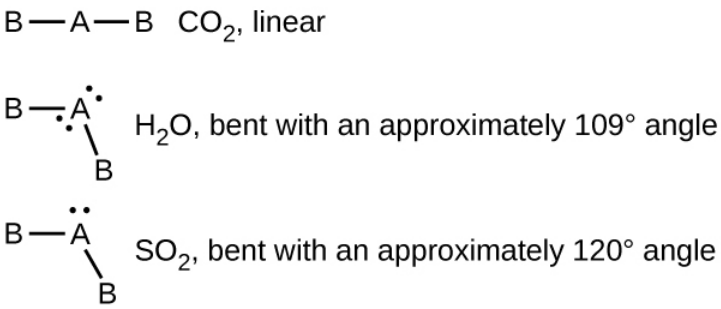


The C–C single bonds are longest.

6.E.2.6: Molecular Structure and Polarity

1. 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



2. Predict the electron pair geometry and the molecular structure of each of the following molecules or ions:
    1. SF_6
    2. PCl_5
    3. (c) 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. (c) Both the electron geometry and the molecular structure are linear.
    4. Both the electron geometry and the molecular structure are trigonal planar.

3. 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. (c) Cl_2CO (C is the central atom)
    4. Cl_2SO (S is the central atom)

    answer

    (a) electron-pair geometry: trigonal planar, molecular structure: bent (120°); (b) electron-pair geometry: linear, molecular structure: linear; (c) electron-pair geometry: trigonal planar, molecular structure: (d) trigonal planar; electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal

4. Which of the following molecules have dipole moments?
    1. CS_2
    2. SeS_2
    3. (c) 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.

5. 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. (c) the oxygen atom in hydrogen peroxide, HOOH
    4. the nitrogen atom in nitric acid, HNO_3 [$HONO_2$]

    answer

    (a) tetrahedral; (b) trigonal pyramidal; (c) bent (109°); (d) trigonal planar; bent (109°);

6. 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°.

This page titled 6.E: Chemical Bonding and Molecular Geometry- Homework is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

CHAPTER OVERVIEW

7: Advanced Theories of Covalent Bonding

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

General Chemistry

We have examined the basic ideas of bonding, showing that atoms share electrons to form molecules with stable Lewis structures and that we can predict the shapes of those molecules by valence shell electron pair repulsion (VSEPR) theory. These ideas provide an important starting point for understanding chemical bonding. But these models sometimes fall short in their abilities to predict the behavior of real substances. How can we reconcile the geometries of *s*, *p*, and *d* atomic orbitals with molecular shapes that show angles like 120° and 109.5°? Furthermore, we know that electrons and magnetic behavior are related through electromagnetic fields.

7.1: Valence Bond Theory and Hybrid Orbitals

7.2: Multiple Bonds

7.3: Molecular Orbital Theory

7.E: Advanced Theories of Covalent Bonding- Homework

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 7: Advanced Theories of Covalent Bonding is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

7.1: Valence Bond Theory and Hybrid Orbitals

Learning Objectives

- Describe the formation of covalent bonds in terms of atomic orbital overlap
- Define and give examples of σ and π bonds
- Explain the concept of atomic orbital hybridization
- Determine the hybrid orbitals associated with various molecular geometries

7.1.1: Valence Bond Theory

We have examined the basic ideas of bonding, showing that atoms share electrons to form molecules with stable Lewis structures and that we can predict the shapes of those molecules by valence shell electron pair repulsion (VSEPR) theory. These ideas provide an important starting point for understanding chemical bonding. But these models sometimes fall short in their abilities to predict the behavior of real substances. How can we reconcile the geometries of *s*, *p*, and *d* atomic orbitals with molecular shapes that show angles like 120° and 109.5°?

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 7.1.1 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 is attracted to the nucleus in the other atom. In addition, the electrons begin to repel each other, as do the nuclei. As the atoms move closer together, the overlap increases, so the attraction of the nuclei for the electrons increases and the energy of the system decreases. This is the formation of a bond. As the atoms move close together the nuclei, which both have a positive charge, repel each other. When the atoms are widely separated the attraction is stronger than the repulsion and the atoms are pulled together. At some point the repulsions get stronger than the attraction and the atoms start to push apart. There is an optimum distance where the attraction and repulsion are balanced, this is the bond distance for an H_2 molecule. The bond is stable because at this point because pulling the atoms apart requires adding enough energy to overcome the attraction. This corresponds to the depth of the energy well in Figure 7.1.1.

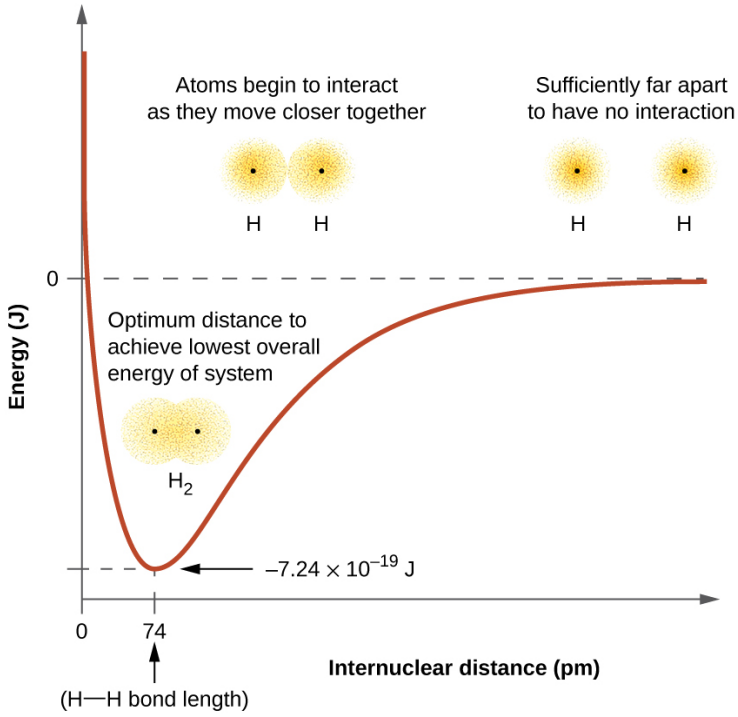


Figure 7.1.1: The interaction of two hydrogen atoms changes as a function of distance. The energy of the system changes as the atoms interact. The lowest (most stable) energy occurs at a distance of 74 pm, which is the bond length observed for the H_2 molecule.

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 7.1.1, 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. Multiplying this by avagadro's number gives a bond energy for H_2 of $4.36 \times 10^5\ J/mol$. Table 7.1.1 shows average bond lengths and energies for several different common bond types. It is important to note that these values are averages. For example Table 7.1.1 lists the average CH bond energy is 413 kJ/mole, but breaking the first C–H bond in CH_4 requires 439.3 kJ/mol while breaking the first C–H bond in $H\text{–}CH_2C_6H_5$ (a common paint thinner) requires 375.5 kJ/mol.

Table 7.1.1: 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
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

For H_2 the overlap between the s orbitals does not depend on the orientation of the molecule. However, for most molecules both the distance between the atoms and the orientation of the orbitals affects the formation of the bond. Greater overlap is possible

when orbitals are oriented in a direct line between the two nuclei. Figure 7.1.2 illustrates this for two *p* orbitals when they overlap end to end or at an angle. The overlap is greater when the orbitals overlap end to end rather than at an angle.

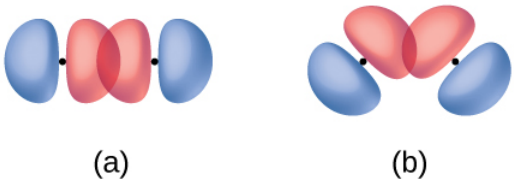


Figure 7.1.2: (a) The overlap of two p orbitals is greatest when the orbitals are directed end to end. (b) Any other arrangement results in less overlap. The dots indicate the locations of the nuclei.

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 7.1.3. 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.

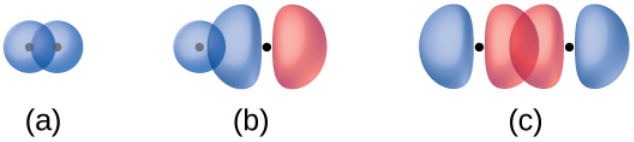


Figure 7.1.3: Sigma (σ) bonds form from the overlap of the following: (a) two s orbitals, (b) an s orbital and a p orbital, and (c) two p orbitals. The dots indicate the locations of the nuclei.

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 7.1.4. 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. Although this figure shows the orbitals overlapping in two places for a π bond, this is still one bond.

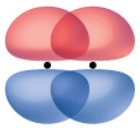
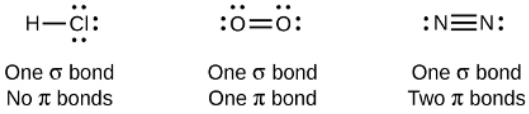


Figure 7.1.4: Pi (π) bonds form from the side-by-side overlap of two p orbitals. The dots indicate the location of the nuclei.

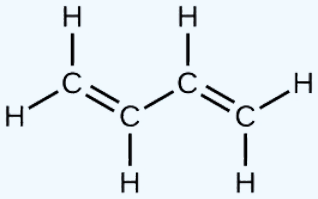
While all single bonds are σ bonds, multiple bonds consist of both σ and π bonds. As the Lewis structures suggest, O_2 contains a double bond, and N_2 contains a triple bond. The double bond consists of one σ bond and one π bond, and the triple bond consists of one σ bond and two π bonds. Between any 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.



As seen in Table 7.1.1, an average carbon-carbon single bond energy is 347 kJ/mol. In a carbon-carbon double bond, the π bond increases the bond strength by 267 kJ/mol. Adding an second π bond to form a carbon-carbon tripple bond causes a additional increase of 225 kJ/mol. The σ and π bonds between other atoms follow the same trend and each individual π bond is weaker than the σ bond between the same two atoms. This happens because a σ bond has more overlap to generate attraction between the two atoms than in a π bond.

Example 7.1.1: 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

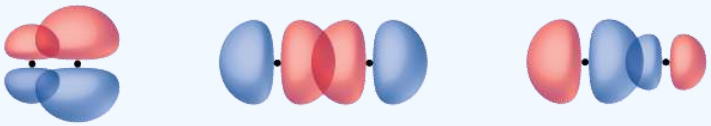
Solution

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 7.1.1

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.

7.1.2: Hybrid Orbitals

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. Since the p orbitals are aligned along the x, y, and z axis, this should result in a 90° bond angle, as shown in Figure 7.1.1. This is different from the bond angle predicted by VSEPR - since the oxygen atom has four electron pairs around it VSEPR predicts a 109.5° bond angle, maybe a bit smaller to accommodate the two sets of lone pair electrons taking more space. VSEPR is consistent with experimental evidence which shows the bond angle is 104.5°. The oxygen atomic orbitals are not oriented to allow the correct molecular geometry using valence bond theory. A different model is needed.

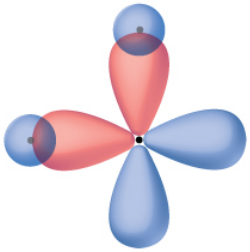


Figure 7.1.1: The hypothetical overlap of two of the 2p orbitals on an oxygen atom (red) with the 1s orbitals of two hydrogen atoms (blue) would produce a bond angle of 90°. This is not consistent with experimental evidence.[1]

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, describes the shape of each orbital using the wavelike properties of electrons. When atoms are bound together in a molecule, the wave functions combine and create new wave functions 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*. The new orbitals that result are called hybrid orbitals and they can explain the molecular geometry of the water molecule. 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 7.1.2). Consequently, the overlap of the O and H orbitals should result in a tetrahedral bond angle (109.5°) as predicted by VSEPR. 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 explain molecular geometry.

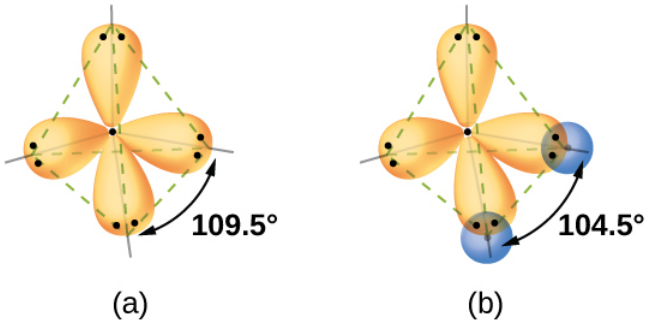


Figure 7.1.2: (a) A water molecule has four regions of electron density, so VSEPR theory predicts a tetrahedral arrangement of hybrid orbitals. (b) Two of the hybrid orbitals on oxygen contain lone pairs, and the other two overlap with the 1s orbitals of hydrogen atoms to form the O–H bonds in H_2O. This description is more consistent with the experimental structure.

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 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 p orbitals overlap to form π bonds.

In the following sections, we shall discuss the common types of hybrid orbitals.

7.1.2.1: 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. According to VSEPR these two electron domains will result in a linear molecular geometry. To generate this geometry two of the Be atom's four valence orbitals 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 the linear geometry shown in Figure 7.1.3. 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 new *sp* orbitals, which are half filled. The half-filled hybrid orbitals in $BeCl_2$, overlap with orbitals from the chlorine atoms to form two identical σ bonds.

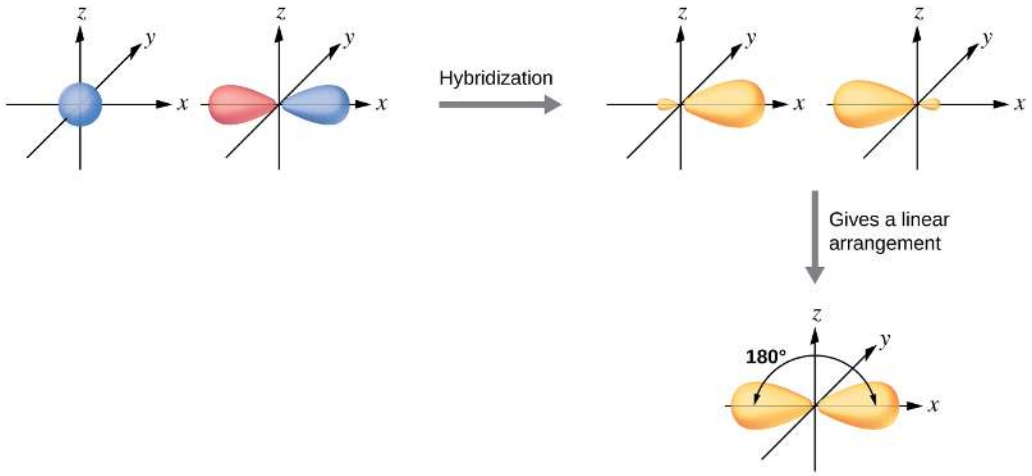


Figure 7.1.3: Hybridization of an s orbital (blue) and a p orbital (red) of the same atom produces two sp hybrid orbitals (yellow). Each hybrid orbital is oriented primarily in just one direction. Note that each sp orbital contains one lobe that is significantly larger than the other. The set of two sp orbitals are oriented at 180°, which is consistent with the geometry for linear molecules.

We illustrate the electronic differences in an isolated Be atom and in the bonded Be atom in the orbital energy-level diagram in Figure 7.1.4. 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.

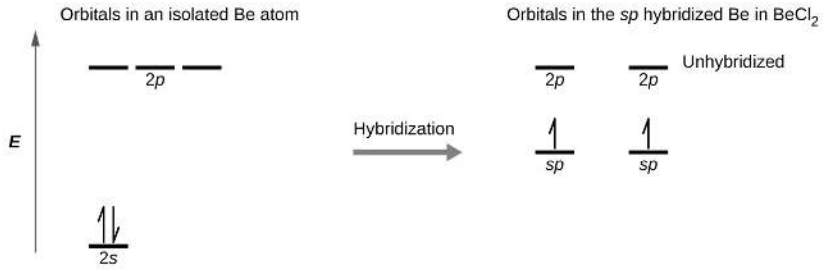


Figure 7.1.4: This orbital energy-level diagram shows the sp hybridized orbitals on Be in the linear $BeCl_2$ molecule. Each of the two sp hybrid orbitals holds one electron and is thus half filled and available for bonding via overlap with a Cl 3p orbital.

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.

7.1.2.2: sp^2 Hybridization

The valence orbitals of a central atom surrounded by three regions of electron density create a trigonal planer geometry in VSEPR. 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 7.1.5). This geometry is creates a central atom with a set of three sp^2 hybrid orbitals and one unhybridized *p* orbital.

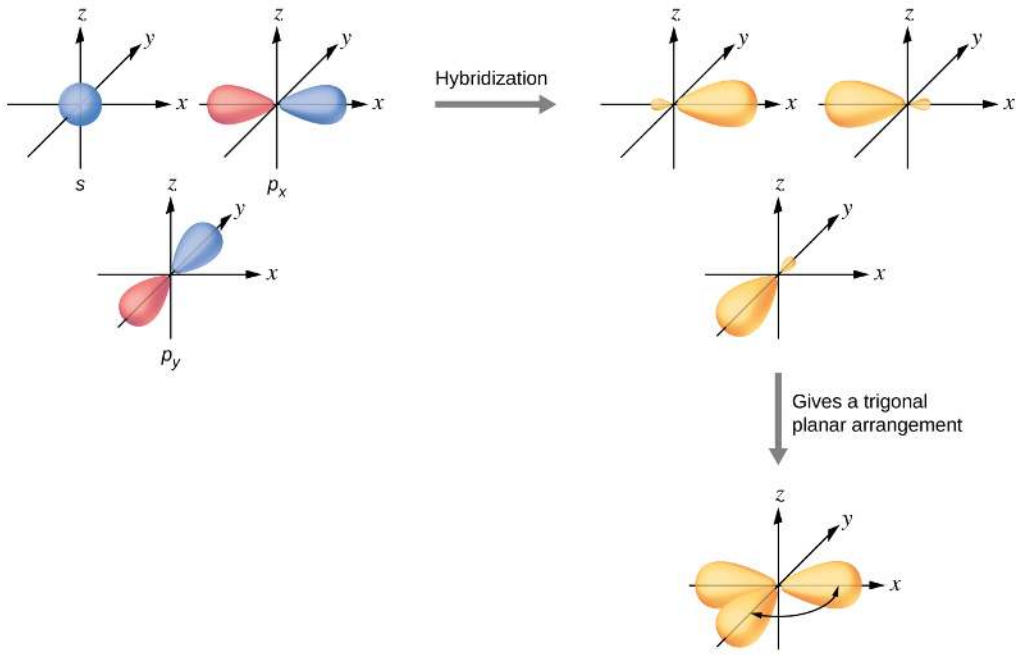


Figure 7.1.5: The hybridization of an s orbital (blue) and two p orbitals (red) produces three equivalent sp^2 hybridized orbitals (yellow) oriented at 120° with respect to each other. The remaining unhybridized p orbital is not shown here, but is located along the z axis.

Although quantum mechanics yields the "plump" orbital lobes as depicted in Figure 7.1.5, sometimes for clarity these orbitals are drawn thinner and without the minor lobes, as in Figure 7.1.6, 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.

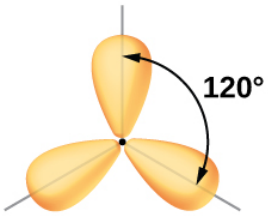


Figure 7.1.6: This alternate way of drawing the trigonal planar sp^2 hybrid orbitals is sometimes used in more crowded figures.

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 7.1.7).

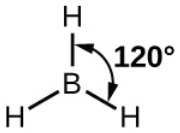


Figure 7.1.7: BH_3 is an electron-deficient molecule with a trigonal planar structure.

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 7.1.8. 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.

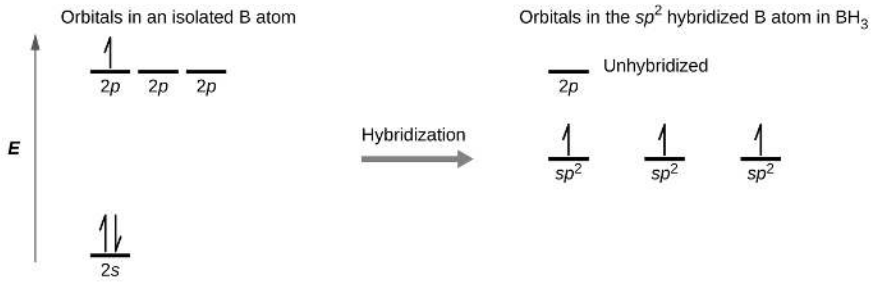


Figure 7.1.8: In an isolated B atom, there are one 2s and three 2p valence orbitals. When boron is in a molecule with three regions of electron density, three of the orbitals hybridize and create a set of three sp^2 orbitals and one unhybridized 2p orbital. The three half-filled hybrid orbitals each overlap with an orbital from a hydrogen atom to form three σ bonds in BH_3.

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 7.1.9), 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.

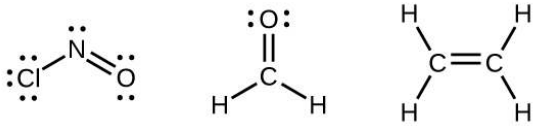


Figure 7.1.9: The central atom(s) in each of the structures shown contain three regions of electron density and are sp^2 hybridized. As we know from the discussion of VSEPR theory, a region of electron density contains all of the electrons that point in one direction. A lone pair, an unpaired electron, a single bond, or a multiple bond would each count as one region of electron density.

7.1.2.3: 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 7.1.10). Each of these hybrid orbitals points toward a different corner of a tetrahedron.

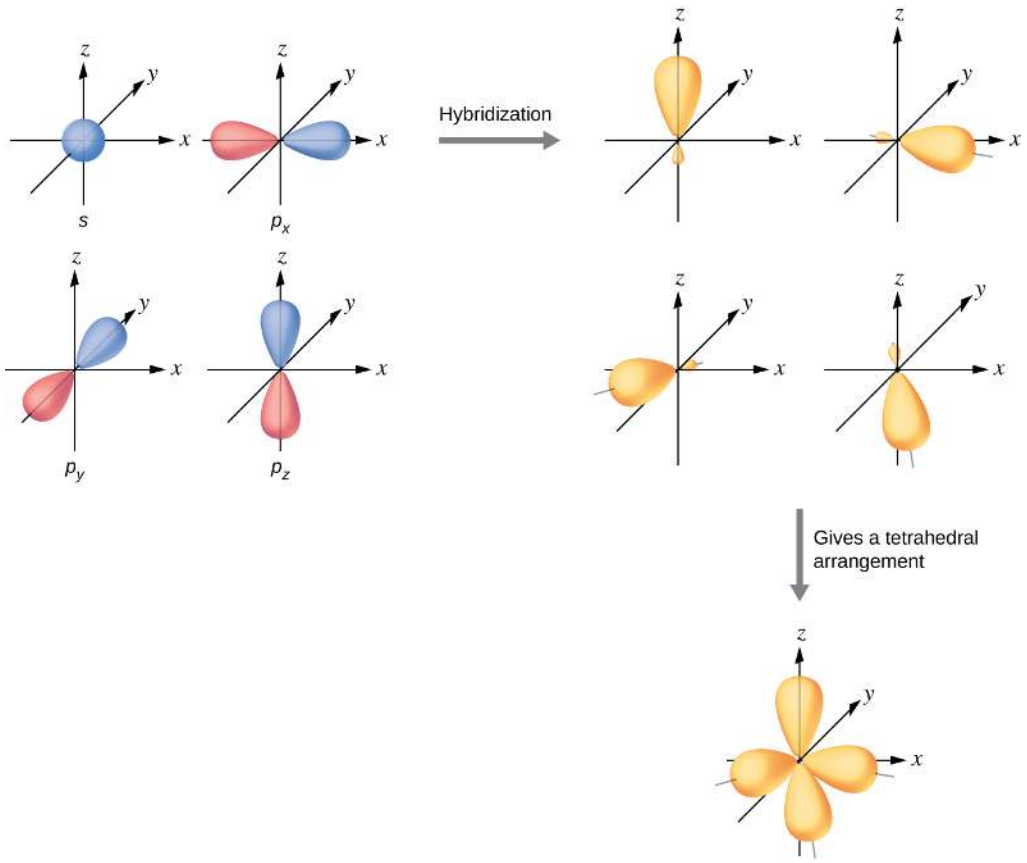


Figure 7.1.10: The hybridization of an s orbital (blue) and three p orbitals (red) produces four equivalent sp^3 hybridized orbitals (yellow) oriented at 109.5° with respect to each other.

A 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 7.1.11. 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.

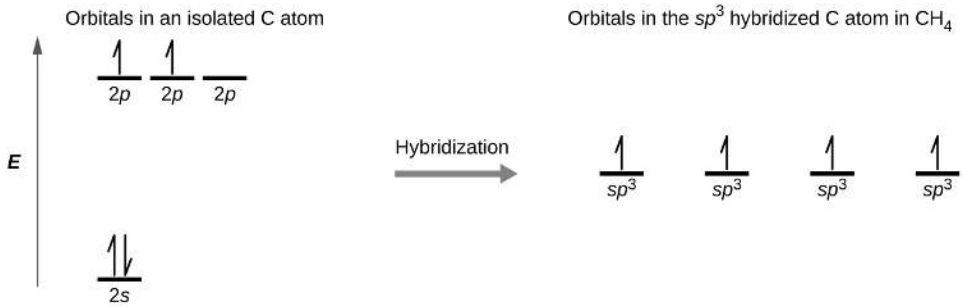


Figure 7.1.11: The four valence atomic orbitals from an isolated carbon atom all hybridize when the carbon bonds in a molecule like CH_4 with four regions of electron density. This creates four equivalent sp^3 hybridized orbitals. Overlap of each of the hybrid orbitals with a hydrogen orbital creates a C–H σ bond.

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 7.1.10). 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 7.1.12. 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.

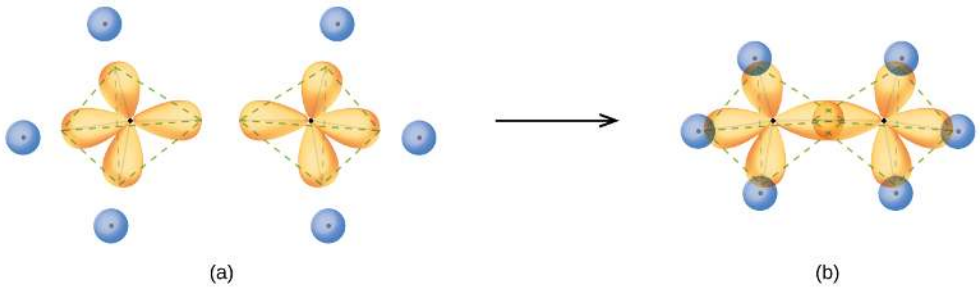


Figure 7.1.12: (a) In the ethane molecule, C_2H_6, each carbon has four sp^3 orbitals. (b) These four orbitals overlap to form seven σ bonds.

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 because the lone pair electrons occupy more space than the bonding electrons. Other examples of sp^3 hybridization include CCl_4, PCl_3, and NCl_3.

7.1.2.4: sp^3d 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. These hybridizations are only possible for atoms that have *d* orbitals in their valence subshells. Elements in the first and second period of the periodic table can not form sp^3d hybrid orbitals.

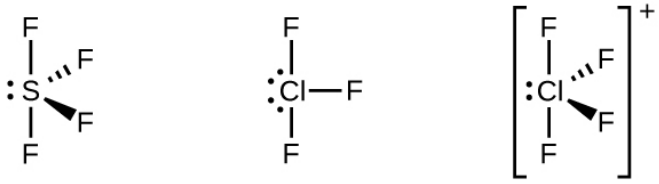


Figure 7.1.13: The three compounds pictured exhibit sp^3d hybridization in the central atom and a trigonal bipyramid form. SF_4 and ClF_4^+ *have one lone pair of electrons on the central atom, and* ClF_3 *has two lone pairs giving it the T-shape shown.*

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 7.1.13) 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.)

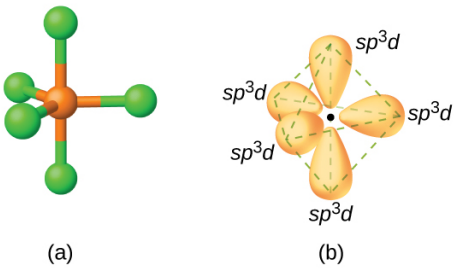


Figure 7.1.14: (a) The five regions of electron density around phosphorus in PCl_5 require five hybrid sp^3d orbitals. (b) These orbitals combine to form a trigonal bipyramidal structure with each large lobe of the hybrid orbital pointing at a vertex. As before, there are also small lobes pointing in the opposite direction for each orbital (not shown for clarity).

7.1.3: sp^3d^2 Hybridization

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. Elements in the first and second period of the periodic table can not form sp^3d^2 hybrid orbitals.

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.

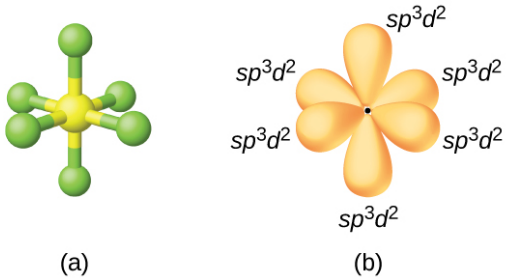


Figure 7.1.15: (a) Sulfur hexafluoride, SF_6, has an octahedral structure that requires sp^3d^2 hybridization. (b) The six sp^3d^2 orbitals form an octahedral structure around sulfur. Again, the minor lobe of each orbital is not shown for clarity.

7.1.4: 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 7.1.16. 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 electron-pair geometry using VSEPR. Single bonds, multiple bonds, radicals, and lone pairs each count as one region.
3. Assign the set of hybridized orbitals from Figure 7.1.16 that corresponds to this geometry.

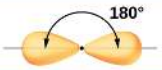
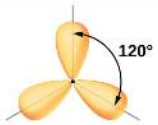
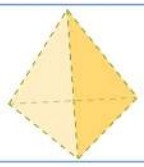
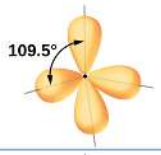
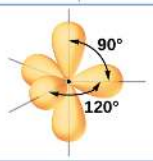
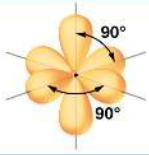
Regions of Electron Density	Arrangement		Hybridization	
2		linear	*sp*	
3		trigonal planar	sp^2	
4		tetrahedral	sp^3	
5		trigonal bipyramidal	sp^3d	
6		octahedral	sp^3d^2	

Figure 7.1.16: 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.

> *It is important to remember that hybridization was devised to rationalize experimentally observed molecular geometries, not the other way around.*

Example 7.1.1: 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.

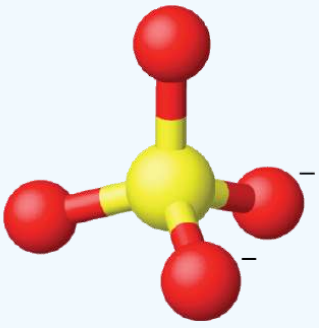
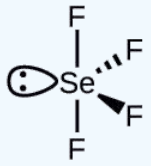


Figure 7.1.16).

Exercise 7.1.1

What is the hybridization of the selenium atom in SeF_4?



Answer

The selenium atom is sp^3d hybridized.

Example 7.1.2: 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

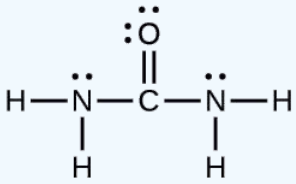


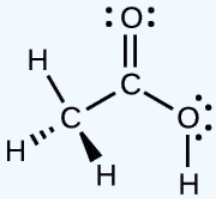
Figure 7.1.16). This is the hybridization of the nitrogen atoms in urea.

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 7.1.16), which is the hybridization of the carbon atom in urea.

The nitrogen atoms are both surrounded by four regions of electron density, three bonds and a lone pair of electrons. This results in a tetrahedral geometry and requires sp^3 hybridization.

Exercise 7.1.1

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?



Answer

$H_3\underline{C}$, sp^3; $\underline{C}(O)OH$, sp^2

7.1.5: 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.

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).

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

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

***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^3d 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^3d^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

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

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 7.1: Valence Bond Theory and Hybrid Orbitals is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

- **8.2: Valence Bond Theory** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.
- **8.3: Hybrid Atomic Orbitals** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

7.2: 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 accounts for the geometry of molecules with single covalent bonds. It also describes how double and triple bonds form. Molecules with dobule and triple bonds use both σ and π bonds. This section describes how the hybrid orbital model works to visualize the creation of multiple bonds using σ and π bonds.

7.2.1: Double Bonds

The Lewis structure of ethene, C_2H_4, shows each carbon atom is connected to the other carbon atom and to two hydrogen atoms. As a result each carbon atom has trigonal planar geometry - according to VSEPR - and is sp^2 hybridized. Figure 7.2.1 shows the energy diagram for the atomic orbitals and the hybrid orbitals. The sp^2 hybrid orbitals overlap to make σ bonds to the hydrogen atoms and between the carbon atoms.

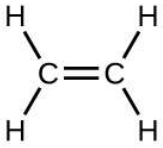


Figure 7.2.2).

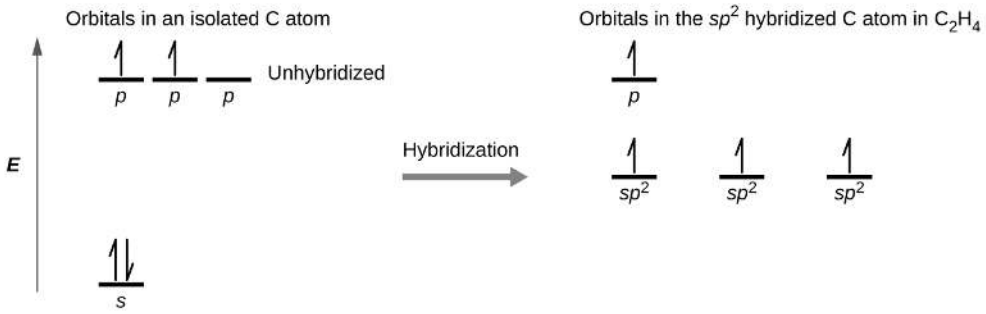


Figure 7.2.1: In ethene, each carbon atom is sp^2 hybridized, and the sp^2 orbitals and the *p* orbital are singly occupied. The hybrid orbitals overlap to form σ bonds, while the *p* orbitals on each carbon atom overlap to form a π bond.

The π bond in the C=C double bond is formed by overlap of the unused 2*p* orbital, only two of the three *p* orbitals are used for hybridization so one is left over. This unhybridized *p* orbital is shown with the red and blue lobes in Figure 7.2.2. This unhybridized 2*p* orbital is perpendicular to the plane of the sp^2 hybrid orbitals. This lets the unhybridized 2*p* orbitals on the carbon atoms overlap side-by-side, above and below the internuclear axis, and form a π bond.

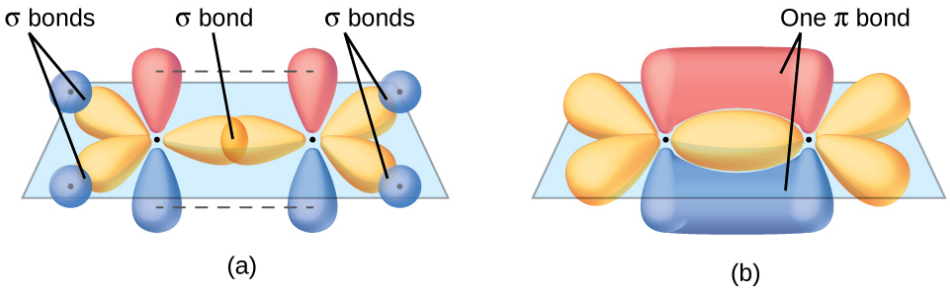


Figure 7.2.2: In the ethene molecule, C_2H_4, there are (a) five σ bonds. One C–C σ bond results from overlap of sp^2 hybrid orbitals on the carbon atom with one sp^2 hybrid orbital on the other carbon atom. Four C–H bonds result from the overlap between the C atoms' sp^2 orbitals with s orbitals on 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.

For the unhybridized 2*p* orbitals in ethene to overlap and form a π bond, the four hydrogen atoms and the two carbon atoms all must be in the same plane so that the ethene molecule is flat. If the molecule is twisted around the C=C bond the *p* orbitals are not overlapping and the π bond can not form. The planar configuration for the ethene molecule occurs because it is the most stable bonding arrangement. This demonstrates a significant difference between σ bonds, which rotate or spin easily, and π bonds, which do not allow rotation. 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 because it would change the overlap of the π bonding orbitals and require breaking the π bond.

7.2.2: Triple Bonds

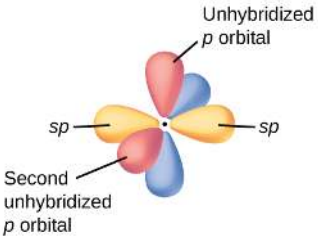


Figure 7.2.3: Diagram of the two linear sp hybrid orbitals of a carbon atom, which lie in a straight line, and the two unhybridized p orbitals at perpendicular angles.

In molecules with sp hybrid orbitals there are two unhybridized p orbitals, shown in Figure 7.2.3 so they are capable of forming two π bonds. Figure 7.2.4 shows the bonding arrangement for acetylene, H−C≡C−H, a linear molecule. The sp hybrid orbitals of the two carbon atoms overlap end to end to form a σ bond between the two carbon atoms. The remaining *sp* orbitals form σ bonds with hydrogen atoms. This leaves two unhybridized *p* orbitals on each carbon atom that can overlap to form two π bonds. The two carbon atoms of acetylene are bound by one σ bond and two π bonds, giving a triple bond.

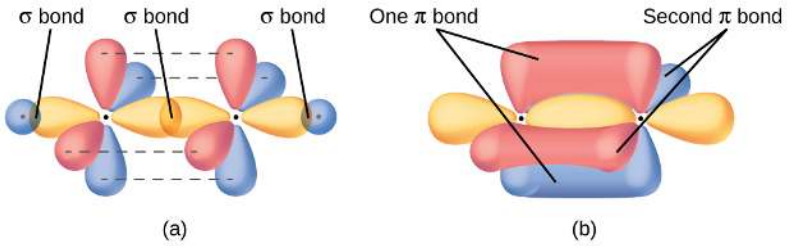


Figure 7.2.4: (a) In the acetylene molecule, C_2H_2, there are two C–H σ bonds and a C≡C triple bond involving one C–C σ bond and two C–C π bonds. The dashed lines, each connecting two lobes, indicate the side-by-side overlap of the four unhybridized p orbitals. (b) This shows the overall outline of 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.

7.2.3: Resonance Structures

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 without changing the three dimensional structure of the molecule. The orientation of the atoms stays the same, so the hybridization is the same for each resonance structure. The difference between resonances structures is the arrangement of π bonds between the unhybridized p orbitals. Resonance does not influence the assignment of hybridization.

For example, benzene has two resonance forms (Figure 7.2.5). Either of these forms show each carbon atom is bonded to three other atoms with no lone pairs, so the hybridization is sp^2. The electrons in the unhybridized *p* orbitals form π bonds but there are two possible configurations. The difference between these two structures is only dependent on which p orbitals are overlapping. Neither resonance structure completely describes the electrons in the π bonds. They are not located in one position or the other, but are in both configurations at the same time.

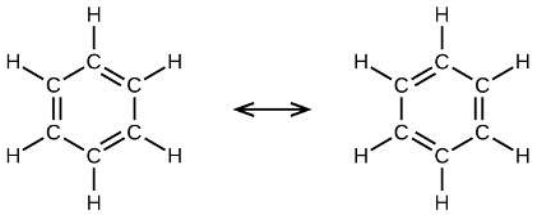


Figure 7.2.5: Each carbon atom in benzene, C_6H_6, is sp^2 hybridized, independently of which resonance form is considered. The electrons in the π bonds are not located in one set of p orbitals or the other, but rather delocalized throughout the molecule.

Example 7.2.1: Assignment of Hybridization Involving Resonance

One component of acid rain is produced by the reaction of sulfur dioxide with atmospheric water vapor to form sulfuric acid. Sulfur dioxide, SO_2, is a major component of volcanic gases and 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



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 7.2.1

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 7.2: Multiple Bonds is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

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

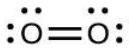
7.3: Molecular Orbital Theory

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

7.3.1: Introduction to MO Theory

For almost any covalent molecule we can now draw the Lewis structure, predict the electron-pair geometry, predict the molecular geometry, and predict bond angles, and use the hybrid orbital model to explain the bonding and structure. However, the behavior of the oxygen molecule O_2 is not consistent with predictions based on these models. We would write the following Lewis structure for O_2:



This electronic structure adheres to all the rules for Lewis theory and we can readily explain the structure and bonding. There is an O=O double bond, and each oxygen atom has eight electrons around it. However, this model is at odds with some experimental results. Although O_2 is not magnetic, it is attracted to magnetic fields. When we pour liquid oxygen past a strong magnet, it collects between the poles of the magnet. This attraction to a magnetic field is called paramagnetism, and it arises in molecules with unpaired electrons. The Lewis structure of O_2 shows all electrons are paired and is not consistent with this experimental observation.

The Lewis dot structure for nitrogen gas, N2, also shows all the electrons are paired. Both N_2 and O_2 have similar Lewis structures with bonds and lone pair electrons that are all paired.



Nitrogen demonstrates very different magnetic behavior than oxygen. We can pour liquid nitrogen through a magnetic field with no visible interactions, while liquid oxygen is attracted to the magnet and floats in the magnetic field. This behavior is not consistent with the Lewis structures and hybrid orbital models. A new model, molecular orbital theory, is needed to explain these observations.

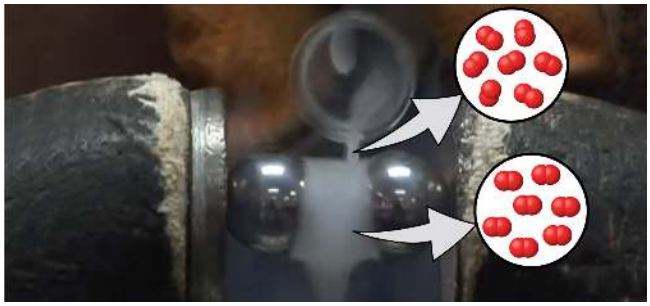


Figure 7.3.1: Oxygen molecules orient randomly most of the time, as shown in the top magnified view. However, when we pour liquid oxygen through a magnet, the molecules line up with the magnetic field, and the attraction allows them to stay suspended between the poles of the magnet where the magnetic field is strongest. Other diatomic molecules (like N_2) flow past the magnet. The detailed explanation of bonding described in this chapter allows us to understand this phenomenon. (credit: modification of work by Jefferson Lab)

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 and more molecules with more complicated bonding 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. MO theory also helps us understand why some substances are electrical conductors, others are semiconductors, and still others are insulators. Table 7.3.1 summarizes the main points of the two complementary bonding theories. Both theories provide different, useful ways of describing molecular structure.

Table 7.3.1 : 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	

7.3.2: Generating Molecular Sigma Orbitals

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). This is similar to the mathematics for creating hybrid orbitals. The wave function describes the wavelike properties of an electron. Molecular orbitals are combinations of atomic orbital wave functions. Figure 7.3.2 shows how combining waves leads to constructive interference, in which peaks line up with peaks, or destructive interference, in which peaks line up with troughs. 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.

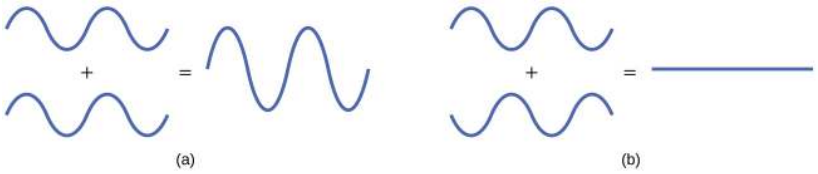


Figure 7.3.2: (a) When in-phase waves combine, constructive interference produces a wave with greater amplitude. (b) When out-of-phase waves combine, destructive interference produces a wave with less (or no) amplitude.

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 7.3.3. 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. This is similar to the overlap between hybrid orbitals to create a sigma bond. The new part in molecular orbital theory is recognizing that 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"). This molecular orbital has a node between the nuclei. Since there is very little electron density between the two nuclei, their positive charge will push the two atoms apart - so this is called an anti-bond. 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 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.

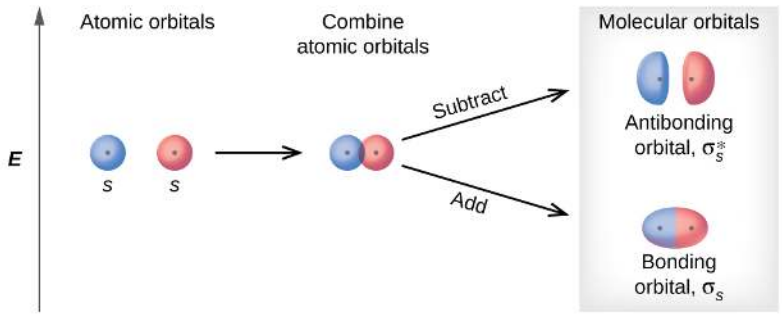


Figure 7.3.3: Sigma (σ) and sigma-star (σ*) molecular orbitals are formed by the combination of two s atomic orbitals. The plus (+) signs indicate the locations of nuclei.

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 7.3.4). 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.

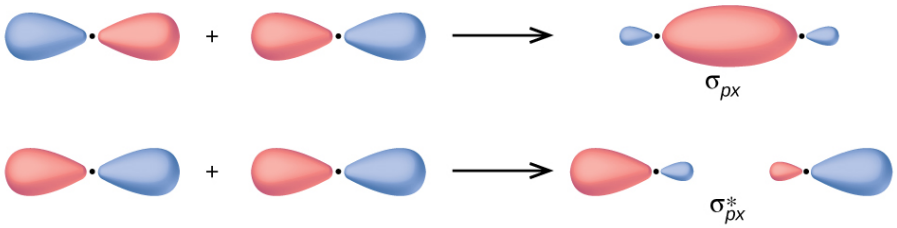


Figure 7.3.4: Combining wave functions of two p atomic orbitals along the internuclear axis creates two molecular orbitals, σp and σ^*_p.

7.3.3: Generating Molecular Pi Orbitals

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 7.3.5. 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.

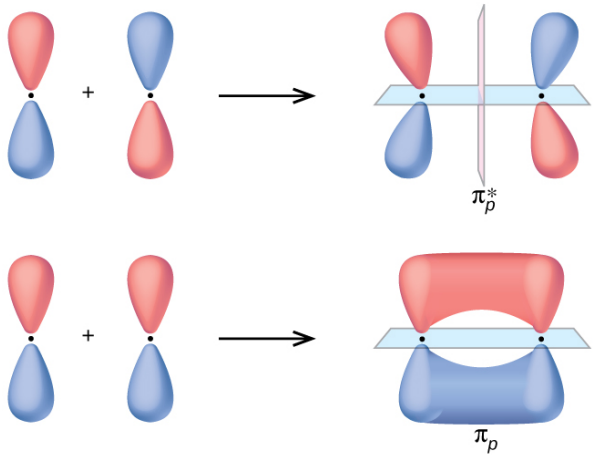
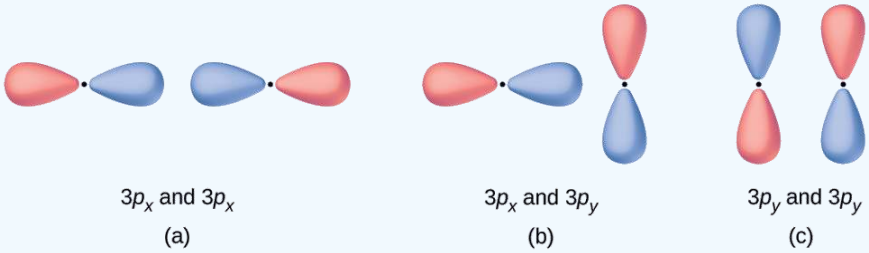


Figure 7.3.5: Side-by-side overlap of each two p orbitals results in the formation of two π molecular orbitals. Combining the out-of-phase orbitals results in an antibonding molecular orbital with two nodes. One contains the internuclear axis, and one is perpendicular to the axis. Combining the in-phase 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.

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 7.3.1: 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.



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 orbitals do not overlap. Only orbitals with the correct alignment can combine.
c. This is an out-of-phase combination, resulting in a π^*_{3p} orbital.

Exercise 7.3.1

Label the molecular orbital shown as σ or π, bonding or antibonding and indicate where the node occurs.



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.



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 7.3.6). 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.

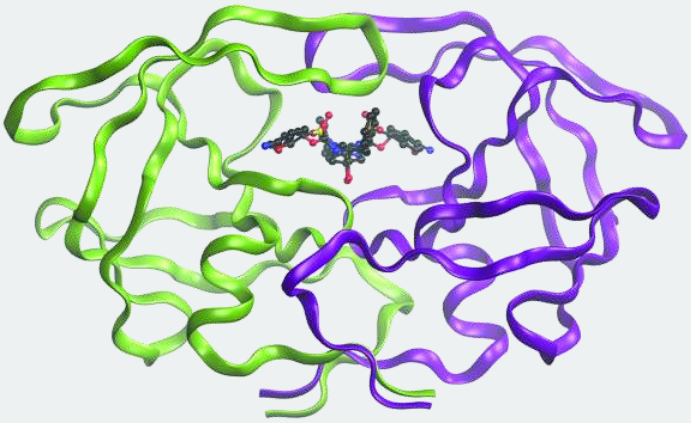


Figure 7.3.6: The molecule shown, HIV-1 protease, is an important target for pharmaceutical research. By designing molecules that bind to this protein, scientists are able to drastically inhibit the progress of the disease.

7.3.4: Molecular Orbital Energy Diagrams

The relative energy levels of atomic and molecular orbitals are typically shown in a molecular orbital diagram (Figure 7.3.7). 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 7.3.7: 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.

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 7.3.7). 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.

7.3.5: 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.

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:

$$\text{bond order} = \frac{(\text{number of bonding electrons}) - (\text{number of antibonding electrons})}{2} \tag{7.3.1}$$

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.

7.3.6: 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 7.3.8) in which a single upward arrow indicates one electron in an orbital, and two (upward and downward) arrows indicate two electrons of opposite spin.

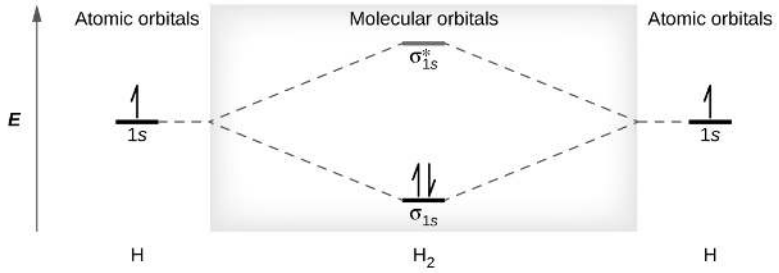


Figure 7.3.8: The molecular orbital energy diagram predicts that H_2 will be a stable molecule with lower energy than the separated atoms.

A dihydrogen molecule contains two bonding electrons and no antibonding electrons so we have

$$\text{bond order in } H_2 = \frac{(2-0)}{2} = 1 \tag{7.3.2}$$

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 7.3.9. 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.

$$\text{bond order in } He_2 = \frac{(2-2)}{2} = 0 \tag{7.3.3}$$

A bond order of zero indicates that no bond is formed between two atoms.

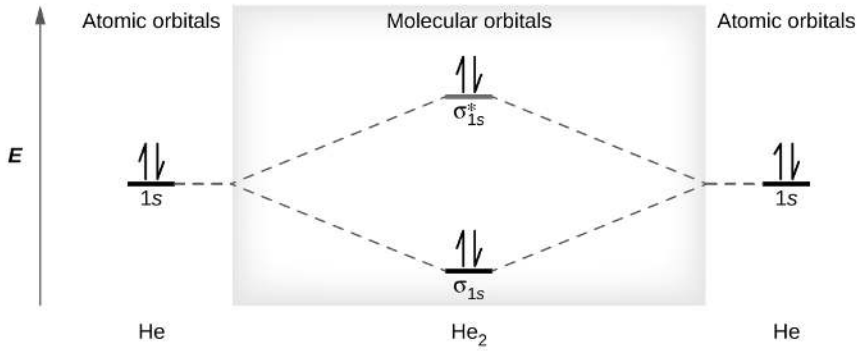


Figure 7.3.9: The molecular orbital energy diagram predicts that He_2 will not be a stable molecule, since it has equal numbers of bonding and antibonding electrons.

7.3.7: 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 7.3.1).

Table 7.3.1: 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.

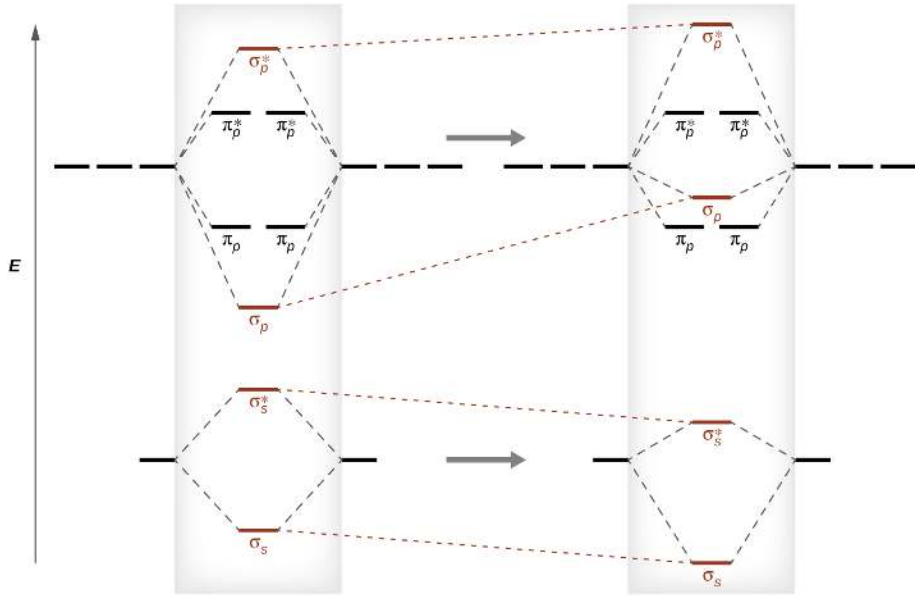


Figure 7.3.10: Without mixing, the MO energy diagram for O_2 to Ne_2 occurs as expected with the diagram on the left where the σ_p orbital lower in energy than the σ_p orbitals. For Li_2 to N_2 the orbitals shift as shown on the right, with the σ_p orbital higher in energy than the π_p orbitals.

Using the MO diagrams shown in Figure 7.3.10, 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 7.3.1, 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 7.3.1 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 7.3.10). 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 7.3.8). 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 7.3.11) shows the bands for three important classes of materials: insulators, semiconductors, and conductors.

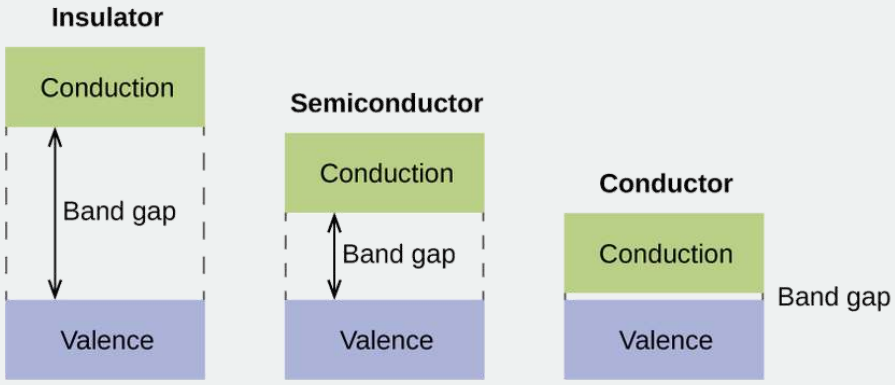


Figure 7.3.11: Molecular orbitals in solids are so closely spaced that they are described as bands. The valence band is lower in energy and the conduction band is higher in energy. The type of solid is determined by the size of the "band gap" between the valence and conduction bands. Only a very small 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.

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 7.3.2: 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 7.3.7. Each oxygen atom contributes six electrons, so the diagram appears as shown in Figure 7.3.7.

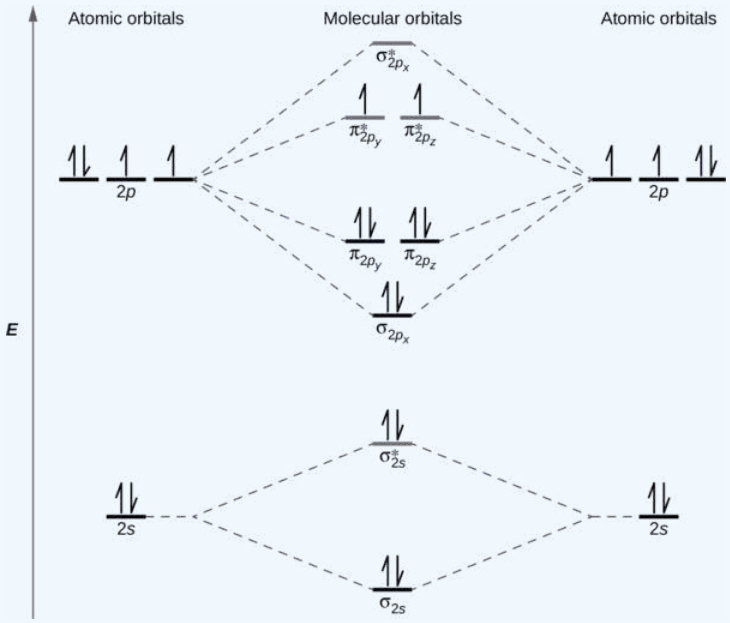


Figure 7.3.12: The molecular orbital energy diagram for O_2 predicts two unpaired electrons.

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 7.3.2

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 7.3.3: 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 7.3.3

How many unpaired electrons would be present on a Be_2^{2-} ion? Would it be paramagnetic or diamagnetic?

Answer

two, paramagnetic

7.3.8: 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.

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 7.3: Molecular Orbital Theory is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

- **8.5: Molecular Orbital Theory** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.
- **8.1: Prelude to Covalent Bonding** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

7.E: Advanced Theories of Covalent Bonding- Homework

7.E.1: Turn in your answers for the following questions - show your work

1. Draw Lewis dot structures, determine the hybridization of each atom and sketch the orbital structure for;
   a. CH_4
   b. NH3
   c. HBr
   d. PCl_5
   e. CO_2
   f. BF_3
   g. C_4H_8O (3 different structures)
2. Draw Lewis dot structures then compare and contrast the Lewis dot, hybrid, and MO models for describing the structure of these molecules.
   a. H_2
   b. O_2

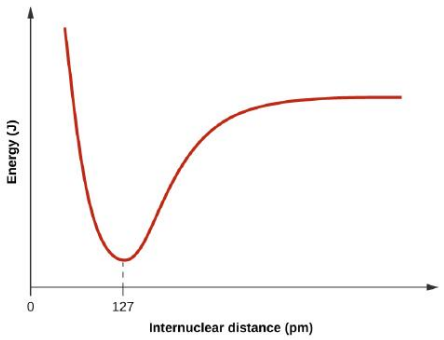
7.E.2: The Following Questions are for your practice - Do Not Turn In. They include answers so you can check your work

7.E.2.1: Valence Bond Theory

1. 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.

$$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)} \quad \Delta H^{\circ}_{rxn} = -184.7\ kJ/mol \tag{7.E.1}$$

answer

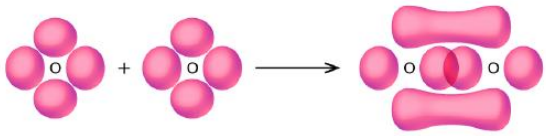


When H and Cl are separate (the x axis) the energy is at a particular value. As they approach, it decreases to a minimum at 127 pm (the bond distance), and then it increases sharply as you get closer.

2. 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

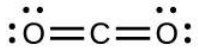
Bonding: One σ bond and one π bond. The *s* orbitals are filled and do not overlap. The *p* orbitals overlap along the axis to form a σ bond and side by side to form the π bond.



3. Draw the Lewis structures for CO_2 and CO, and predict the number of σ and π bonds for each molecule.

answer

a. CO_2; 2 σ 2 π;



b. CO; 1 σ 2 π



7.E.2.2: Hybrid Atomic Orbitals

1. Sulfuric acid is manufactured by a series of reactions represented by the following equations:

$$S_8(s) + 8\,O_2(g) \longrightarrow 8\,SO_2(g)$$

$$2\,SO_2(g) + O_2(g) \longrightarrow 2\,SO_3(g)$$

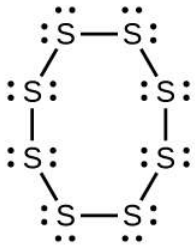
$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(l)$$

Draw a Lewis structure, predict the molecular geometry by VSEPR, and determine the hybridization of sulfur for the following:

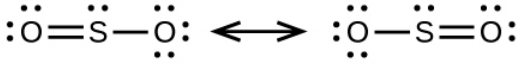
a. circular S_8 molecule
b. SO_2 molecule
c. SO_3 molecule
d. H_2SO_4 molecule (the hydrogen atoms are bonded to oxygen atoms)

answer

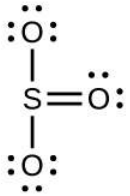
(a) Each S has a bent (109°) geometry, sp^3



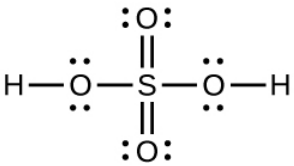
(b) Bent (120°), sp^2



(c) Trigonal planar, sp^2



(d) Tetrahedral, sp^3

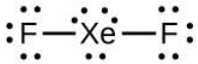


2. For many years after they were discovered, it was believed that the noble gases could not form compounds. Now we know that belief to be incorrect. A mixture of xenon and fluorine gases, confined in a quartz bulb and placed on a windowsill, is found to slowly produce a white solid. Analysis of the compound indicates that it contains 77.55% Xe and 22.45% F by mass.
   1. What is the formula of the compound?
   2. Write a Lewis structure for the compound.
   3. Predict the shape of the molecules of the compound.
   4. What hybridization is consistent with the shape you predicted?

answer

(a) XeF_2

(b)

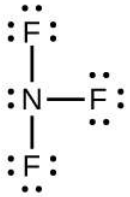


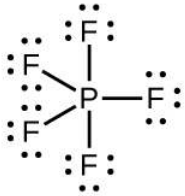
(c) linear

(d) sp^3d

3. 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





7.E.2.3: Multiple Bonds

1. A useful solvent that will dissolve salts as well as organic compounds is the compound acetonitrile, H_3CCN. It is present in paint strippers.

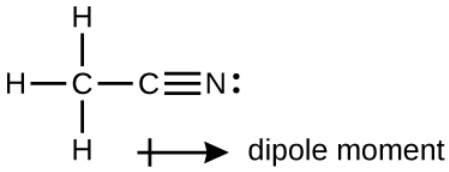
   (a) Write the Lewis structure for acetonitrile, and indicate the direction of the dipole moment in the molecule.

   (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.

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.

2. 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

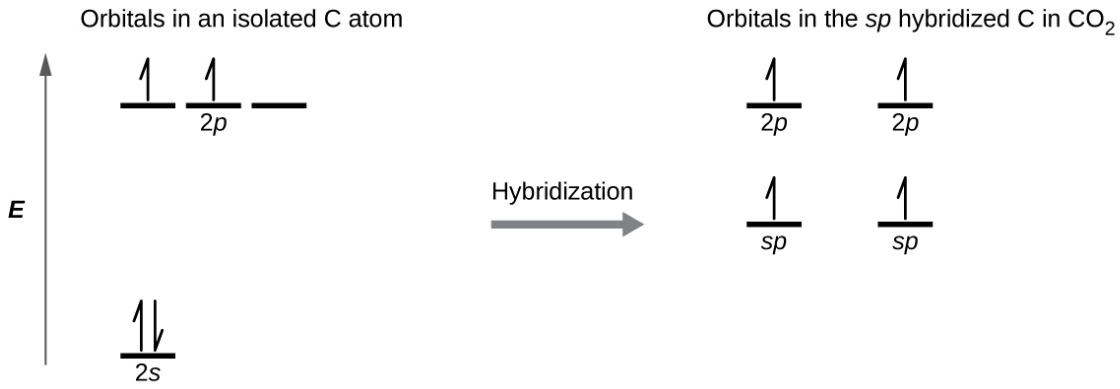
(c) Cl_2CO (C is the central atom)

answer

(a) sp^2; (b) *sp*; (c) sp^2

3. 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.

7.E.2.4: Molecular Orbital Theory

1. 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-}

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+}

This page titled 7.E: Advanced Theories of Covalent Bonding- Homework is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

CHAPTER OVERVIEW

8: Kinetics

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

General Chemistry

Chemical kinetics is the study of rates of chemical processes and includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction.

8.1: Introduction to Chemical Reaction Rates
8.2: Collision Theory and Reaction Mechanisms
8.3: Catalysis
8.E: Kinetics - Homework

This page titled 8: Kinetics 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.

8.1: Introduction to Chemical Reaction Rates



Figure 8.1.1An agama lizard basks in the sun. As its body warms, the chemical reactions of its metabolism speed up.

Learning Objectives

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

- Define chemical reaction rate
- Derive rate expressions from the balanced equation for a given chemical reaction
- Calculate reaction rates from experimental data
- Describe the effects of chemical nature, physical state, temperature, concentration, and catalysis on reaction rates

8.1.1: Introduction

The lizard in the Figure 8.1.1 photograph is not simply enjoying the sunshine or working on its tan. The heat from the sun's rays is critical to the lizard's survival. A warm lizard can move faster than a cold one because the chemical reactions that allow its muscles to move occur more rapidly at higher temperatures. A cold lizard is a slower lizard and an easier meal for predators.

From baking a cake to determining the useful lifespan of a bridge, rates of chemical reactions play important roles in our understanding of processes that involve chemical changes. Two questions are typically posed when planning to carry out a chemical reaction. The first is: "Will the reaction produce the desired products in useful quantities?" The second question is: "How rapidly will the reaction occur?" A third question is often asked when investigating reactions in greater detail: "What specific molecular-level processes take place as the reaction occurs?" Knowing the answer to this question is of practical importance when the yield or rate of a reaction needs to be controlled.

The study of chemical kinetics concerns the second and third questions—that is, the rate at which a reaction yields products and the molecular-scale means by which a reaction occurs. This chapter examines the factors that influence the rates of chemical reactions, the mechanisms by which reactions proceed, and the quantitative techniques used to describe the rates at which reactions occur.

8.1.2: Reaction Rates

A *rate* is a measure of how some property varies with time. Speed is a familiar rate that expresses the distance traveled by an object in a given amount of time. Wage is a rate that represents the amount of money earned by a person working for a given amount of time. Likewise, the rate of a chemical reaction is a measure of how much reactant is consumed, or how much product is produced, by the reaction in a given amount of time.

The rate of reaction is the change in the amount of a reactant or product per unit time. Reaction rates are therefore determined by measuring the time dependence of some property that can be related to reactant or product amounts. Rates of reactions that consume or produce gaseous substances, for example, are conveniently determined by measuring changes in volume or pressure. For reactions involving one or more colored substances, rates may be monitored via measurements of light absorption. For reactions involving aqueous electrolytes, rates may be measured via changes in a solution's conductivity.

For reactants and products in solution, their relative amounts (concentrations) are conveniently used for purposes of expressing reaction rates. For example, the concentration of hydrogen peroxide, H_2O_2, in an aqueous solution changes slowly over time as it decomposes according to the equation:

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

Figure 8.1.2 provides an example of data collected during the decomposition of H_2O_2. To obtain the tabulated results for this decomposition, the concentration of hydrogen peroxide was measured every 6 hours over the course of a day at a constant temperature of 40 °C. The reaction rate between any two measurements is determined by finding the change in concentration, $\Delta[H_2O_2]$, and the change in time, Δt. Reaction rates are, by convention, positive quantities, and so this negative change in concentration is multiplied by −1. Reaction rates were computed for each time interval by dividing the change in concentration by the corresponding time increment, as shown here for the first 6-hour period:

$$\frac{-\Delta[H_2O_2]}{\Delta t} = \frac{-(0.500\ \text{mol/L} - 1.000\ \text{mol/L})}{(6.00\ \text{h} - 0.00\ \text{h})} = 0.0833 \text{mol L}{-1\ \text{h}^{-1}}$$

Notice that the reaction rates vary with time, decreasing as the reaction proceeds. Results for the last 6-hour period yield a reaction rate of:

$$\frac{-\Delta[H_2O_2]}{\Delta t} = \frac{-(0.0625\ \text{mol/L} - 0.125\ \text{mol/L})}{(24.00\ \text{h} - 18.00\ \text{h})} = 0.010\ \text{mol L}^{-1}\ \text{h}^{-1}$$

Time (h)	$[H_2O_2]$ (mol L^{-1})	$\Delta[H_2O_2]$ (mol L^{-1})	Δt (h)	Rate of Decomposition, (mol L^{-1} h^{-1})
0.00	1.000			
		−0.500	6.00	0.0833
6.00	0.500			
		−0.250	6.00	0.0417
12.00	0.250			
		−0.125	6.00	0.0208
18.00	0.125			
		−0.062	6.00	0.010
24.00	0.0625			

Figure 8.1.2The rate of decomposition of H_2O_2 in an aqueous solution decreases as the concentration of H_2O_2 decreases.

This behavior indicates the reaction continually slows with time. Using the concentrations at the beginning and end of a time period over which the reaction rate is changing results in the calculation of an average rate for the reaction over this time interval.

8.1.3: Instantaneous Reaction Rate

The change in concentration with time shown in Figure 8.1.2 can also be made into a graph, as shown in Figure 8.1.3. The slope of the curve in this graph is another way to find the rate of a reaction. At any specific time, the slope of this line is the rate of the reaction.

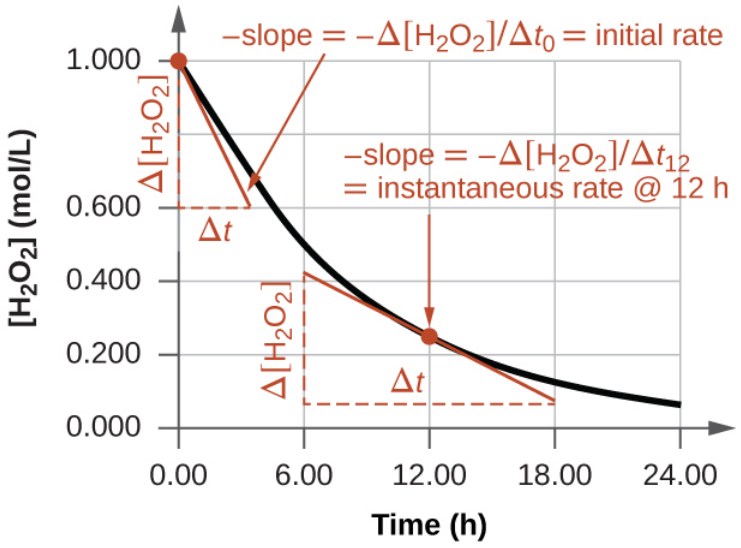


Figure 8.1.3This graph shows a plot of concentration versus time for a 1.000 *M* solution of H_2O_2. The rate at any time is equal to the negative of the slope of a line tangent to the curve at that time. Tangents are shown at t = 0 h ("initial rate") and at t = 12 h ("instantaneous rate" at 12 h).

8.1.3.1: Chemistry in Everyday Life

8.1.3.1.1: Reaction Rates in Analysis: Test Strips for Urinalysis

Physicians often use disposable test strips to measure the amounts of various substances in a patient's urine (Figure 8.1.4). These test strips contain various chemical reagents, embedded in small pads at various locations along the strip, which undergo changes in color upon exposure to sufficient concentrations of specific substances. The usage instructions for test strips often stress that proper read time is critical for optimal results. This emphasis on read time suggests that kinetic aspects of the chemical reactions occurring on the test strip are important considerations.

The test for urinary glucose relies on a two-step process represented by the chemical equations shown here:

$$C_6H_{12}O_6 + O_2 \xrightarrow{\text{catalyst}} C_6H_{10}O_6 + H_2O_2$$

$$2H_2O_2 + 2I^- \xrightarrow{\text{catalyst}} I_2 + 2H_2O + O_2$$

The first equation depicts the oxidation of glucose in the urine to yield glucolactone and hydrogen peroxide. The hydrogen peroxide produced subsequently oxidizes colorless iodide ion to yield brown iodine, which may be visually detected. Some strips include an additional substance that reacts with iodine to produce a more distinct color change.

The two test reactions shown above are inherently very slow, but their rates are increased by special enzymes embedded in the test strip pad. This is an example of *catalysis*, a topic discussed later in this chapter. A typical glucose test strip for use with urine requires approximately 30 seconds for completion of the color-forming reactions. Reading the result too soon might lead one to conclude that the glucose concentration of the urine sample is lower than it actually is (a *false-negative* result). Waiting too long to assess the color change can lead to a *false positive* due to the slower (not catalyzed) oxidation of iodide ion by other substances found in urine.



Figure 8.1.4Test strips are commonly used to detect the presence of specific substances in a person's urine. Many test strips have several pads containing various reagents to permit the detection of multiple substances on a single strip. (credit: Iqbal Osman)

8.1.4: Factors Affecting Reaction Rates

The rates at which reactants are consumed and products are formed during chemical reactions vary greatly. Five factors typically affecting the rates of chemical reactions will be explored in this section: the chemical nature of the reacting substances, the state of subdivision (one large lump versus many small particles) of the reactants, the temperature of the reactants, the concentration of the reactants, and the presence of a catalyst.

8.1.4.1: The Chemical Nature of the Reacting Substances

The rate of a reaction depends on the nature of the participating substances. Reactions that appear similar may have different rates under the same conditions, depending on the identity of the reactants. For example, when small pieces of the metals iron and sodium are exposed to air, the sodium reacts completely with air overnight, whereas the iron is barely affected. The active metals calcium and sodium both react with water to form hydrogen gas and a base. Yet calcium reacts at a moderate rate, whereas sodium reacts so rapidly that the reaction is almost explosive.

8.1.4.2: The Physical States of the Reactants

A chemical reaction between two or more substances requires intimate contact between the reactants. When reactants are in different physical states, or phases (solid, liquid, gaseous, dissolved), the reaction takes place only at the interface between the phases. Consider the heterogeneous reaction between a solid phase and either a liquid or gaseous phase. Compared with the reaction rate for large solid particles, the rate for smaller particles will be greater because the surface area in contact with the other reactant phase is greater. For example, large pieces of iron react more slowly with acids than they do with finely divided iron powder (Figure 8.1.5). Large pieces of wood smolder, smaller pieces burn rapidly, and saw dust burns explosively.



Figure 8.1.5(a) Iron powder reacts rapidly with dilute hydrochloric acid and produces bubbles of hydrogen gas: 2Fe(s) + 6HCl(aq) ⟶ 2$FeCl_3$(aq) + 3H_2(g). (b) An iron nail reacts more slowly because the surface area exposed to the acid is much less.

8.1.4.3: Link to Learning

Watch this video to see the reaction of cesium with water in slow motion and a discussion of how the state of reactants and particle size affect reaction rates.

8.1.4.4: Temperature of the Reactants

Chemical reactions typically occur faster at higher temperatures. Food can spoil quickly when left on the kitchen counter. However, the lower temperature inside of a refrigerator slows that process so that the same food remains fresh for days. Gas burners, hot plates, and ovens are often used in the laboratory to increase the speed of reactions that proceed slowly at ordinary temperatures. For many chemical processes, reaction rates are approximately doubled when the temperature is raised by 10 °C.

8.1.4.5: Concentrations of the Reactants

The rates of many reactions depend on the concentrations of the reactants. Rates usually increase when the concentration of one or more of the reactants increases. For example, calcium carbonate ($CaCO_3$) deteriorates as a result of its reaction with the pollutant sulfur dioxide. The rate of this reaction depends on the amount of sulfur dioxide in the air (Figure 8.1.6). An acidic oxide, sulfur dioxide combines with water vapor in the air to produce sulfurous acid in the following reaction:

$$\mathrm{SO_2}(g) + \mathrm{H_2O}(g) \longrightarrow \mathrm{H_2SO_3}(aq)$$

Calcium carbonate reacts with sulfurous acid as follows:

$$\mathrm{CaCO_3}(s) + \mathrm{H_2SO_3}(aq) \longrightarrow \mathrm{CaSO_3}(aq) + \mathrm{CO_2}(g) + \mathrm{H_2O}(l)$$

In a polluted atmosphere where the concentration of sulfur dioxide is high, calcium carbonate deteriorates more rapidly than in less polluted air. Similarly, phosphorus burns much more rapidly in an atmosphere of pure oxygen than in air, which is only about 20% oxygen.



Figure 8.1.6Statues made from carbonate compounds such as limestone and marble typically weather slowly over time due to the actions of water, and thermal expansion and contraction. However, pollutants like sulfur dioxide can accelerate weathering. As the concentration of air pollutants increases, deterioration of limestone occurs more rapidly. (credit: James P Fisher III)

8.1.4.6: Link to Learning

Phosphorus burns rapidly in air, but it will burn even more rapidly if the concentration of oxygen is higher. Watch this video to see an example.

8.1.4.7: The Presence of a Catalyst

Relatively dilute aqueous solutions of hydrogen peroxide, H_2O_2, are commonly used as topical antiseptics. Hydrogen peroxide decomposes to yield water and oxygen gas according to the equation:

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

Under typical conditions, this decomposition occurs very slowly. When dilute H_2O_2(aq) is poured onto an open wound, however, the reaction occurs rapidly and the solution foams because of the vigorous production of oxygen gas. This dramatic difference is caused by the presence of substances within the wound's exposed tissues that accelerate the decomposition process. Substances that function to increase the rate of a reaction are called catalysts, a topic treated in greater detail later in this chapter.

8.1.4.8: Link to Learning

Chemical reactions occur when molecules collide with each other and undergo a chemical transformation. Before physically performing a reaction in a laboratory, scientists can use molecular modeling simulations to predict how the parameters discussed earlier will influence the rate of a reaction. Use the PhET Reactions & Rates interactive to explore how temperature, concentration, and the nature of the reactants affect reaction rates.

This page titled 8.1: Introduction to Chemical Reaction Rates 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: Collision Theory and Reaction Mechanisms

Learning Objectives

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

- Use the postulates of collision theory to explain the effects of physical state, temperature, and concentration on reaction rates
- Define the concepts of activation energy and transition state
- Distinguish net reactions from elementary reactions (steps)
- Identify the molecularity of elementary reactions
- Write a balanced chemical equation for a process given its reaction mechanism

8.2.1: Introduction to Collision Theory

We should not be surprised that atoms, molecules, or ions must collide before they can react with each other. Atoms must be close together to form chemical bonds. This simple premise is the basis for a very powerful theory that explains many observations regarding chemical kinetics, including factors affecting reaction rates.

Collision theory is based on the following postulates:

1. The rate of a reaction is proportional to the rate of reactant collisions.
2. The reacting species must collide in an orientation that allows contact between the atoms that will become bonded together in the product.
3. The collision must occur with adequate energy to permit mutual penetration of the reacting species' valence shells so that the electrons can rearrange and form new bonds (and new chemical species).

The first postulate for collision theory explains why most reaction rates increase as concentrations increase. With an increase in the concentration of any reacting substance, the chances for collisions between molecules are increased because there are more molecules per unit of volume. More collisions mean a faster reaction rate, assuming the energy of the collisions is adequate.

To explain the second and third postulates, the orientation and energy of collisions, consider the reaction of carbon monoxide with oxygen:

$$2\ CO(g) + O_2(g) \longrightarrow 2\ CO_2(g)$$

Carbon monoxide is a pollutant produced by the combustion of hydrocarbon fuels. To reduce this pollutant, automobiles have catalytic converters that use a catalyst to carry out this reaction. If carbon monoxide and oxygen are present in sufficient amounts, the reaction will occur at high temperature and pressure. The first step in the gas-phase reaction between carbon monoxide and oxygen is a collision between the two molecules:

$$CO(g) + O_2(g) \longrightarrow CO_2(g) + O(g)$$

Although there are many different possible orientations the two molecules can have relative to each other, consider the two presented in Figure 8.2.1. In the first case, the oxygen side of the carbon monoxide molecule collides with the oxygen molecule. In the second case, the carbon side of the carbon monoxide molecule collides with the oxygen molecule. The second case is clearly more likely to result in the formation of carbon dioxide, which has a central carbon atom bonded to two oxygen atoms $(O = C = O)$. This shows how important the orientation of the collision is in terms of creating the desired product of the reaction.

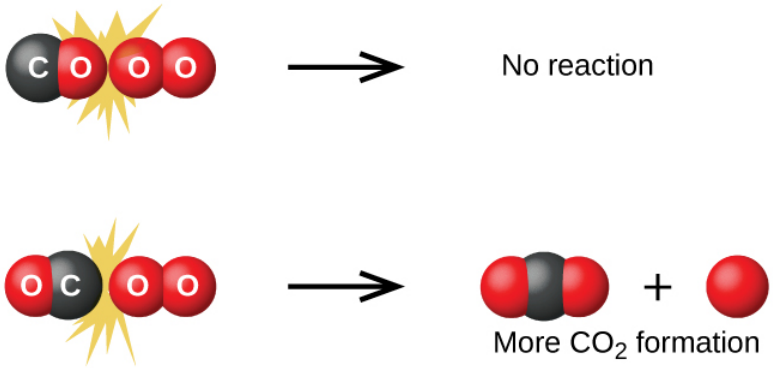


Figure 8.2.1Illustrated are two collisions that might take place between carbon monoxide and oxygen molecules. The orientation of the colliding molecules partially determines whether a reaction between the two molecules will occur.

If the collision does take place with the correct orientation, there is still no guarantee that the reaction will proceed to form carbon dioxide. In addition to a proper orientation, the collision must also occur with sufficient energy to result in product formation. When reactant species collide with both proper orientation and adequate energy, they combine to form an unstable species called an activated complex or a transition state. These species are very short lived and usually undetectable by most analytical instruments. In some cases, sophisticated spectral measurements have been used to observe transition states.

8.2.2: Activation Energy

The minimum energy necessary to form a product during a collision between reactants is called the activation energy (E_a). The magnitude of the activation energy compared to the kinetic energy from colliding reactant molecules is an important factor determining the rate of a chemical reaction. If the activation energy is much larger than the average kinetic energy of the collisions, the reaction occurs slowly since only a few molecules move fast enough to have enough energy to react. If the activation energy is much smaller than the average kinetic energy of the molecules, a large fraction of molecules have enough kinetic energy to react when they collide.

Figure 8.2.2 shows how the energy of a chemical system changes as it undergoes a reaction converting reactants to products according to the equation

$$A + B \longrightarrow C + D$$

These reaction diagrams are widely used in chemical kinetics to illustrate various properties of the reaction of interest. Viewing the diagram from left to right, the system initially comprises reactants only, $A + B$. Reactant molecules with sufficient energy can collide to form a high-energy activated complex or transition state. The unstable transition state can then subsequently decay to yield stable products, $C + D$. The diagram depicts the reaction's activation energy, E_a, as the energy difference between the reactants and the transition state. Using a specific energy, the *enthalpy* (see chapter on thermochemistry), the enthalpy change of the reaction, ΔH, is estimated as the energy difference between the reactants and products. In this case, the reaction is exothermic ($\Delta H < 0$) since it yields a decrease in system enthalpy.

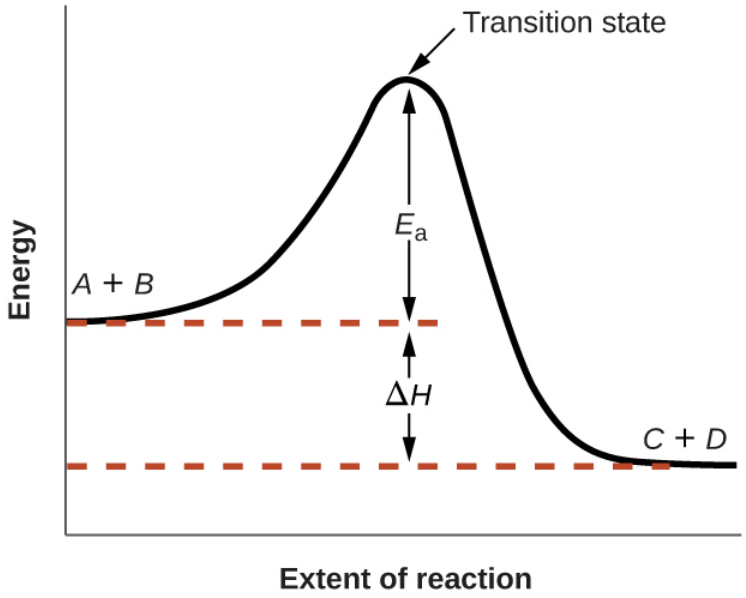


Figure 8.2.2Reaction diagram for the exothermic reaction $A + B \longrightarrow C + D$.

8.2.3: Boltzman Distribution

The energy required to overcome the activation energy is provided by the kinetic energy of the molecules when they collide. As a result, the rate of the reaction - how many molecules can overcome the activation energy barrier - depends upon the temperature. The boltzmann distribution shown in Figure $8.2.3a$ describes the number of molecules as a function of kinetic energy at a specific temperature. When the temperature changes as shown in Figure $8.2.3b$ the distribution changes, so the number of molecules with enough kinetic energy to overcome the activation energy barrier changes.

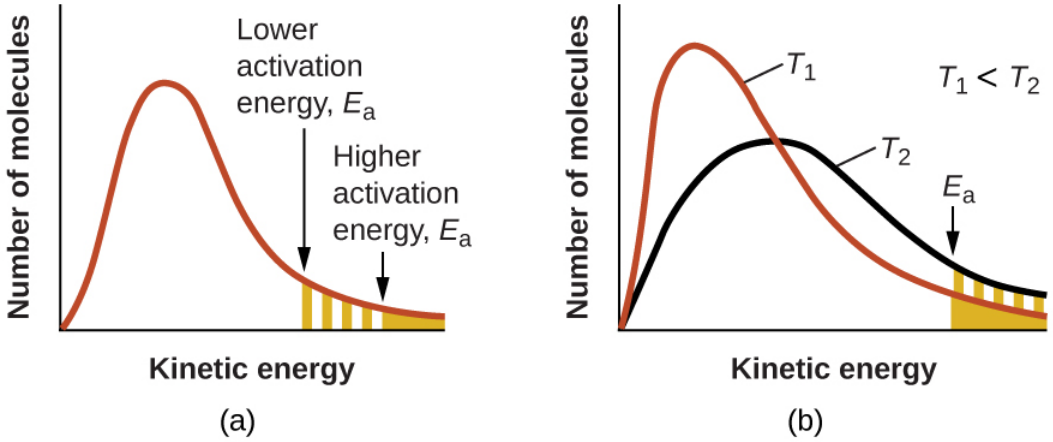


Figure 8.2.3Molecular energy distributions showing numbers of molecules with energies exceeding (a) two different activation energies at a given temperature, and (b) a given activation energy at two different temperatures.

8.2.4: Reaction Mechanisms

Chemical reactions very often occur in a step-wise fashion, involving two or more distinct reactions taking place in sequence. A balanced equation indicates what is reacting and what is produced, but it reveals no details about how the reaction actually takes

place. The reaction mechanism (or reaction path) provides details regarding the precise, step-by-step process by which a reaction occurs.

The decomposition of ozone, for example, appears to follow a mechanism with two steps:

$$\mathrm{O_{3(g)} \longrightarrow O_{2(g)} + O}$$
$$\mathrm{O + O_{3(g)} \longrightarrow 2O_{2(g)}}$$

Each of the steps in a reaction mechanism is an elementary reaction. These elementary reactions occur precisely as represented in the step equations, and they must sum to yield the balanced chemical equation representing the overall reaction:

$$\mathrm{2O_{3(g)} \longrightarrow 3O_{2(g)}}$$

Notice that the oxygen atom produced in the first step of this mechanism is consumed in the second step and therefore does not appear as a product in the overall reaction. Species that are produced in one step and consumed in a subsequent step are called intermediates. Intermediates are different from transition states because the intermediates are longer lived and can be detected in many reactions. A transition state is at the top of the reaction energy diagram - as shown in Figure 8.2.2. Figure 8.2.4 shows the O_3 starting material, the first transition state is the excited state ozone molecule, O_3^*, the reaction intermediate O in the valley between the two transition state peaks, the second transition state O-O_3^*, and the final products O_2. T

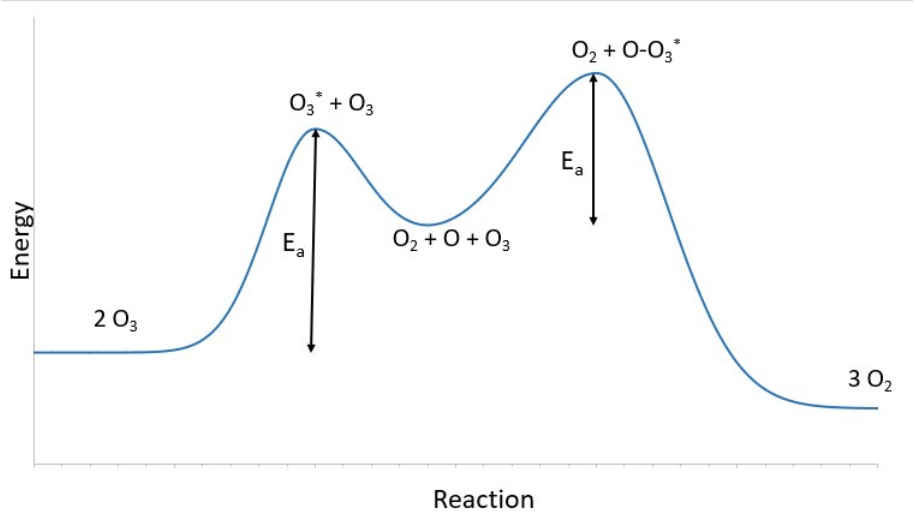


Figure 8.2.4:Energy diagram for ozone decomposition.

While the overall reaction equation for the decomposition of ozone indicates that two molecules of ozone react to give three molecules of oxygen, the mechanism of the reaction *does not involve the direct collision and reaction of two ozone molecules*. Instead, one O_3 decomposes to yield O_2 and an oxygen atom, and a second O_3 molecule subsequently reacts with the oxygen atom to yield two additional O_2 molecules.

Unlike balanced equations representing an overall reaction, the equations for elementary reactions are explicit representations of the chemical change taking place. The reactant(s) in an elementary reaction's equation undergo only the bond-breaking and/or making events depicted to yield the product(s).

8.2.4.1: Unimolecular Elementary Reactions

The molecularity of an elementary reaction is the number of reactant species (atoms, molecules, or ions). For example, a unimolecular reaction involves the reaction of a *single* reactant species to produce one or more molecules of product:

$$\mathrm{A \longrightarrow products}$$

The rate law for a unimolecular reaction is first order because it only depends upon the amount of one reaction:

$$\mathrm{rate} = k[A]$$

A unimolecular reaction may be one of several elementary reactions in a complex mechanism. For example, the reaction:

$$O_3\ (g) \text{ -> } O_2\ (g) + O$$

illustrates a unimolecular elementary reaction that occurs as one part of a two-step reaction mechanism as described above. However, in some cases the overall reaction is also an elementary reaction. For some unimolecular reactions are the only step of a single-step reaction mechanism. For example, the gas-phase decomposition of cyclobutane, C_4H_8, to ethylene, C_2H_4, is represented by the chemical equation in Figure 8.2.4:

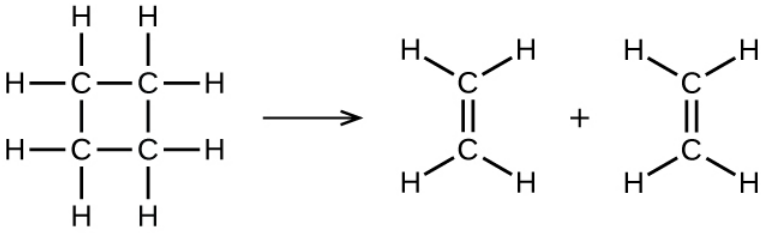


Figure 8.2.5. Decomposition of cyclobutane.

This equation represents the overall reaction observed, and it might also represent a legitimate unimolecular elementary reaction. The rate law predicted from this equation, assuming it is an elementary reaction, turns out to be the same as the rate law derived experimentally for the overall reaction, namely, one showing first-order behavior:

$$\text{rate} = k[C_4H_8]$$

This agreement between observed and predicted rate laws is interpreted to mean that the proposed unimolecular, single-step process is a reasonable mechanism for the butadiene reaction.

8.2.4.2: Bimolecular Elementary Reactions

A bimolecular reaction involves two reactant species, for example:

$$A + A \longrightarrow \text{products}$$

OR

$$A + B \longrightarrow \text{products}$$

For the first type, in which the two reactant molecules are different, the rate law is first-order in *A* and first order in *B* (second-order overall):

$$\text{RATE} = k[A][B]$$

For the second type, in which two identical molecules collide and react, the rate law is second order in *A*:

$$\text{RATE} = k[A][A] = k[A]^2$$

Some chemical reactions occur by mechanisms that consist of a single bimolecular elementary reaction. One example is the reaction of nitrogen dioxide with carbon monoxide shown in Figure 8.2.6

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$



Figure 8.2.6The probable mechanism for the reaction between NO_2 and CO to yield NO and CO_2.

Bimolecular elementary reactions may also be involved as steps in a multistep reaction mechanism. The reaction of atomic oxygen with ozone is the second step of the two-step ozone decomposition mechanism discussed earlier in this section.

8.2.4.3: Relating Reaction Mechanisms to Rate Laws

It's often the case that one step in a multistep reaction mechanism has a much higher activation energy, so it is significantly slower than the others. Because a reaction cannot proceed faster than its slowest step, this step will limit the rate at which the overall

reaction occurs. The slowest step is therefore called the rate-limiting step (or rate-determining step) of the reaction. Figure 8.2.7 shows a cattle chute, which is the rate-determining step for moving cattle between two pens.



Figure 8.2.7A cattle chute is a nonchemical example of a rate-determining step. Cattle can only be moved from one holding pen to another as quickly as one animal can make its way through the chute. (credit: Loren Kerns)

As described earlier, rate laws may be derived directly from the chemical equations for elementary reactions. However, most chemical reactions are not elementary reactions so and they are often the result of several elementary reaction steps. Together these steps make up the reaction mechanism. In every case, the rate law must be determined from experimental data and the reaction mechanism subsequently deduced from the rate law (and sometimes from other data). The reaction of NO_2 and CO provides an illustrative example:

$$NO_2(g)+CO(g)\longrightarrow CO_2(g)+NO(g)$$

For temperatures above 225 °C, the rate law is:

$$\text{rate} = k\,[NO_2][CO]$$

The reaction is first order with respect to NO_2 and first-order with respect to CO. This is consistent with a single-step bimolecular mechanism and it is *possible* that this is the mechanism for this reaction at high temperatures.

At temperatures below 225 °C, the reaction is described by a rate law that is second order with respect to NO_2:

$$\text{rate}=k[NO_2]^2$$

This rate law is not consistent with the single-step mechanism, but is consistent with the following two-step mechanism:

$$NO_2(g)+NO_2(g)\longrightarrow NO_3(g)+NO(g)\ \text{(slow)}$$
$$NO_3(g)+CO(g)\longrightarrow NO_2(g)+CO_2(g)\ \text{(fast)}$$

The rate-determining (slower) step gives a rate law showing second-order dependence on the NO_2 concentration, and the sum of the two equations gives the net overall reaction. This shows the reaction using different mechanisms depending upon the temperature. The two reaction mechanisms are shown in Figure 8.2.8.

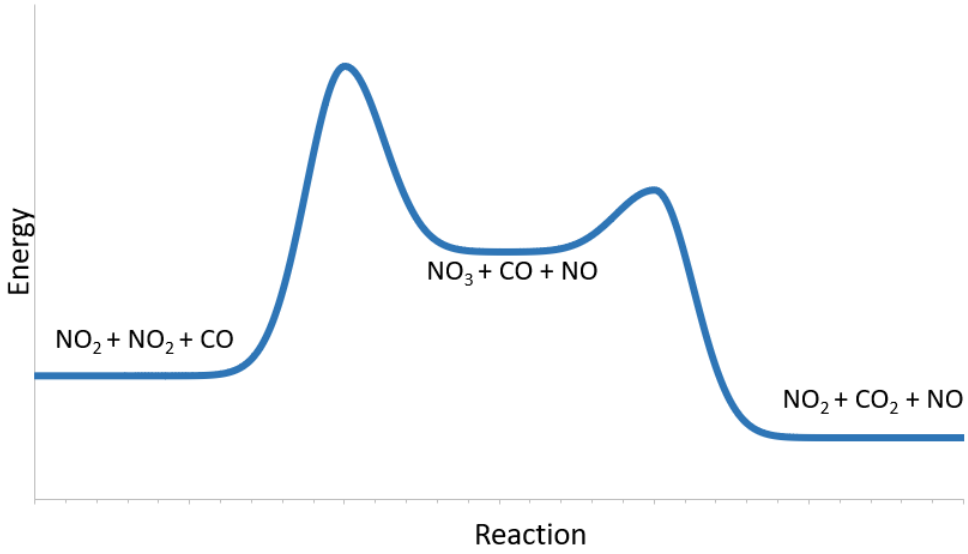


Figure 8.2.8: Copy and Paste Caption here. (Copyright; author via source)

In general, when the rate-determining (slower) step is the first step in a mechanism, the rate law for the overall reaction is the same as the rate law for this step. However, when the rate-determining step is preceded by a step involving a rapidly reversible reaction the rate law for the overall reaction may be more difficult to derive.

This page titled 8.2: Collision Theory and Reaction Mechanisms 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: Catalysis

Learning Objectives

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

- Explain the function of a catalyst in terms of reaction mechanisms and potential energy diagrams
- List examples of catalysis in natural and industrial processes

Among the factors affecting chemical reaction rates discussed earlier in this chapter was the presence of a *catalyst*, a substance that can increase the reaction rate without being consumed in the reaction. The concepts introduced in the previous section on reaction mechanisms provide the basis for understanding how catalysts are able to accomplish this very important function.

Figure 8.3.1 shows reaction diagrams for a chemical process in the absence and presence of a catalyst. Inspection of the diagrams reveals several traits of these reactions. Consistent with the fact that the two diagrams represent the same overall reaction, both curves begin and end at the same energies (in this case, because products are more energetic than reactants, the reaction is endothermic). The reaction mechanisms, however, are clearly different. The uncatalyzed reaction proceeds via a one-step mechanism (one transition state observed), whereas the catalyzed reaction follows a two-step mechanism (two transition states observed) with *a notably lesser activation energy*. This difference illustrates the means by which a catalyst functions to accelerate reactions, namely, by providing an alternative reaction mechanism with a lower activation energy. Although the catalyzed reaction mechanism for a reaction needn't necessarily involve a different number of steps than the uncatalyzed mechanism, it must provide a reaction path whose rate determining step is faster (lower E_a).

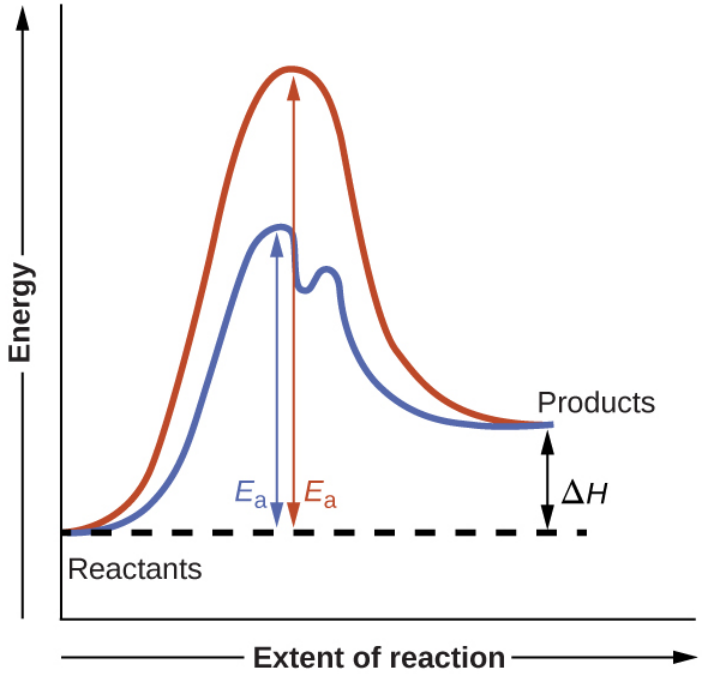
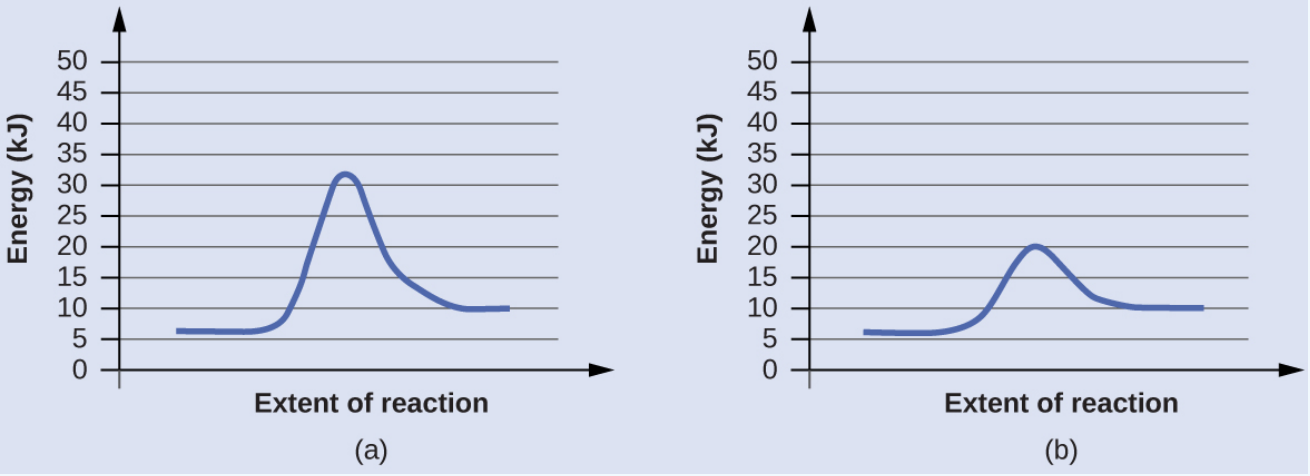


Figure 8.3.1 Reaction diagrams for an endothermic process in the absence (red curve) and presence (blue curve) of a catalyst. The catalyzed pathway involves a two-step mechanism (note the presence of two transition states) and an intermediate species (represented by the valley between the two transitions states).

8.3.0.1: Example 12.15

8.3.0.0.1: Reaction Diagrams for Catalyzed Reactions

The two reaction diagrams here represent the same reaction: one without a catalyst and one with a catalyst. Estimate the activation energy for each process, and identify which one involves a catalyst.



8.3.0.0.1: Solution

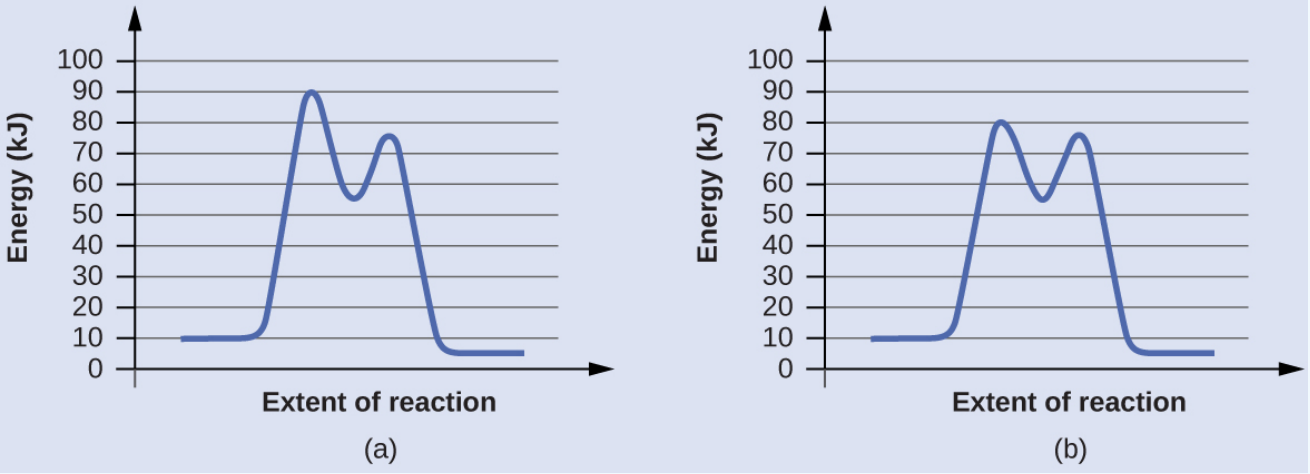
Activation energies are calculated by subtracting the reactant energy from the transition state energy.

$$\text{diagram (a): } E_a = 32\ \text{kJ} - 6\ \text{kJ} = 26\ \text{kJ}$$
$$\text{diagram (b): } E_a = 20\ \text{kJ} - 6\ \text{kJ} =$$

The catalyzed reaction is the one with lesser activation energy, in this case represented by diagram b.

8.3.0.0.1: Check Your Learning

Reaction diagrams for a chemical process with and without a catalyst are shown below. Both reactions involve a two-step mechanism with a rate-determining first step. Compute activation energies for the first step of each mechanism, and identify which corresponds to the catalyzed reaction. How do the second steps of these two mechanisms compare?



8.3.0.1: Answer:

For the first step, E_a = 80 kJ for (a) and 70 kJ for (b), so diagram (b) depicts the catalyzed reaction. Activation energies for the second steps of both mechanisms are the same, 20 kJ.

8.3.0.1: Homogeneous Catalysts

A homogeneous catalyst is present in the same phase as the reactants. It interacts with a reactant to form an intermediate substance, which then decomposes or reacts with another reactant in one or more steps to regenerate the original catalyst and form product.

As an important illustration of homogeneous catalysis, consider the earth's ozone layer. Ozone in the upper atmosphere, which protects the earth from ultraviolet radiation, is formed when oxygen molecules absorb ultraviolet light and undergo the reaction:

$$3O_2(g) \rightarrow h\nu \;\; 2O_3(g)$$

Ozone is a relatively unstable molecule that decomposes to yield diatomic oxygen by the reverse of this equation. This decomposition reaction is consistent with the following two-step mechanism:

$$O_3 \longrightarrow O_2 + O$$

$$O + O_3 \longrightarrow 2O_2$$

A number of substances can catalyze the decomposition of ozone. For example, the nitric oxide–catalyzed decomposition of ozone is believed to occur via the following three-step mechanism:

$$\begin{aligned} NO(g) + O_3(g) &\longrightarrow NO_2(g) + O_2(g) \\ O_3(g) &\longrightarrow O_2(g) + O(g) \\ NO_2(g) + O(g) &\longrightarrow NO(g) + O_2(g) \end{aligned}$$

As required, the overall reaction is the same for both the two-step uncatalyzed mechanism and the three-step NO-catalyzed mechanism:

$$2O_3(g) \longrightarrow 3O_2(g)$$

Notice that NO is a reactant in the first step of the mechanism and a product in the last step. This is another characteristic trait of a catalyst: Though it participates in the chemical reaction, it is not consumed by the reaction.

8.3.0.1: Portrait of a Chemist

8.3.0.0.1: Mario J. Molina

The 1995 Nobel Prize in Chemistry was shared by Paul J. Crutzen, Mario J. Molina (Figure 8.3.2), and F. Sherwood Rowland "for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone."[1] Molina, a Mexican citizen, carried out the majority of his work at the Massachusetts Institute of Technology (MIT).

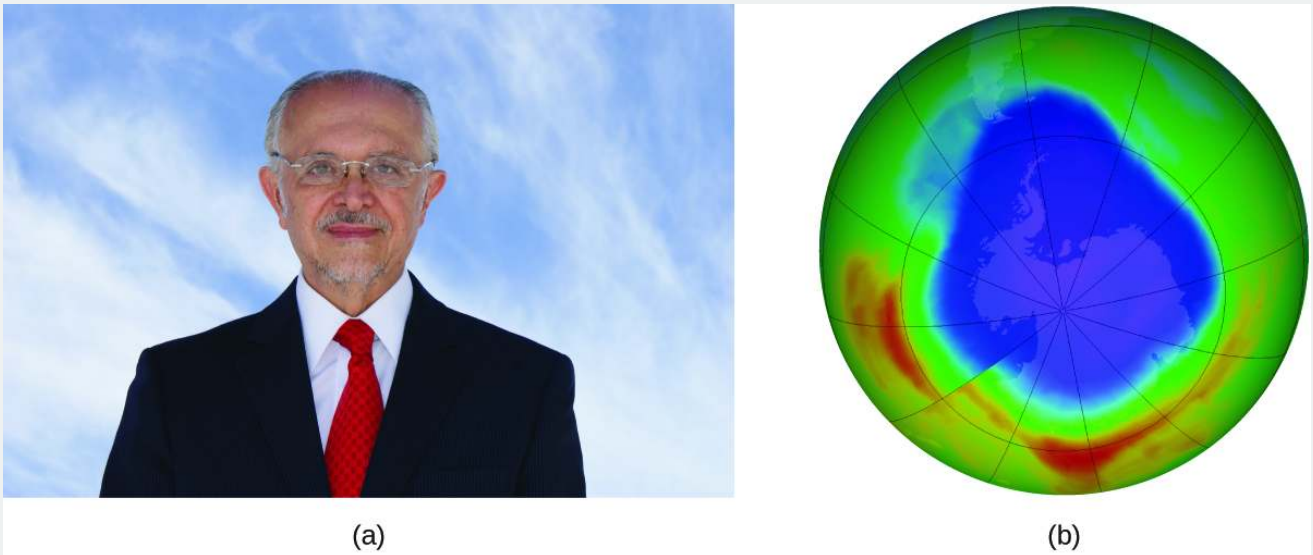


Figure 8.3.2(a) Mexican chemist Mario Molina (1943 –) shared the Nobel Prize in Chemistry in 1995 for his research on (b) the Antarctic ozone hole. (credit a: courtesy of Mario Molina; credit b: modification of work by NASA)

In 1974, Molina and Rowland published a paper in the journal *Nature* detailing the threat of chlorofluorocarbon gases to the stability of the ozone layer in earth's upper atmosphere. The ozone layer protects earth from solar radiation by absorbing ultraviolet light. As chemical reactions deplete the amount of ozone in the upper atmosphere, a measurable "hole" forms above Antarctica, and an increase in the amount of solar ultraviolet radiation— strongly linked to the prevalence of skin cancers—

reaches earth's surface. The work of Molina and Rowland was instrumental in the adoption of the Montreal Protocol, an international treaty signed in 1987 that successfully began phasing out production of chemicals linked to ozone destruction.

Molina and Rowland demonstrated that chlorine atoms from human-made chemicals can catalyze ozone destruction in a process similar to that by which NO accelerates the depletion of ozone. Chlorine atoms are generated when chlorocarbons or chlorofluorocarbons—once widely used as refrigerants and propellants—are photochemically decomposed by ultraviolet light or react with hydroxyl radicals. A sample mechanism is shown here using methyl chloride:

$$\mathrm{CH_3Cl + OH \longrightarrow Cl + \text{other products}}$$

Chlorine radicals break down ozone and are regenerated by the following catalytic cycle:

$$\mathrm{Cl + O_3 \longrightarrow ClO + O_2}$$
$$\mathrm{ClO + O \longrightarrow Cl + O_2}$$
$$\mathrm{\text{overall Reaction: } O_3 + O \longrightarrow 2O_2}$$

A single monatomic chlorine can break down thousands of ozone molecules. Luckily, the majority of atmospheric chlorine exists as the catalytically inactive forms Cl_2 and $ClONO_2$.

Since receiving his portion of the Nobel Prize, Molina has continued his work in atmospheric chemistry at MIT.

8.3.0.1: How Sciences Interconnect

8.3.0.0.2: Glucose-6-Phosphate Dehydrogenase Deficiency

Enzymes in the human body act as catalysts for important chemical reactions in cellular metabolism. As such, a deficiency of a particular enzyme can translate to a life-threatening disease. G6PD (glucose-6-phosphate dehydrogenase) deficiency, a genetic condition that results in a shortage of the enzyme glucose-6-phosphate dehydrogenase, is the most common enzyme deficiency in humans. This enzyme, shown in Figure 8.3.3, is the rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells (Figure 8.3.4).

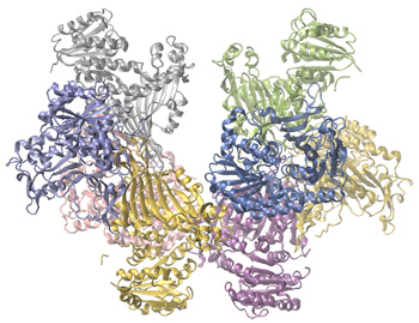


Figure 8.3.3Glucose-6-phosphate dehydrogenase is a rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells.

A disruption in this pathway can lead to reduced glutathione in red blood cells; once all glutathione is consumed, enzymes and other proteins such as hemoglobin are susceptible to damage. For example, hemoglobin can be metabolized to bilirubin, which leads to jaundice, a condition that can become severe. People who suffer from G6PD deficiency must avoid certain foods and medicines containing chemicals that can trigger damage their glutathione-deficient red blood cells.

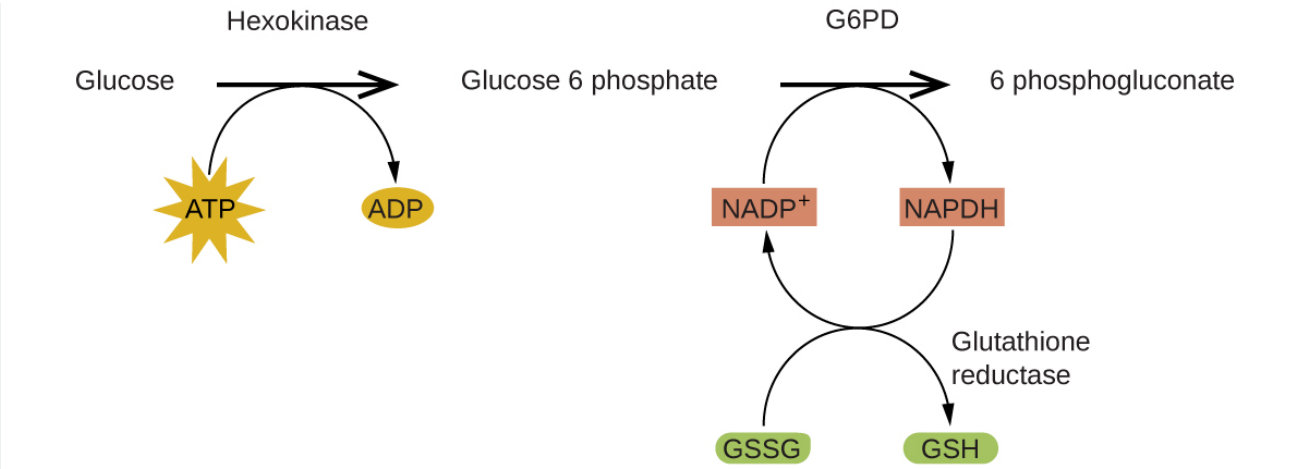


Figure 8.3.4In the mechanism for the pentose phosphate pathway, G6PD catalyzes the reaction that regulates NADPH, a co-enzyme that regulates glutathione, an antioxidant that protects red blood cells and other cells from oxidative damage.

8.3.0.1: Heterogeneous Catalysts

A heterogeneous catalyst is a catalyst that is present in a different phase (usually a solid) than the reactants. Such catalysts generally function by furnishing an active surface upon which a reaction can occur. Gas and liquid phase reactions catalyzed by heterogeneous catalysts occur on the surface of the catalyst rather than within the gas or liquid phase.

Heterogeneous catalysis typically involves the following processes:

1. Adsorption of the reactant(s) onto the surface of the catalyst
2. Activation of the adsorbed reactant(s)
3. Reaction of the adsorbed reactant(s)
4. Desorption of product(s) from the surface of the catalyst

Figure 8.3.5 illustrates the steps of a mechanism for the reaction of compounds containing a carbon–carbon double bond with hydrogen on a nickel catalyst. Nickel is the catalyst used in the hydrogenation of polyunsaturated fats and oils (which contain several carbon–carbon double bonds) to produce saturated fats and oils (which contain only carbon–carbon single bonds).

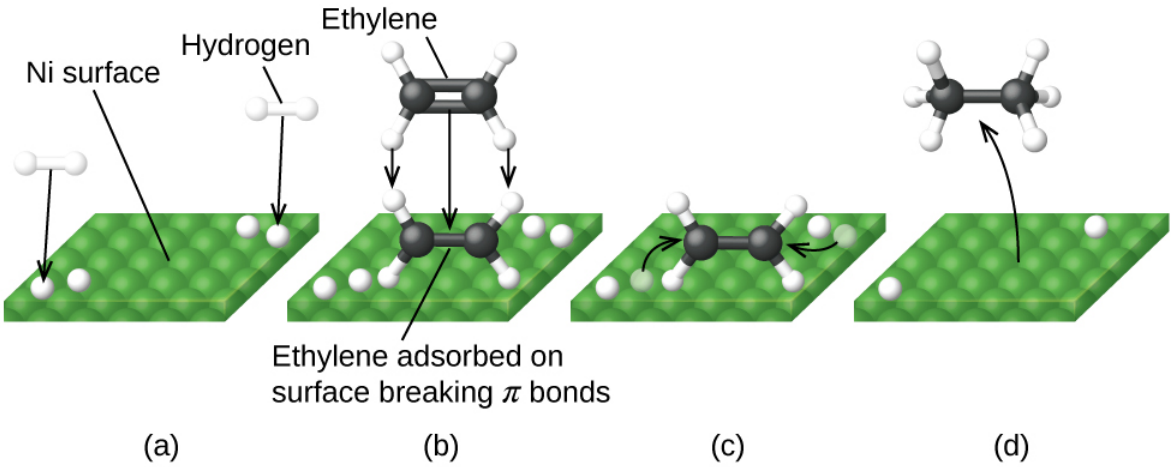


Figure 8.3.5Mechanism for the Ni-catalyzed reaction $C_2H_4 + H_2 \longrightarrow C_2H_6$. (a) Hydrogen is adsorbed on the surface, breaking the H–H bonds and forming Ni–H bonds. (b) Ethylene is adsorbed on the surface, breaking the C–C π-bond and forming Ni–C bonds. (c) Atoms diffuse across the surface and form new C–H bonds when they collide. (d) C_2H_6 molecules desorb from the Ni surface.

Many important chemical products are prepared via industrial processes that use heterogeneous catalysts, including ammonia, nitric acid, sulfuric acid, and methanol. Heterogeneous catalysts are also used in the catalytic converters found on most gasoline-powered automobiles (Figure 8.3.6).

8.3.0.1: Chemistry in Everyday Life

8.3.0.0.1: Automobile Catalytic Converters

Scientists developed catalytic converters to reduce the amount of toxic emissions produced by burning gasoline in internal combustion engines. By utilizing a carefully selected blend of catalytically active metals, it is possible to effect complete combustion of all carbon-containing compounds to carbon dioxide while also reducing the output of nitrogen oxides. This is particularly impressive when we consider that one step involves adding more oxygen to the molecule and the other involves removing the oxygen (Figure 8.3.6).

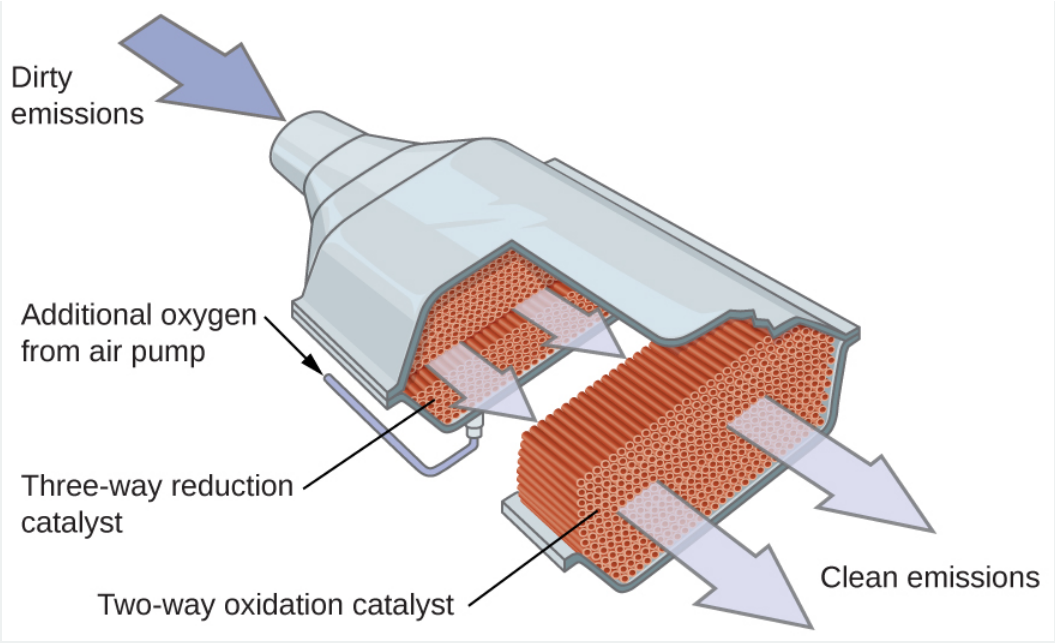


Figure 8.3.6A catalytic converter allows for the combustion of all carbon-containing compounds to carbon dioxide, while at the same time reducing the output of nitrogen oxide and other pollutants in emissions from gasoline-burning engines.

Most modern, three-way catalytic converters possess a surface impregnated with a platinum-rhodium catalyst, which catalyzes the conversion of nitric oxide into dinitrogen and oxygen as well as the conversion of carbon monoxide and hydrocarbons such as octane into carbon dioxide and water vapor:

$$2NO_2(g) \longrightarrow N_2(g) + 2O_2(g)$$
$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$$
$$2C_8H_{18}(g) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(g)$$

In order to be as efficient as possible, most catalytic converters are preheated by an electric heater. This ensures that the metals in the catalyst are fully active even before the automobile exhaust is hot enough to maintain appropriate reaction temperatures.

8.3.0.1: Link to Learning

The University of California at Davis' "ChemWiki" provides a thorough explanation of how catalytic converters work.

8.3.0.1: How Sciences Interconnect

8.3.0.0.2: Enzyme Structure and Function

The study of enzymes is an important interconnection between biology and chemistry. Enzymes are usually proteins (polypeptides) that help to control the rate of chemical reactions between biologically important compounds, particularly those that are involved in cellular metabolism. Different classes of enzymes perform a variety of functions, as shown in Table 12.3.

Classes of Enzymes and Their Functions

Class	Function
oxidoreductases	redox reactions
transferases	transfer of functional groups
hydrolases	hydrolysis reactions
lyases	group elimination to form double bonds
isomerases	isomerization
ligases	bond formation with ATP hydrolysis

Table 12.3

Enzyme molecules possess an active site, a part of the molecule with a shape that allows it to bond to a specific substrate (a reactant molecule), forming an enzyme-substrate complex as a reaction intermediate. There are two models that attempt to explain how this active site works. The most simplistic model is referred to as the lock-and-key hypothesis, which suggests that the molecular shapes of the active site and substrate are complementary, fitting together like a key in a lock. The induced fit hypothesis, on the other hand, suggests that the enzyme molecule is flexible and changes shape to accommodate a bond with the substrate. This is not to suggest that an enzyme's active site is completely malleable, however. Both the lock-and-key model and the induced fit model account for the fact that enzymes can only bind with specific substrates, since in general a particular enzyme only catalyzes a particular reaction (Figure 8.3.7).

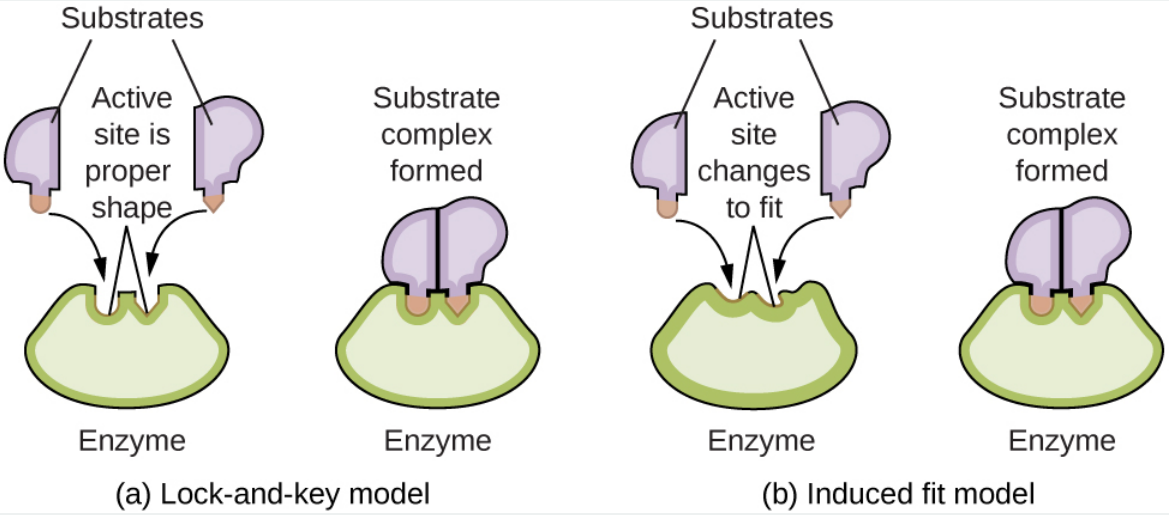


Figure 8.3.7(a) According to the lock-and-key model, the shape of an enzyme's active site is a perfect fit for the substrate. (b) According to the induced fit model, the active site is somewhat flexible, and can change shape in order to bond with the substrate.

8.3.0.1: Link to Learning

The Royal Society of Chemistry provides an excellent introduction to enzymes for students and teachers.

8.3.0.1: Footnotes

- 1"The Nobel Prize in Chemistry 1995," Nobel Prize.org, accessed February 18, 2015, http://www.nobelprize.org/nobel_priz...aureates/1995/.

This page titled 8.3: Catalysis 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.E: Kinetics - Homework

8.E.0.1: Chemical Reaction Rates

1. A study of the rate of dimerization of C_4H_6 gave the data shown in the table. Determine the average rate of dimerization between 0 s and 1600 s, and between 1600 s and 3200 s.

Time (s)	0	1600	3200	4800	6200
$[C_4H_6]$ (M)	1.00×10^{-2}	5.04×10^{-3}	3.37×10^{-3}	2.53×10^{-3}	2.08×10^{-3}

answer

$5.03x10^{-3}$ M/s
$2.08x10^{-3}$ M/s

8.E.0.1: Factors Affecting Reaction Rates

1. Describe the effect of each of the following on the rate of the reaction of magnesium metal with a solution of hydrochloric acid: the molarity of the hydrochloric acid, the temperature of the solution, and the size of the pieces of magnesium.

answer

HCl molarity - will increase reaction rate
Temperature - will increase reaction rate
Size of Mg - will reduce reaction rate

2. Go to the PhET Reactions & Rates interactive. Use the Single Collision tab to represent how the collision between monatomic oxygen (O) and carbon monoxide (CO) results in the breaking of one bond and the formation of another. Pull back on the red plunger to release the atom and observe the results. Then, click on “Reload Launcher” and change to “Angled shot” to see the difference.
   a. What happens when the angle of the collision is changed?
   b. Explain how this is relevant to rate of reaction.

answer

orientation is not correct for reaction to occur, slows down reaction rate

8.E.0.1: Collision Theory

1. Chemical reactions occur when reactants collide. What are two factors that may prevent a collision from producing a chemical reaction?

answer

collision energy and collision orientation

2. What is the activation energy of a reaction, and how is this energy related to the activated complex of the reaction?

answer

the energy required for the collision to create the activated complex so that a reaction can occur.

3. How does an increase in temperature affect rate of reaction? Explain this effect in terms of the collision theory of the reaction rate.

answer

increasing temperature increases the kinetic energy of the molecules so that there is more energy available in the collision.

4. Use the PhET Reactions & Rates interactive simulation to simulate a system. On the “Single collision” tab of the simulation applet, enable the “Energy view” by clicking the “+” icon. Select the first $A + BC \longrightarrow AB + C$ reaction (A is yellow, B is purple, and C is navy blue). Using the “straight shot” default option, try launching the A atom with varying amounts of energy.

What changes when the Total Energy line at launch is below the transition state of the Potential Energy line? Why? What happens when it is above the transition state? Why?

answer

there is not enough energy to overcome the activation energy barrier and no reaction occurs. Above the transition state, there is enough energy for the reaction to overcome the activation energy barrier.

8.E.0.1: Reaction Mechanisms

1. In general, can we predict the effect of doubling the concentration of *A* on the rate of the overall reaction $A+$? Can we predict the effect if the reaction is known to be an elementary reaction?

answer

I depends upon knowing the rate law, which can be determined experimentally or if it is known to be an elementary reaction. If this is an elementary reaction, doubling the concentration of A will double the reaction rate.

2. Write the rate law for each of the following elementary reactions:

a. $\mathrm{O_3} \overset{\text{sunlight}}{\longrightarrow} \mathrm{O_2 + O}$
b. $\mathrm{O_3 + Cl \longrightarrow O_2 + ClO}$
c. $\mathrm{ClO + O \longrightarrow Cl + O_2}$
d. $\mathrm{O_3 + NO \longrightarrow NO_2 + O_2}$
e. $\mathrm{NO_2 + O \longrightarrow NO + O_2}$

answer

answer here

8.E.0.1: Catalysis

1. Consider this scenario and answer the following questions: Chlorine atoms resulting from decomposition of chlorofluoromethanes, such as $\mathrm{CCl_2F_2}$, catalyze the decomposition of ozone in the atmosphere. One simplified mechanism for the decomposition is:

$$\begin{aligned} \mathrm{O_3} &\overset{\text{sunlight}}{\longrightarrow} \mathrm{O_2 + O} \\ \mathrm{O_3 + Cl} &\longrightarrow \mathrm{O_2 + ClO} \\ \mathrm{ClO + O} &\longrightarrow \mathrm{Cl + O_2} \end{aligned}$$

a. Explain why chlorine atoms are catalysts in the gas-phase transformation:

$$\mathrm{2O_3} \overset{\text{sunlight}}{\longrightarrow} \mathrm{3O_2} \tag{8.E.1}$$

answer

The chlorine atoms are used in the second step of the reaction but are reformed in the third step of the reaction, so the chlorine atoms are not consumed.

b. Nitric oxide is also involved in the decomposition of ozone by the mechanism:

$$\begin{aligned} \mathrm{O_3} &\overset{\text{sunlight}}{\longrightarrow} \mathrm{O_2 + O} \\ \mathrm{O_3 + NO} &\longrightarrow \mathrm{NO_2 + O_2} \\ \mathrm{NO_2 + O} &\longrightarrow \mathrm{NO + O_2} \end{aligned}$$

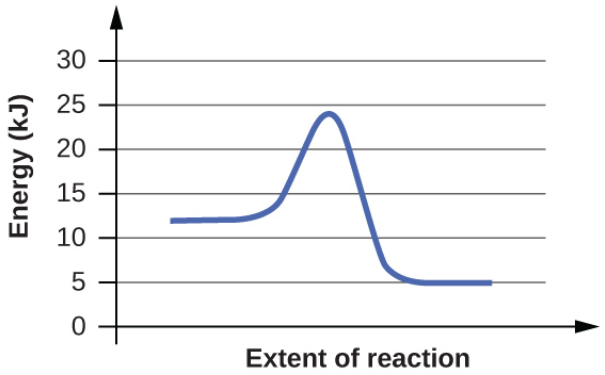
Is NO a catalyst for the decomposition? Explain your answer.

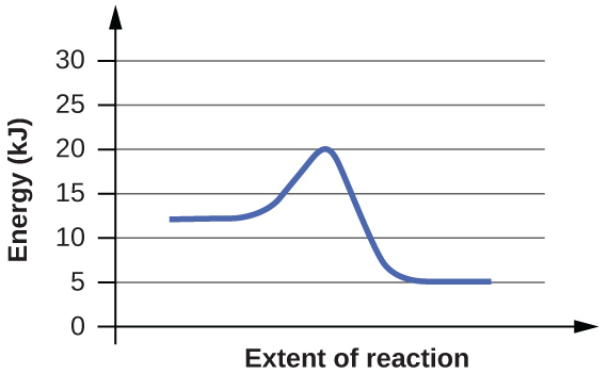
answer

Yes, the NO is required for the second step of the reaction mechanism. But is reformed in the third step.

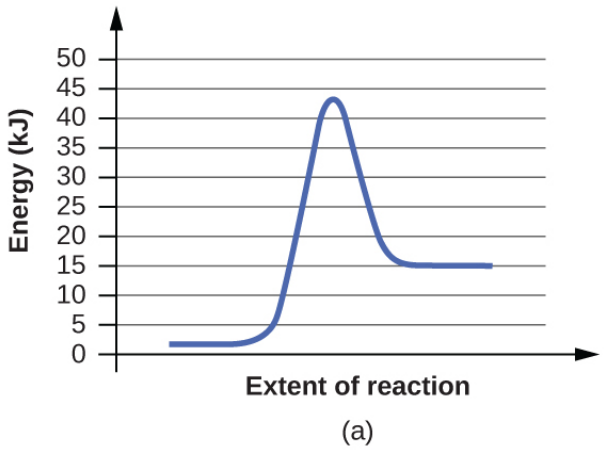
2. For each of the following pairs of reaction diagrams, identify which of the pair is catalyzed:

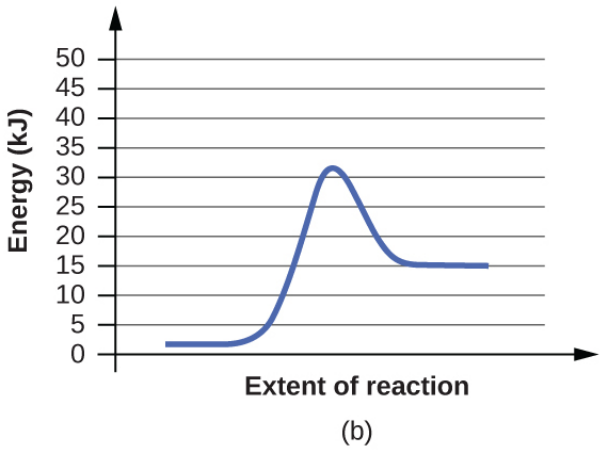
a.





b.



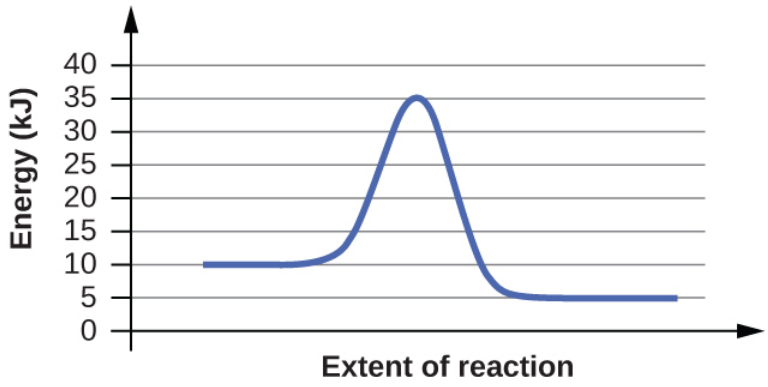


answer

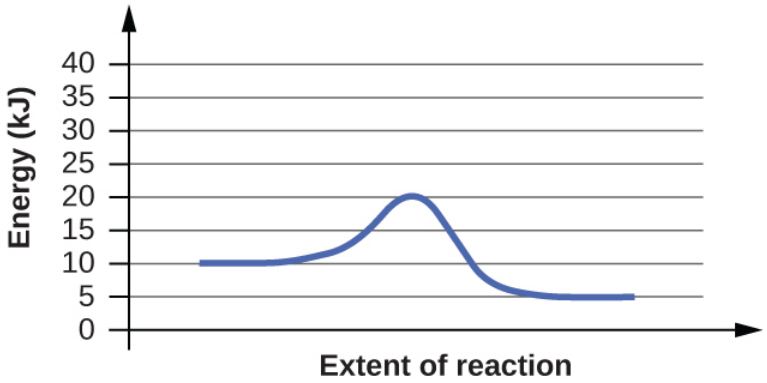
a) reaction b b) reaction b both have lower activation energies.

3. For each of the following reaction diagrams, estimate the activation energy (E_a) of the reaction:

a.



https://chem.libretexts.org/@go/page/431446



b.

answer

a) 25 kJ/mole b) 10 kJ/mole

This page titled 8.E: Kinetics - Homework 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

9: Fundamental Equilibrium Concepts

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

General Chemistry

In this chapter, you will learn how to predict the position of the balance and the yield of a product of a reaction under specific conditions, how to change a reaction's conditions to increase or reduce yield, and how to evaluate an equilibrium system's reaction to disturbances.

9.1: Chemical Equilibria

9.2: Equilibrium Constants

9.E: Fundamental Equlibrium Concepts - Homework

This page titled 9: Fundamental Equilibrium Concepts 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.

9.1: Chemical Equilibria

Learning Objectives

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

- Describe the nature of equilibrium systems
- Explain the dynamic nature of a chemical equilibrium

9.1.1: Introduction

Imagine a beach populated with sunbathers and swimmers. As those basking in the sun get too hot, they enter the surf to swim and cool off. As the swimmers tire, they return to the beach to rest. If the rate at which sunbathers enter the surf were to equal the rate at which swimmers return to the sand, then the numbers (though not the identities) of sunbathers and swimmers would remain constant. This scenario illustrates a dynamic phenomenon known as *equilibrium*, in which opposing processes occur at equal rates. Chemical and physical processes are subject to this phenomenon; these processes are at equilibrium when the forward and reverse reaction rates are equal. Equilibrium systems are pervasive in nature; the various reactions involving carbon dioxide dissolved in blood are examples (see Figure 13.1). This chapter provides a thorough introduction to the essential aspects of chemical equilibria. Figure 9.1.1 shows the equilibrium system responsible for the removal of carbon dioxide in respiration.

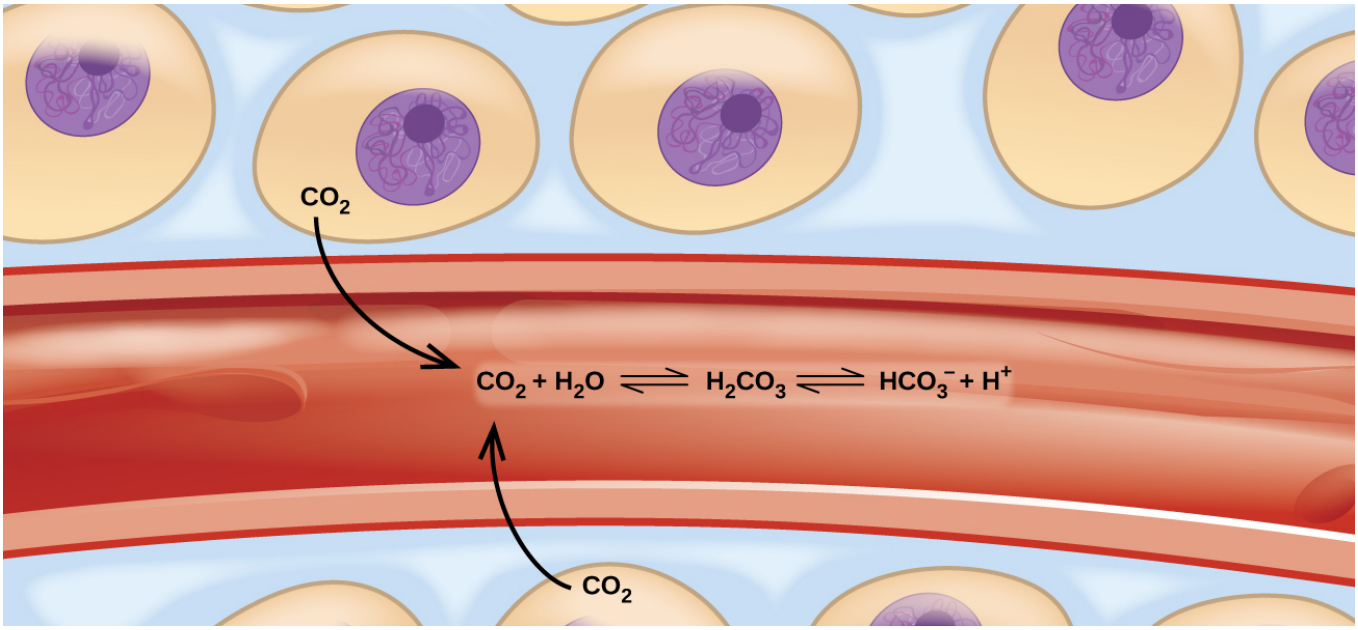


Figure 9.1.1: Transport of carbon dioxide in the body involves several reversible chemical reactions, including hydrolysis and acid ionization (among others).

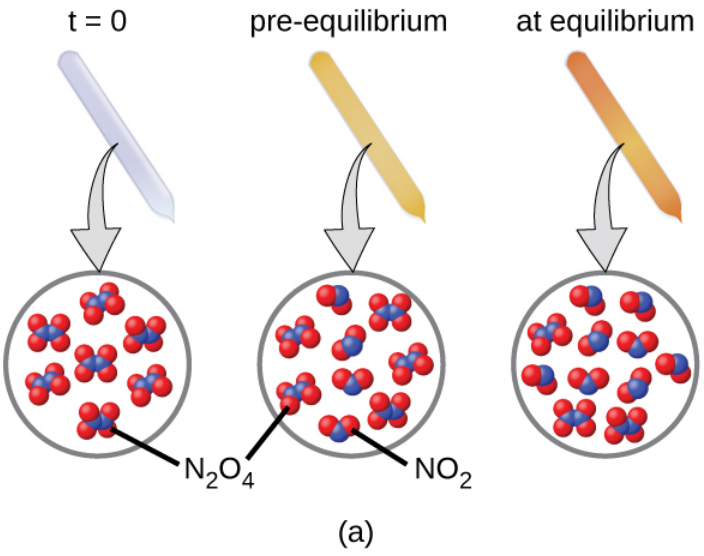
9.1.2: Equilibrium Concepts

The convention for writing chemical equations involves placing reactant formulas on the left side of a reaction arrow and product formulas on the right side. By this convention, and the definitions of “reactant” and “product,” a chemical equation represents the reaction in question as proceeding from left to right. Reversible reactions, however, may proceed in both forward (left to right) and reverse (right to left) directions. When the rates of the forward and reverse reactions are equal, the concentrations of the reactant and product species remain constant over time and the system is at equilibrium. The relative concentrations of reactants and products in equilibrium systems vary greatly; some systems contain mostly products at equilibrium, some contain mostly reactants, and some contain appreciable amounts of both.

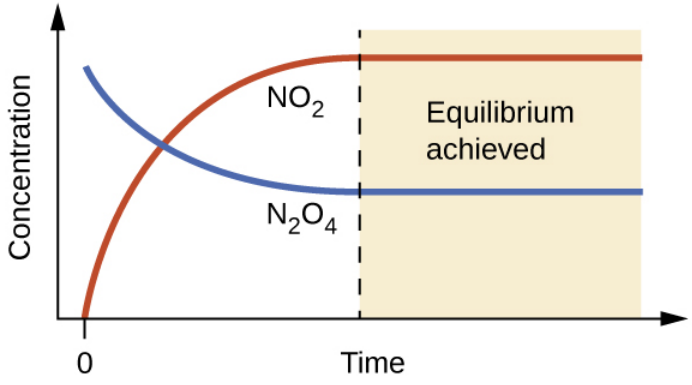
Figure 9.1.2 illustrates fundamental equilibrium concepts using the reversible decomposition of colorless dinitrogen tetroxide to yield brown nitrogen dioxide, an elementary reaction described by the equation:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

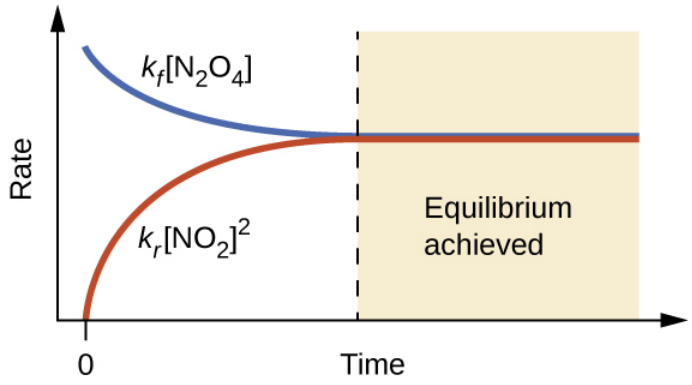
Note that a special double arrow is used to emphasize the reversible nature of the reaction.



(a)



(b)



(c)

Figure 9.1.2(a) A sealed tube containing colorless N_2O_4 darkens as it decomposes to yield brown NO_2. (b) Changes in concentration over time as the decomposition reaction achieves equilibrium. (c) At equilibrium, the forward and reverse reaction rates are equal.

For this reaction the rate for the forward and the reverse reactions are defined by the following equations:

$$\text{rate}_f = k_f[\mathrm{N_2O_4}]$$
$$\text{rate}_r = k_r[\mathrm{NO_2}]^2$$

As the reaction begins (t = 0), the concentration of the N_2O_4 reactant is finite and that of the NO_2 product is zero, so the forward reaction proceeds at a finite rate while the reverse reaction rate is zero. As time passes, N_2O_4 is consumed and its concentration falls, while NO_2 is produced and its concentration increases (Figure 9.1.2 **b**). The decreasing concentration of the reactant slows the forward reaction rate, and the increasing product concentration speeds the reverse reaction rate (Figure 9.1.2 **c**). This process continues until *the forward and reverse reaction rates become equal*, at which time the reaction has reached equilibrium, as characterized by constant concentrations of its reactants and products (shaded areas of Figure 9.1.2 **b** and Figure 9.1.2 **c**). It's important to emphasize that chemical equilibria are dynamic; a reaction at equilibrium has not "stopped," but is proceeding in the forward and reverse directions at the same rate. This dynamic nature is essential to understanding equilibrium behavior as discussed in this and subsequent chapters of the text.



Figure 13.3 A two-person juggling act illustrates the dynamic aspect of chemical equilibria. Each person is throwing and catching clubs at the same rate, and each holds a (approximately) constant number of clubs.

Physical changes, such as phase transitions, are also reversible and may establish equilibria. This concept was introduced in another chapter of this text through discussion of the vapor pressure of a condensed phase (liquid or solid). As one example, consider the vaporization of bromine:

$$\mathrm{Br_2}(l) \rightleftharpoons \mathrm{Br_2}(g)$$

When liquid bromine is added to an otherwise empty container and the container is sealed, the forward process depicted above (vaporization) will commence and continue at a roughly constant rate as long as the exposed surface area of the liquid and its temperature remain constant. As increasing amounts of gaseous bromine are produced, the rate of the reverse process (condensation) will increase until it equals the rate of vaporization and equilibrium is established. A photograph showing this phase transition equilibrium is provided in Figure 9.1.4.



Figure 9.1.4A sealed tube containing an equilibrium mixture of liquid and gaseous bromine. (credit: http://images-of-elements.com/bromine.php)

This page titled 9.1: Chemical Equilibria 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.

9.2: Equilibrium Constants

Learning Objectives

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

- Derive reaction quotients from chemical equations
- Calculate values of reaction quotients and equilibrium constants
- Relate the magnitude of an equilibrium constant to properties of the chemical system
- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Chatelier's principle

The status of a reversible reaction is conveniently assessed by evaluating its reaction quotient (Q). For a reversible reaction described by

$$mA + nB \rightleftharpoons xC + yD \tag{9.2.1}$$

the reaction quotient is derived directly from the stoichiometry of the balanced equation where the subscript c denotes the use of molar concentrations in the expression as

$$Q_c = \frac{[C]^x[D]^y}{[A]^m[B]^n} \tag{9.2.2}$$

9.2.0.1: Example

9.2.0.0.1: Writing Reaction Quotient Expressions

Write the concentration-based reaction quotient expression for each of the following reactions:

(a) $3O_2(g) \rightleftharpoons 2O_3(g)$

(b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(c) $4NH_3(g) + 7O_2(g) \rightleftharpoons 4NO_2(g) + 6H_2O(g)$

9.2.0.0.1: Solution

(a) $Q_c = \frac{[O_3]^2}{[O_2]^3}$

(b) $Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$

(c) $Q_c = \frac{[NO_2]^4[H_2O]^6}{[NH_3]^4[O_2]^7}$

9.2.0.0.1: Check Your Learning

Write the concentration-based reaction quotient expression for each of the following reactions:

(a) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

(b) $C_4H_8(g) \rightleftharpoons 2C_2H_4(g)$

(c) $2C_4H_{10}(g) + 13O_2(g) \rightleftharpoons 8CO_2(g) + 10H_2O(g)$

9.2.0.1: Answer:

(a) $Q_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$

(b) $Q_c = \frac{[C_2H_4]^2}{[C_4H_8]}$

(c) $Q_c = \frac{[CO_2]^8[H_2O]^{10}}{[C_4H_10]^2[O_2]^{13}}$

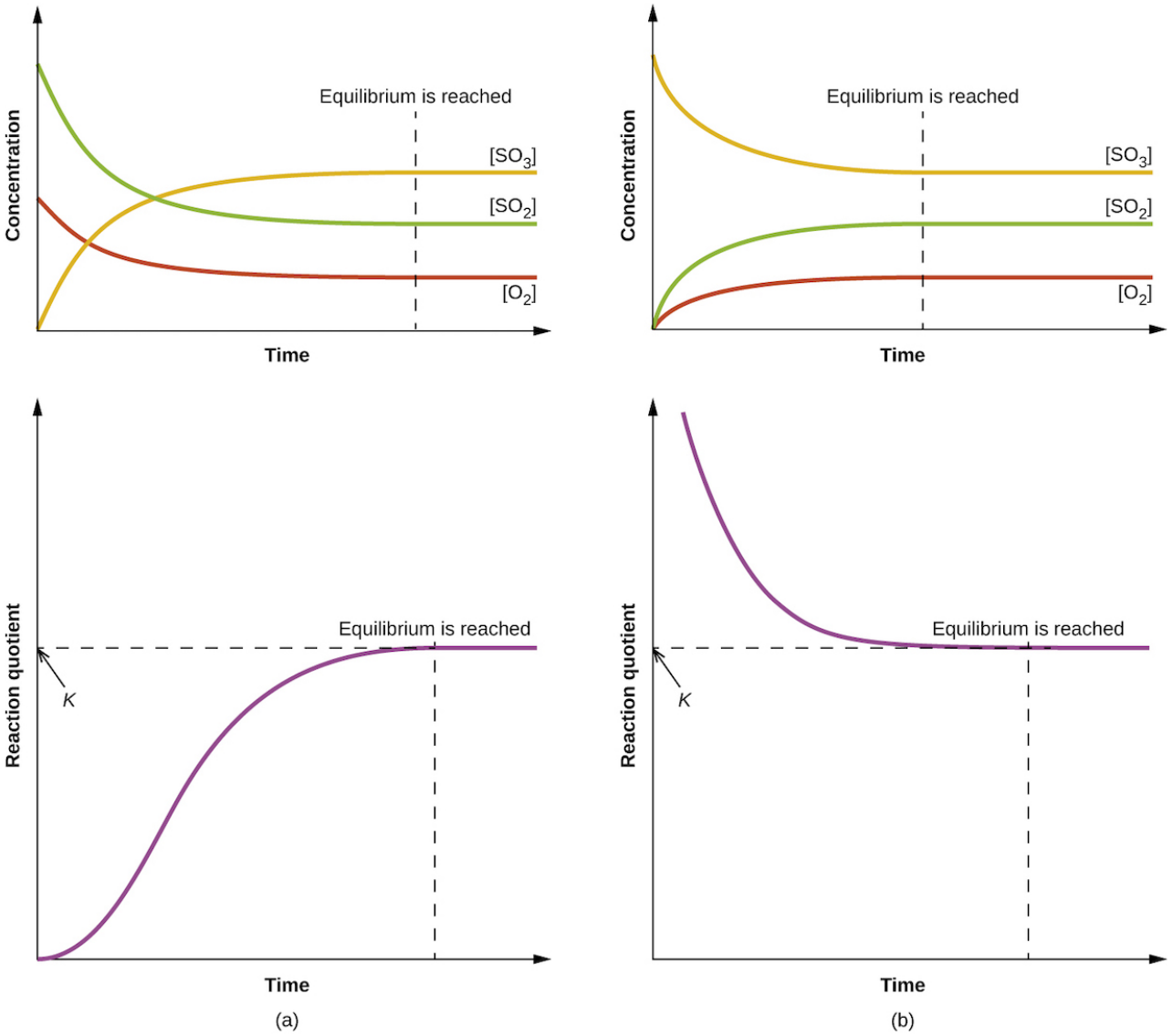


Figure 9.2.1 Changes in concentrations and Q_c for a chemical equilibrium achieved beginning with (a) a mixture of reactants only and (b) products only.

The numerical value of Q varies as a reaction proceeds towards equilibrium; therefore, it can serve as a useful indicator of the reaction's status. To illustrate this point, consider the oxidation of sulfur dioxide:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

Two different experimental scenarios are depicted in Figure 9.2.1, one in which this reaction is initiated with a mixture of reactants only, SO_2 and O_2, and another that begins with only product, SO_3. For the reaction that begins with a mixture of reactants only, Q is initially equal to zero:

$$Q_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{0^2}{[SO_2]^2[O_2]} = 0 \tag{9.2.3}$$

As the reaction proceeds toward equilibrium in the forward direction, reactant concentrations decrease (as does the denominator of Q_c), product concentration increases (as does the numerator of Q_c), and the reaction quotient consequently increases. When

equilibrium is achieved, the concentrations of reactants and product remain constant, as does the value of Q_c.

If the reaction begins with only product present, the value of Q_c is initially undefined (immeasurably large, or infinite):

$$Q_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{[SO_3]}{0} = \infty \tag{9.2.4}$$

In this case, the reaction proceeds toward equilibrium in the reverse direction. The product concentration and the numerator of Q_c decrease with time, the reactant concentrations and the denominator of Q_c increase, and the reaction quotient consequently decreases until it becomes constant at equilibrium.

The constant value of Q exhibited by a system at equilibrium is called the equilibrium constant, K:

$$K \equiv q\ at\ equlibrium \tag{9.2.5}$$

Comparison of the data plots in Figure 9.2.1 shows that both experimental scenarios resulted in the same value for the equilibrium constant. This is a general observation for all equilibrium systems, known as the law of mass action: At a given temperature, the reaction quotient for a system at equilibrium is constant.

9.2.0.1: Example

9.2.0.0.1: Evaluating a Reaction Quotient

Gaseous nitrogen dioxide forms dinitrogen tetroxide according to this equation:

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

When 0.10 mol NO_2 is added to a 1.0-L flask at 25 °C, the concentration changes so that at equilibrium, [NO_2] = 0.016 *M* and [N_2O_4] = 0.042 *M*.

(a) What is the value of the reaction quotient before any reaction occurs?

(b) What is the value of the reaction quotent when the system reacheconstant for the reaction?

9.2.0.0.1: Solution

As for all equilibrium calculations in this text, use the simplified equations for *Q* and *K* and disregard any concentration or pressure units, as noted previously in this section.

(a) Before any product is formed, $[NO_2] = \frac{0.10\ \text{mol}}{1.0\ \text{L}} = 0.10\ M$, and [$N_2O_4$] = 0 *M*. Thus,

$$Q_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{0}{0.10^2} =$$

(b) At equilibrium, $K_c = Q_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{0.042}{0.016^2} = 1.6 \times 10^2$. The reaction quotient is 1.6×10^2.

9.2.0.0.1: Check Your Learning

For the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, the concentrations at equilibrium are [SO_2] = 0.90 *M*, [O_2] = 0.35 *M*, and [SO_3] = 1.1 *M*. What is the value of the reaction quotient at equlibrium?

9.2.0.1: Answer:

Q_c = 4.3

By its definition, the reaction quotient at equilibrium is called the equilibrium constant. the magnitude of an equilibrium constant explicitly reflects the composition of a reaction mixture at equilibrium, and it may be interpreted with regard to the extent of the forward reaction. A reaction exhibiting a large equilibrium constant will reach equilibrium when most of the reactant has been

converted to product, whereas a small equilibrium constant indicates the reaction achieves equilibrium after very little reactant has been converted. It's important to keep in mind that the magnitude of the equilibrium constant does *not* indicate how rapidly or slowly equilibrium will be reached. Some equilibria are established so quickly as to be nearly instantaneous, and others so slowly that no perceptible change is observed over the course of days, years, or longer.

The equilibrium constant for a reaction can be used to predict the behavior of mixtures containing its reactants and/or products. As demonstrated by the sulfur dioxide oxidation process described above, a chemical reaction will proceed in whatever direction is necessary to achieve equilibrium. Comparing *Q* to the equilibrium constant for an equilibrium system of interest allows prediction of what reaction (forward or reverse), if any, will occur.

To further illustrate this important point, consider the reversible reaction shown below, K_c is the symbol for the equilibrium constant:

$$\mathrm{CO}(g)+\mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO_2}(g)+\mathrm{H_2}(g) \qquad K_c = 0.640 \qquad \mathrm{T} = 800\ ^\circ$$

The bar charts in Figure 9.2.2 represent changes in reactant and product concentrations for three different reaction mixtures. The reaction quotients for mixtures 1 and 3 are initially lesser than the reaction's equilibrium constant, so each of these mixtures will experience a net forward reaction to achieve equilibrium. The reaction quotient for mixture 2 is initially greater than the equilibrium constant, so this mixture will proceed in the reverse direction until equilibrium is established.

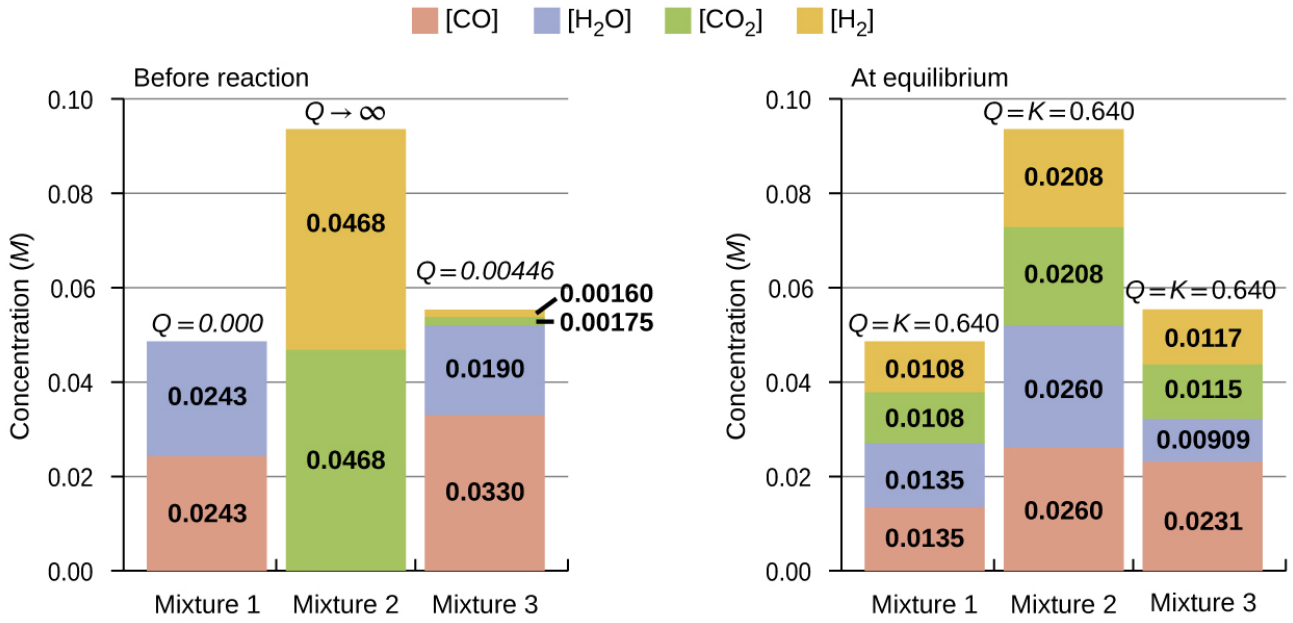


Figure 9.2.2Compositions of three mixtures before ($Q_c \neq K_c$) and after ($Q_c = K_c$) equilibrium is established for the reaction $\mathrm{CO}(g)+\mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO_2}(g)+\mathrm{H_2}(g)$.

9.2.0.1: Example

9.2.0.0.1: Predicting the Direction of Reaction

Given here are the starting concentrations of reactants and products for three experiments involving this reaction:

$$\mathrm{CO}(g)+\mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO_2}(g)+\mathrm{H_2}(g)$$

$$K_c = 0.64$$

Determine in which direction the reaction proceeds as it goes to equilibrium in each of the three experiments shown.

Reactants/Products	Experiment 1	Experiment 2	Experiment 3
$[\mathrm{CO}]_i$	0.020 *M*	0.011 *M*	0.0094 *M*

Reactants/Products	Experiment 1	Experiment 2	Experiment 3
$[H_2O]_i$	0.020 *M*	0.0011 *M*	0.0025 *M*
$[CO_2]_i$	0.0040 *M*	0.037 *M*	0.0015 *M*
$[H_2]_i$	0.0040 *M*	0.046 *M*	0.0076 *M*

9.2.0.0.1: Solution

Experiment 1:

$$Q_c = \frac{[CO_2]\ [H_2]}{[CO]\ [H_2O]} = \frac{(0.0040)\,(0.0040)}{(0.020)\,(0.020)} = 0.040.$$

$Q_c < K_c$ (0.040 < 0.64)

The reaction will proceed in the forward direction.

Experiment 2:

$$Q_c = \frac{[CO_2]\ [H_2]}{[CO]\ [H_2O]} = \frac{(0.037)\,(0.046)}{(0.011)\,(0.0011)} = 1.4 \times 10^2$$

$Q_c > K_c$ (140 > 0.64)

The reaction will proceed in the reverse direction.

Experiment 3:

$$Q_c = \frac{[CO_2]\ [H_2]}{[CO]\ [H_2O]} = \frac{(0.0015)\,(0.0076)}{(0.0094)\,(0.0025)} = 0.48$$

$Q_c < K_c$ (0.48 < 0.64)

The reaction will proceed in the forward direction.

9.2.0.0.1: Check Your Learning

Calculate the reaction quotient and determine the direction in which each of the following reactions will proceed to reach equilibrium.

(a) A 1.00-L flask containing 0.0500 mol of NO(g), 0.0155 mol of Cl_2(g), and 0.500 mol of NOCl:

$$2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g) \qquad K_c = 4.6 \times 10^4$$

(b) A 5.0-L flask containing 17 g of NH_3, 14 g of N_2, and 12 g of H_2:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad K_c = 0.060$$

(c) A 2.00-L flask containing 230 g of SO_3(g):

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g) \qquad K_c = 0.230$$

9.2.0.1: Answer:

(a) Q_c = 6.45 × 10^3, forward. (b) Q_c = 0.23, reverse. (c) Q_c = 0, forward.

9.2.1: Predicting the Direction of a Reversible Reaction

As we saw in the previous section, reactions proceed in both directions (reactants go to products and products go to reactants). We can tell a reaction is at equilibrium if the reaction quotient (Q) is equal to the equilibrium constant (K). We next address what happens when a system at equilibrium is disturbed so that Q is no longer equal to K. If a system at equilibrium is subjected to a perturbance or stress (such as a change in concentration) the position of equilibrium changes. Since this stress affects the concentrations of the reactants and the products, the value of Q will no longer equal the value of K. To re-establish equilibrium, the system will either shift toward the products (if $Q < K$) or the reactants (if $Q > K$) until Q returns to the same value as K.

This process is described by Le Chatelier's principle: When a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance. As described in the previous paragraph, the disturbance causes a change in Q; the reaction will shift to re-establish $Q = K$.

Le Chatelier's principle can be used to predict changes in equilibrium concentrations when a system that is at equilibrium is subjected to a stress. However, if we have a mixture of reactants and products that have not yet reached equilibrium, the changes necessary to reach equilibrium may not be so obvious. In such a case, we can compare the values of *Q* and *K* for the system to predict the changes.

> A chemical system at equilibrium can be **temporarily** shifted out of equilibrium by adding or removing one or more of the reactants or products. The concentrations of both reactants and products then undergo additional changes to return the system to equilibrium.

The stress on the system in Figure $9.2.3$ is the reduction of the equilibrium concentration of SCN^- (lowering the concentration of one of the reactants would cause *Q* to be larger than *K*). As a consequence, Le Chatelier's principle leads us to predict that the concentration of $Fe(SCN)^{2+}$ should decrease, increasing the concentration of SCN^- part way back to its original concentration, and increasing the concentration of Fe^{3+} above its initial equilibrium concentration.



Figure 9.2.1: (a) The test tube contains 0.1 M Fe^{3+}. (b) Thiocyanate ion has been added to solution in (a), forming the red $Fe(SCN)^{2+}$ ion. $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$. *(c) Silver nitrate has been added to the solution in (b), precipitating some of the SCN− as the white solid AgSCN.* $Ag^+(aq) + SCN^-(aq) \rightleftharpoons AgSCN(s)$ *The decrease in the SCN− concentration shifts the first equilibrium in the solution to the left, decreasing the concentration (and lightening color) of the* $Fe(SCN)^{2+}$. *(credit: modification of work by Mark Ott).*

The effect of a change in concentration on a system at equilibrium is illustrated further by the equilibrium of this chemical reaction:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2\,HI_{(g)} \tag{9.2.6}$$

$$K_c = 50.0 \text{ at } 400^\circ C \tag{9.2.7}$$

The numeric values for this example have been determined experimentally. A mixture of gases at 400 °C with $[H_2] = [I_2] = 0.221\ M$ and $[HI] = 1.563\ M$ is at equilibrium; for this mixture, $Q_c = K_c = 50.0$. If H_2 is introduced into the system so quickly that its concentration doubles before it begins to react (new $[H_2] = 0.442\ M$), the reaction will shift so that a new equilibrium is reached, at which

- $[H_2] = 0.374\ M$,
- $[I_2] = 0.153\ M$, and
- $[HI] = 1.692\ M$.

This gives:

$$Q_c = \frac{[\mathrm{HI}]^2}{[\mathrm{H_2}][\mathrm{I_2}]} = \frac{(1.692)^2}{(0.374)(0.153)} = 50.0 = K_c \tag{9.2.8}$$

We have stressed this system by introducing additional $\mathrm{H_2}$. The stress is relieved when the reaction shifts to the right, using up some (but not all) of the excess $\mathrm{H_2}$, reducing the amount of uncombined $\mathrm{I_2}$, and forming additional HI.

9.2.2: Effect of Change in Pressure on Equilibrium

Sometimes we can change the position of equilibrium by changing the pressure of a system. However, changes in pressure have a measurable effect only in systems in which gases are involved, and then only when the chemical reaction produces a change in the total number of gas molecules in the system. An easy way to recognize such a system is to look for different numbers of moles of gas on the reactant and product sides of the equilibrium. While evaluating pressure (as well as related factors like volume), it is important to remember that equilibrium constants are defined with regard to concentration (for K_c) or partial pressure (for K_P). Some changes to total pressure, like adding an inert gas that is not part of the equilibrium, will change the total pressure but not the partial pressures of the gases in the equilibrium constant expression. Thus, addition of a gas not involved in the equilibrium will not perturb the equilibrium.

As we increase the pressure of a gaseous system at equilibrium, either by decreasing the volume of the system or by adding more of one of the components of the equilibrium mixture, we introduce a stress by increasing the partial pressures of one or more of the components. In accordance with Le Chatelier's principle, a shift in the equilibrium that reduces the total number of molecules per unit of volume will be favored because this relieves the stress. The reverse reaction would be favored by a decrease in pressure.

Consider what happens when we increase the pressure on a system in which NO, $\mathrm{O_2}$, and $\mathrm{NO_2}$ are at equilibrium:

$$2\,\mathrm{NO(g)} + \mathrm{O_2(g)} \rightleftharpoons 2\,\mathrm{NO_2(g)} \tag{9.2.9}$$

The formation of additional amounts of $\mathrm{NO_2}$ decreases the total number of molecules in the system because each time two molecules of $\mathrm{NO_2}$ form, a total of three molecules of NO and $\mathrm{O_2}$ are consumed. This reduces the total pressure exerted by the system and reduces, but does not completely relieve, the stress of the increased pressure. On the other hand, a decrease in the pressure on the system favors decomposition of $\mathrm{NO_2}$ into NO and $\mathrm{O_2}$, which tends to restore the pressure.

Now consider this reaction:

$$\mathrm{N_2(g)} + \mathrm{O_2(g)} \rightleftharpoons 2\,\mathrm{NO(g)} \tag{9.2.10}$$

Because there is no change in the total number of molecules in the system during reaction, a change in pressure does not favor either formation or decomposition of gaseous nitrogen monoxide.

9.2.3: Effect of Change in Temperature on Equilibrium

Changing concentration or pressure perturbs an equilibrium because the reaction quotient is shifted away from the equilibrium value. Changing the temperature of a system at equilibrium has a different effect: A change in temperature actually changes the value of the equilibrium constant. However, we can qualitatively predict the effect of the temperature change by treating it as a stress on the system and applying Le Chatelier's principle.

When hydrogen reacts with gaseous iodine, heat is evolved.

$$\mathrm{H_2(g)} + \mathrm{I_2(g)} \rightleftharpoons 2\,\mathrm{HI(g)} \quad \Delta H = -9.4\ \mathrm{kJ\ (exothermic)} \tag{9.2.11}$$

Because this reaction is exothermic, we can write it with heat as a product.

$$\mathrm{H_2(g)} + \mathrm{I_2(g)} \rightleftharpoons 2\,\mathrm{HI(g)} + \mathrm{heat} \tag{9.2.12}$$

Increasing the temperature of the reaction increases the internal energy of the system. Thus, increasing the temperature has the effect of increasing the amount of one of the products of this reaction. The reaction shifts to the left to relieve the stress, and there is an increase in the concentration of $\mathrm{H_2}$ and $\mathrm{I_2}$ and a reduction in the concentration of HI. Lowering the temperature of this system reduces the amount of energy present, favors the production of heat, and favors the formation of hydrogen iodide.

When we change the temperature of a system at equilibrium, the equilibrium constant for the reaction changes. Lowering the temperature in the HI system increases the equilibrium constant: At the new equilibrium the concentration of HI has increased and the concentrations of $\mathrm{H_2}$ and $\mathrm{I_2}$ decreased. Raising the temperature decreases the value of the equilibrium constant, from 67.5 at 357 °C to 50.0 at 400 °C.

Temperature affects the equilibrium between NO_2 and N_2O_4 in this reaction

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \quad \Delta H = 57.20 \text{ kJ} \tag{9.2.13}$$

The positive ΔH value tells us that the reaction is endothermic and could be written

$$\text{heat} + N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \tag{9.2.14}$$

At higher temperatures, the gas mixture has a deep brown color, indicative of a significant amount of brown NO_2 molecules. If, however, we put a stress on the system by cooling the mixture (withdrawing energy), the equilibrium shifts to the left to supply some of the energy lost by cooling. The concentration of colorless N_2O_4 increases, and the concentration of brown NO_2 decreases, causing the brown color to fade.

9.2.4: Catalysts Do Not Affect Equilibrium

As we learned during our study of kinetics, a catalyst can speed up the rate of a reaction. Though this increase in reaction rate may cause a system to reach equilibrium more quickly (by speeding up the forward and reverse reactions), a catalyst has no effect on the value of an equilibrium constant nor on equilibrium concentrations.

The interplay of changes in concentration or pressure, temperature, and the lack of an influence of a catalyst on a chemical equilibrium is illustrated in the industrial synthesis of ammonia from nitrogen and hydrogen according to the equation

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \tag{9.2.15}$$

A large quantity of ammonia is manufactured by this reaction. Each year, ammonia is among the top 10 chemicals, by mass, manufactured in the world. About 2 billion pounds are manufactured in the United States each year. Ammonia plays a vital role in our global economy. It is used in the production of fertilizers and is, itself, an important fertilizer for the growth of corn, cotton, and other crops. Large quantities of ammonia are converted to nitric acid, which plays an important role in the production of fertilizers, explosives, plastics, dyes, and fibers, and is also used in the steel industry.

Fritz Haber

Haber was born in Breslau, Prussia (presently Wroclaw, Poland) in December 1868. He went on to study chemistry and, while at the University of Karlsruhe, he developed what would later be known as the Haber process: the catalytic formation of ammonia from hydrogen and atmospheric nitrogen under high temperatures and pressures.



The work of Nobel Prize recipient Fritz Haber revolutionized agricultural practices in the early 20th century. His work also affected wartime strategies, adding chemical weapons to the artillery.

For this work, Haber was awarded the 1918 Nobel Prize in Chemistry for synthesis of ammonia from its elements. The Haber process was a boon to agriculture, as it allowed the production of fertilizers to no longer be dependent on mined feed stocks such as sodium nitrate.

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

Currently, the annual production of synthetic nitrogen fertilizers exceeds 100 million tons and synthetic fertilizer production has increased the number of humans that arable land can support from 1.9 persons per hectare in 1908 to 4.3 in 2008. The availability of nitrogen is a strong limiting factor to the growth of plants. Despite accounting for 78% of air, diatomic nitrogen (N_2) is nutritionally unavailable due the tremendous stability of the nitrogen-nitrogen triple bond. For plants to use atmospheric nitrogen, the nitrogen must be converted to a more bioavailable form (this conversion is called nitrogen fixation).

In addition to his work in ammonia production, Haber is also remembered by history as one of the fathers of chemical warfare. During World War I, he played a major role in the development of poisonous gases used for trench warfare. Regarding his role in these developments, Haber said, “During peace time a scientist belongs to the World, but during war time he belongs to his country.”[1] Haber defended the use of gas warfare against accusations that it was inhumane, saying that death was death, by whatever means it was inflicted. He stands as an example of the ethical dilemmas that face scientists in times of war and the double-edged nature of the sword of science.

Like Haber, the products made from ammonia can be multifaceted. In addition to their value for agriculture, nitrogen compounds can also be used to achieve destructive ends. Ammonium nitrate has also been used in explosives, including improvised explosive devices. Ammonium nitrate was one of the components of the bomb used in the attack on the Alfred P. Murrah Federal Building in downtown Oklahoma City on April 19, 1995.

9.2.5: Summary

Systems at equilibrium can be disturbed by changes to temperature, concentration, and, in some cases, volume and pressure; volume and pressure changes will disturb equilibrium if the number of moles of gas is different on the reactant and product sides of the reaction. The system's response to these disturbances is described by Le Chatelier's principle: The system will respond in a way that counteracts the disturbance. Not all changes to the system result in a disturbance of the equilibrium. Adding a catalyst affects the rates of the reactions but does not alter the equilibrium, and changing pressure or volume will not significantly disturb systems with no gases or with equal numbers of moles of gas on the reactant and product side.

Table 9.2.1: Effects of Disturbances of Equilibrium and K

Disturbance	Observed Change as Equilibrium is Restored	Direction of Shift	Effect on K
reactant added	added reactant is partially consumed	toward products	none
product added	added product is partially consumed	toward reactants	none
decrease in volume/increase in gas pressure	pressure decreases	toward side with fewer moles of gas	none
increase in volume/decrease in gas pressure	pressure increases	toward side with more moles of gas	none
temperature increase	heat is absorbed	toward products for endothermic, toward reactants for exothermic	changes
temperature decrease	heat is given off	toward reactants for endothermic, toward products for exothermic	changes

Footnotes

1. Herrlich, P. “The Responsibility of the Scientist: What Can History Teach Us About How Scientists Should Handle Research That Has the Potential to Create Harm?” *EMBO Reports* 14 (2013): 759–764.

9.2.6: Glossary

equilibrium

state of a reversible reaction in which the forward and reverse processes occur at equal rates

equilibrium constant (*K*)

value of the reaction quotient for a system at equilibrium; may be expressed using concentrations (K_c) or partial pressures (K_p)

heterogeneous equilibria
equilibria in which reactants and products occupy two or more different phases

homogeneous equilibria
equilibria in which all reactants and products occupy the same phase

law of mass action
when a reversible reaction has attained equilibrium at a given temperature, the reaction quotient remains constant

Le Châtelier's principle
an equilibrium subjected to stress will shift in a way to counter the stress and re-establish equilibrium

reaction quotient (*Q*)
mathematical function describing the relative amounts of reactants and products in a reaction mixture; may be expressed in terms of concentrations (Q_c) or pressures (Q_p)

reversible reaction
chemical reaction that can proceed in both the forward and reverse directions under given conditions

---

This page titled 9.2: Equilibrium Constants 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.

- **13.4: Shifting Equilibria - Le Chatelier's Principle** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

9.E: Fundamental Equlibrium Concepts - Homework

9.E.0.1: Chemical Equilibria

1. Is a system at equilibrium if the rate constants of the forward and reverse reactions are equal?

Answer

yes

2. If the concentrations of products and reactants are equal, is the system at equilibrium?

Answer

no

9.E.0.1: Equilibrium Constants

1. Explain why there may be an infinite number of values for the reaction quotient of a reaction at a given temperature but there can be only one value for the equilibrium constant at that temperature.

Answer

the reaction quotient depends upon the concentration of the products and reactants, which can have an infinate number of values. The equilibrium constant is a constant - so it only has one value

2. Explain why an equilibrium between $Br_2(l)$ and $Br_2(g)$ would not be established if the container were not a closed vessel shown in Figure 7.1.4.

Answer

in an open vessel the bromine gas can escape and is not able to condense back into a liquid - so the system can not go in both directions

3. If you observe the following reaction at equilibrium, is it possible to tell whether the reaction started with pure NO_2 or with pure N_2O_4? $2NO_2 \rightleftharpoons N_2O_4$

Answer

no

4. Write the mathematical expression for the reaction quotient, Q_c, for the following reaction:
$CH_4(g) + Cl_2(g) \rightleftharpoons CH_3Cl(g) + HCl(g)$

Answer

$$Q = \frac{[CH_3Cl][HCl]}{[CH_4][Cl_2]} \tag{9.E.1}$$

5. Determine if the following system is at equilibrium. If not, in which direction will the system need to shift to reach equilibrium?
$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$; $[SO_2Cl_2] = 0.12\ M$, $[Cl_2] = 0.16\ M$ and $[SO_2] = 0.050\ M$. K_c for the reaction is 0.078.

Answer

Q=0.66, Q is less than K so the reaction will go forward, increasing the concentration of products and reducing the concentration of reactants.

9.E.0.1: Shifting Equilibria: Le Châtelier's Principle

1. Methanol can be prepared from carbon monoxide and hydrogen at high temperature and pressure in the presence of a suitable catalyst.

$$H_2(g) + CO(g) \rightleftharpoons CH_3OH(g) \tag{9.E.2}$$

a. (a) Write the expression for the equilibrium constant (K) for the reversible reaction

Answer

$$Q = \frac{[CH_3OH]}{[H_2][CO]} \tag{9.E.3}$$

b. (b) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more H_2 is added?

Answer

H_2 and CO will decrease, CH_3OH will increase

c. (c) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CO is removed?

Answer

H_2 and CO will increase, CH_3OH will decrease

d. (d) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CH_3OH is added?

Answer

H_2 and CO will increase, CH_3OH will decrease

e. (e) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if the temperature of the system is increased (Δ H = -90.2 kJ)?

Answer

H_2 and CO will increase, CH_3OH will decrease

f. (f) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more catalyst is added?

Answer

no change

2. Water gas, a mixture of H_2 and CO, is an important industrial fuel produced by the reaction of steam with red hot coke, essentially pure carbon.

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \tag{9.E.4}$$

a. (a) Write the expression for the equilibrium constant for the reversible reaction

Answer

$$Q = \frac{[CO][H_2]}{[H_2O]} \tag{9.E.5}$$

b. (b) What will happen to the concentration of each reactant and product at equilibrium if more C is added?

Answer

no change, since C is a solid and is not in the equlibrium constant expression

c. (c) What will happen to the concentration of each reactant and product at equilibrium if H_2O is removed?

Answer

amount of C will increase, concentration of H_2O will increase, CO and H_2 will decrease

d. (d) What will happen to the concentration of each reactant and product at equilibrium if CO is added?

Answer

amount of C will increase, concentration of H_2O will increase, CO and H_2 will decrease

e. (e) What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased? $\Delta H = 131.30$ kJ

Answer

amount of C will decrease, concentration of H_2O will decrease, CO and H_2 will increase

---

This page titled 9.E: Fundamental Equlibrium Concepts - Homework 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

10: Acid-Base Equilibria

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

General Chemistry

This chapter will illustrate the chemistry of acid-base reactions and equilibria, and provide you with tools for quantifying the concentrations of acids and bases in solutions.

10.1: Introduction to Brønsted-Lowry Acids and Bases
10.2: pH, pOH, and Relative Strengths of Acids and Bases
10.3: Hydrolysis of Salt Solutions
10.4: Buffers
10.E: Acid-Base Equilibria - Homework

This page titled 10: Acid-Base Equilibria 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.

10.1: Introduction to Brønsted-Lowry Acids and Bases



Figure 10.1.1Sinkholes such as this are the result of reactions between acidic groundwaters and basic rock formations, like limestone. (credit: modification of work by Emil Kehnel)

Introduction

Liquid water is essential to life on our planet, and chemistry involving the characteristic ions of water, H^+ and OH^-, is widely encountered in nature and society. As introduced in another chapter of this text, acid-base chemistry involves the transfer of hydrogen ions from donors (acids) to acceptors (bases). These H^+ transfer reactions are reversible, and the equilibria established by acid-base systems are essential aspects of phenomena ranging from sinkhole formation (Figure 10.1.1) to oxygen transport in the human body. This chapter will further explore acid-base chemistry with an emphasis on the equilibrium aspects of this important reaction class.

Introduction to Equilibrium Reactions

Acid base reactions can go in both the forward and the reverse directions. The rate that the reaction goes in either direction depends upon the activation energy - discussed in the chapter on kinteics. For some acid base reactions the forward reaction is much faster, so the reaction ends up with more product. For other acid base reactions the reverse reaction is much faster so the reaction produces little product. Because acid/base reactions are very fast this equlibrium between forward and reverse reactions is reached quickly. For a reaction where:

$$\text{reactant} \rightleftharpoons \text{product}$$

The ratio of concentrations of the reactants and products is a constant at equilibrium. This equilibrium constant takes the form of this equation:

$$K = \frac{[\text{Products}]}{[\text{Reactant}]} \tag{10.1.1}$$

If K is large, the reaction favors the product, and if K is small the reaction favors the reactant.

Brønsted-Lowry acids and Bases

Learning Objectives

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

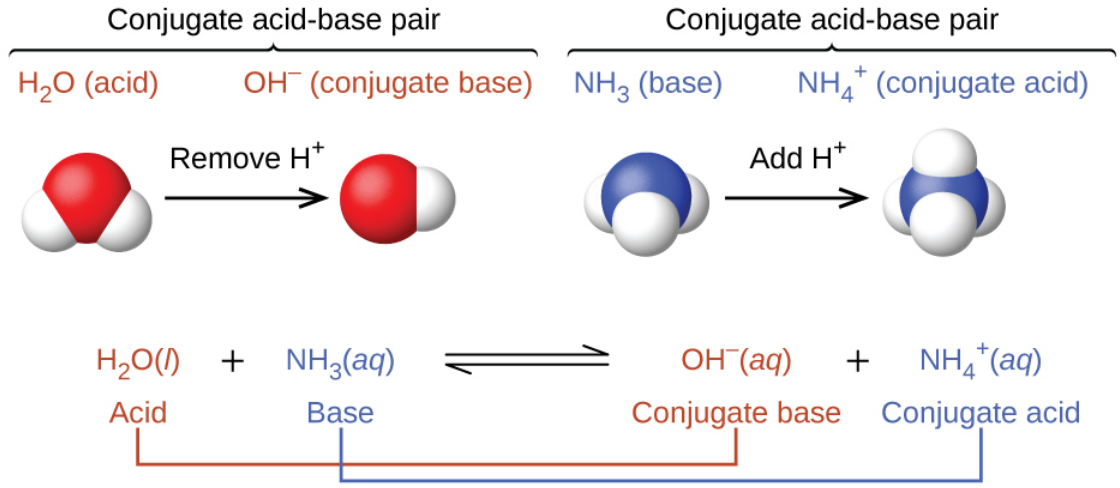
- Identify acids, bases, and conjugate acid-base pairs according to the Brønsted-Lowry definition
- Write equations for acid and base ionization reactions
- Use the ion-product constant for water to calculate hydronium and hydroxide ion concentrations

- Describe the acid-base behavior of amphiprotic substances

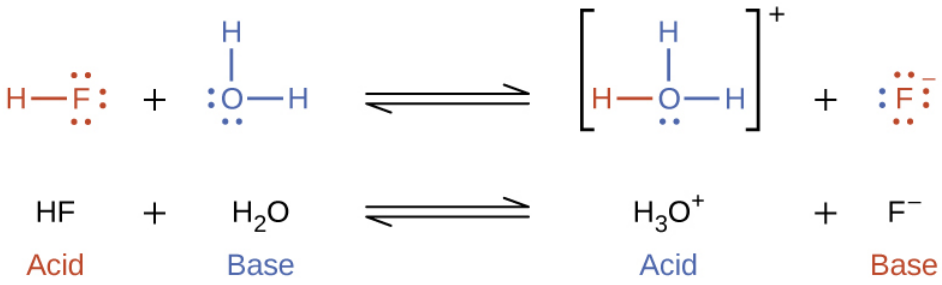
The acid-base reaction class has been studied for quite some time. In 1680, Robert Boyle reported traits of acid solutions that included their ability to dissolve many substances, to change the colors of certain natural dyes, and to lose these traits after coming in contact with alkali (base) solutions. In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be CO_2), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. The significance of hydrogen was reemphasized in 1884 when Svante Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions) and a base as a compound that dissolves in water to yield hydroxide anions.

Johannes Brønsted and Thomas Lowry proposed a more general description in 1923 in which acids and bases were defined in terms of the transfer of hydrogen ions, H^+. (Note that these hydrogen ions are often referred to simply as *protons*, since that subatomic particle is the only component of cations derived from the most abundant hydrogen isotope, ^1H.) A compound that donates a proton to another compound is called a Brønsted-Lowry acid, and a compound that accepts a proton is called a Brønsted-Lowry base. An acid-base reaction is, thus, the transfer of a proton from a donor (acid) to an acceptor (base).

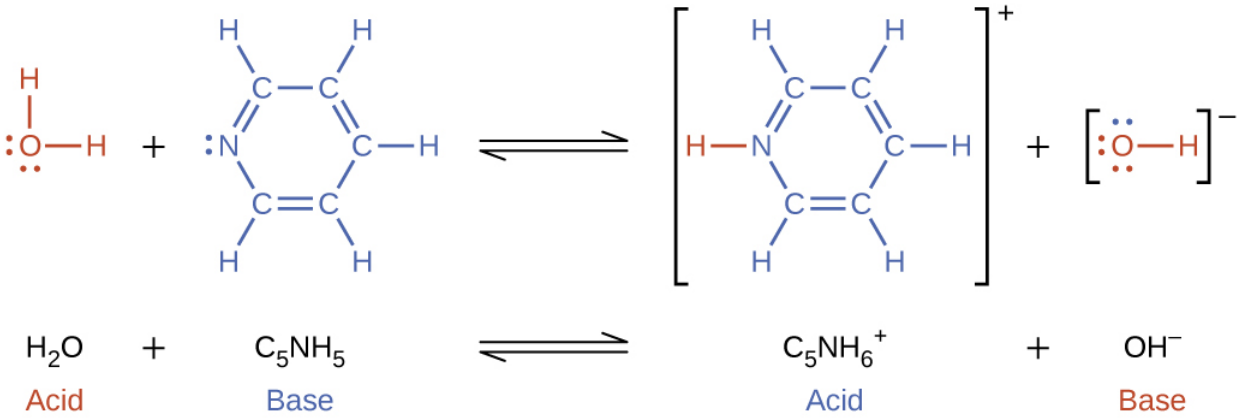
The concept of *conjugate pairs* is useful in describing Brønsted-Lowry acid-base reactions (and other reversible reactions, as well). When an acid donates H^+, the species that remains is called the **conjugate base** of the acid because it reacts as a proton acceptor in the reverse reaction. Likewise, when a base accepts H^+, it is converted to its **conjugate acid**. The reaction between water and ammonia illustrates this idea. In the forward direction, water acts as an acid by donating a proton to ammonia and subsequently becoming a hydroxide ion, OH^-, the conjugate base of water. The ammonia acts as a base in accepting this proton, becoming an ammonium ion, NH_4^+, the conjugate acid of ammonia. In the reverse direction, a hydroxide ion acts as a base in accepting a proton from ammonium ion, which acts as an acid.



The reaction between a Brønsted-Lowry acid and water is called acid ionization. For example, when hydrogen fluoride dissolves in water and ionizes, protons are transferred from hydrogen fluoride molecules to water molecules, yielding hydronium ions, H_3O^+, and fluoride ions:

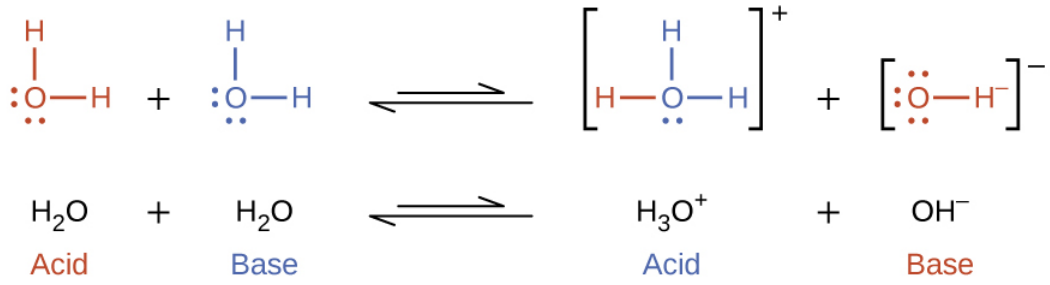


Base ionization of a species occurs when it accepts protons from water molecules. In the example below, pyridine molecules, C_5NH_5, undergo base ionization when dissolved in water, yielding hydroxide and pyridinium ions:



The preceding ionization reactions suggest that water may function as both a base (as in its reaction with hydrogen fluoride) and an acid (as in its reaction with ammonia or pyridine). Species capable of either donating or accepting protons are called amphiprotic, or more generally, amphoteric, a term that may be used for acids and bases per definitions other than the Brønsted-Lowry one.

In the liquid state, molecules of an amphiprotic substance can react with one another as illustrated for water in the equations below:



The process in which like molecules react to yield ions is called autoionization. Liquid water undergoes autoionization to a very slight extent; at 25 °C, approximately two out of every billion water molecules are ionized. The extent of the water autoionization process is reflected in the value of its equilibrium constant, the ion-product constant for water, K_w:

$$\mathrm{H_2O}(l) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O}(aq) + \mathrm{OH^-}(aq) \qquad K_w = [\mathrm{H_3O}][\mathrm{OH^-}]$$

Notice that the concentration of water is not included in the equlibrium constant, since the concentration of water is so great that it does not change. The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C, K_w has a value of 1.0×10^{-14}. The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium ion and hydroxide ion increase with temperature. For example, at 100 °C, the value for K_w is about 5.6×10^{-13}, roughly 50 times larger than the value at 25 °C.

Example 14.1

Ion Concentrations in Pure Water

What are the hydronium ion concentration and the hydroxide ion concentration in pure water at 25 °C?

Solution

The autoionization of water yields the same number of hydronium and hydroxide ions. Therefore, in pure water, $[H_3O^+] = [OH^-] = x$. At 25 °C:

$$K_w = [\mathrm{H_3O+}][\mathrm{OH^-}] = (x)(x) = x^2 = 1.0 \times 10^{-14}$$

So:

$$x = [\mathrm{H_3O+}] = [\mathrm{OH^-}] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}$$

The hydronium ion concentration and the hydroxide ion concentration are the same, $1.0 \times 10^{-7}\ M$.

Check Your Learning

The ion product of water at 80 °C is 2.4×10^{-13}. What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?

Answer:

$[H_3O^+] = [OH^-] = 4.9 \times 10^{-7}\ M$

Example 14.2

The Inverse Relation between $[H_3O^+]$ and $[OH^-]$

A solution of an acid in water has a hydronium ion concentration of $2.0 \times 10^{-6}\ M$. What is the concentration of hydroxide ion at 25 °C?

Solution

Use the value of the ion-product constant for water at 25 °C

$$2H_2O(l) \rightleftharpoons H_3O+(aq) + OH^-(aq) \qquad K_w = [H_3O+][OH^-] = 1.0 \times 10^{-14}$$

to calculate the missing equilibrium concentration.

Rearrangement of the K_w expression shows that $[OH^-]$ is inversely proportional to $[H_3O^+]$:

$$[OH^-] = \frac{K_w}{[H_3O+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9}$$

Compared with pure water, a solution of acid exhibits a higher concentration of hydronium ions (due to ionization of the acid) and a proportionally lower concentration of hydroxide ions. This may be explained via Le Chatelier's principle as a left shift in the water autoionization equilibrium resulting from the stress of increased hydronium ion concentration.

Substituting the ion concentrations into the K_w expression confirms this calculation, resulting in the expected value:

$$K_w = [H_3O+][OH^-] = (2.0 \times 10^{-6})(5.0 \times 10^{-9}) = 1.0 \times 10^{-14}$$

Check Your Learning

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 M at 25 °C?

Answer:

$[H_3O^+] = 1 \times 10^{-11}\ M$

10.1: Introduction to Brønsted-Lowry Acids and Bases is shared under a CC BY license and was authored, remixed, and/or curated by LibreTexts.

10.2: pH, pOH, and Relative Strengths of Acids and Bases

Learning Objectives

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

- Explain the characterization of aqueous solutions as acidic, basic, or neutral
- Express hydronium and hydroxide ion concentrations on the pH and pOH scales
- Perform calculations relating pH and pOH
- Assess the relative strengths of acids and bases according to their ionization constants
- Rationalize trends in acid–base strength in relation to molecular structure
- Carry out equilibrium calculations for weak acid–base systems

As discussed earlier, hydronium and hydroxide ions are present both in pure water and in all aqueous solutions, and their concentrations are inversely proportional as determined by the ion product of water (K_w). The concentrations of these ions in a solution are often critical determinants of the solution's properties and the chemical behaviors of its other solutes, and specific vocabulary has been developed to describe these concentrations in relative terms. A solution is neutral if it contains equal concentrations of hydronium and hydroxide ions; acidic if it contains a greater concentration of hydronium ions than hydroxide ions; and basic if it contains a lesser concentration of hydronium ions than hydroxide ions.

A common means of expressing quantities that may span many orders of magnitude is to use a logarithmic scale. One such scale that is very popular for acid and base concentrations is the p-function, defined as shown where "X" is the quantity of interest and "log" is the base-10 logarithm. The pH of a solution is therefore defined as shown here, where $[H_3O^+]$ is the molar concentration of hydronium ion in the solution:

$$\mathrm{pH} = -\log\left[\mathrm{H_3O+}\right]$$

Rearranging this equation to isolate the hydronium ion molarity yields the equivalent expression:

$$[\mathrm{H_3O}] = 10^{-\mathrm{pH}}$$

Likewise, the hydroxide ion molarity may be expressed as a p-function, or pOH:

$$\mathrm{pOH} = -\log\left[\mathrm{OH^-}\right]$$

or

$$\left[\mathrm{OH^-}\right] = 10^{-\mathrm{pOH}}$$

Finally, the relation between these two ion concentration expressed as p-functions is easily derived from the K_w expression:

$$K_w = [\mathrm{H_3O}]$$

$$=\mathrm{pH}+\mathrm{pOH}$$

At 25 °C, the value of K_w is 1.0×10^{-14}, and so:

$$14.00 = \mathrm{pH} + \mathrm{pOH}$$

As was shown in Example 14.1, the hydronium ion molarity in pure water (or any neutral solution) is 1.0×10^{-7} *M* at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

$$\mathrm{pH} = -\log\left[\mathrm{H_3O}\right] = -\log\left(1.0 \times 10^{-7}\right) = 7.00$$

$$\mathrm{pOH} = -\log\left[\mathrm{OH^-}\right] = -\log\left(1.0 \times 10^{-7}\right) = 7.00$$

And so, *at this temperature*, acidic solutions are those with hydronium ion molarities greater than 1.0×10^{-7} *M* and hydroxide ion molarities less than 1.0×10^{-7} *M* (corresponding to pH values less than 7.00 and pOH values greater than 7.00). Basic solutions

are those with hydronium ion molarities less than 1.0×10^{-7} M and hydroxide ion molarities greater than 1.0×10^{-7} M (corresponding to pH values greater than 7.00 and pOH values less than 7.00).

Figure 10.2.1 shows the relationships between $[H_3O^+]$, $[OH^-]$, pH, and pOH for solutions classified as acidic, basic, and neutral.

$[H_3O^+]$ (M)	$[OH^-]$ (M)	pH	pOH	Sample Solution
10^{1}	10^{-15}	–1	15	
10^{0} or 1	10^{-14}	0	14	1 M HCl
10^{-1}	10^{-13}	1	13	
10^{-2}	10^{-12}	2	12	gastric juice; lime juice; 1 M CH_3CO_2H (vinegar)
10^{-3}	10^{-11}	3	11	stomach acid
10^{-4}	10^{-10}	4	10	wine; orange juice
10^{-5}	10^{-9}	5	9	coffee
10^{-6}	10^{-8}	6	8	rain water
10^{-7}	10^{-7}	7	7	pure water
10^{-8}	10^{-6}	8	6	blood; ocean water; baking soda
10^{-9}	10^{-5}	9	5	
10^{-10}	10^{-4}	10	4	Milk of Magnesia
10^{-11}	10^{-3}	11	3	
10^{-12}	10^{-2}	12	2	household ammonia, NH_3
10^{-13}	10^{-1}	13	1	bleach
10^{-14}	10^{0} or 1	14	0	1 M NaOH
10^{-15}	10^{1}	15	–1	

Figure 10.2.1 The pH and pOH scales represent concentrations of H_3O^+ and OH^-, respectively. The pH and pOH values of some common substances at 25 °C are shown in this chart.

10.2.0.1: Example 14.4

10.2.0.0.1: Calculation of pH from $[H_3O^+]$

What is the pH of stomach acid, a solution of HCl with a hydronium ion concentration of 1.2×10^{-3} M?

10.2.0.0.1: Solution

$$\begin{aligned} \text{pH} &= -\log\left[\text{H}_3\text{O}+\right] \\ &= -\log(1.2 \times 10^{-3}) \\ &= -(-2.92) = 2.92 \end{aligned}$$

(The use of logarithms is explained in Appendix B. When taking the log of a value, keep as many decimal places in the result as there are significant figures in the value.)

10.2.0.0.1: Check Your Learning

Water exposed to air contains carbonic acid, H_2CO_3, due to the reaction between carbon dioxide and water:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

Air-saturated water has a hydronium ion concentration caused by the dissolved CO_2 of 2.0×10^{-6} M, about 20-times larger than that of pure water. Calculate the pH of the solution at 25 °C.

10.2.0.1: Answer:

5.70

10.2.0.1: Example 14.5

10.2.0.0.1: Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of blood, the pH of which is 7.3.

10.2.0.0.1: Solution

$$\begin{gathered} \text{pH} = -\log\left[H_3O^+\right] = 7.3 \\ \log\left[H_3O^+\right] = -7.3 \\ \left[H_3O^+\right] = 10^{-7.3} \text{ or } \left[H_3O^+\right] = \text{ antilog of } -7.3 \\ \left[H_3O^+\right] = 5 \times 10^{-8} M \end{gathered}$$

(On a calculator take the antilog, or the "inverse" log, of −7.3, or calculate $10^{-7.3}$.)

10.2.0.0.1: Check Your Learning

Calculate the hydronium ion concentration of a solution with a pH of −1.07.

10.2.0.1: Answer:

12 M

10.2.0.1: How Sciences Interconnect

10.2.0.0.1: Environmental Science

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved CO_2 which forms carbonic acid:

$$H_2O(l) + CO_2(g) \longrightarrow H_2CO_3(aq)$$

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3{}^-(aq)$$

Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including CO_2, SO_2, SO_3, NO, and NO_2 being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:

$$H_2O(l) + SO_3(g) \longrightarrow H_2SO_4(aq)$$

$$H_2SO_4(aq) \longrightarrow H+(aq) + HSO_4{}^-(aq)$$

Carbon dioxide is naturally present in the atmosphere because most organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also originates from burning fossil fuels, which have traces of sulfur, and from the process of "roasting" ores of metal sulfides in metal-refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (Figure 10.2.2). Regulations limiting the amount of sulfur and nitrogen oxides that can be released into the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.

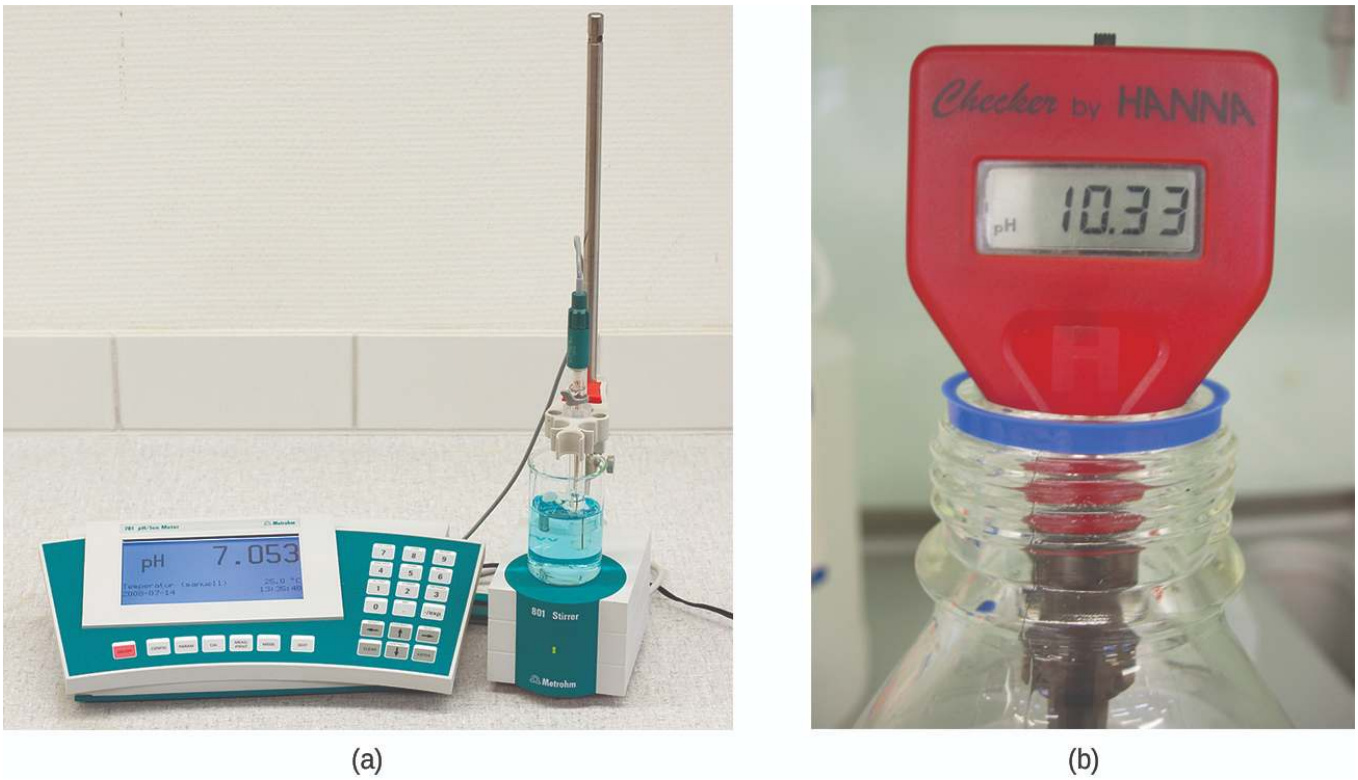
For further information on acid rain, visit this website hosted by the US Environmental Protection Agency.



Figure 10.2.2(a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also is corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by “Eden, Janine and Jim”/Flickr)

10.2.0.1: Measuring pH

The acidity of a solution is typically assessed experimentally by measurement of its pH. The pOH of a solution is not usually measured, as it is easily calculated from an experimentally determined pH value. The pH of a solution can be directly measured using a pH meter (Figure 10.2.3).



(a) (b)

Figure 10.2.3(a) A research-grade pH meter used in a laboratory can have a resolution of 0.001 pH units, an accuracy of ± 0.002 pH units, and may cost in excess of $1000. (b) A portable pH meter has lower resolution (0.01 pH units), lower accuracy (± 0.2 pH units), and a far lower price tag. (credit b: modification of work by Jacopo Werther)

The pH of a solution may also be visually estimated using colored indicators (Figure 10.2.4). The acid-base equilibria that enable use of these indicator dyes for pH measurements are described in a later section of this chapter.



Figure 10.2.4(a) A solution containing a dye mixture, called universal indicator, takes on different colors depending upon its pH. (b) Convenient test strips, called pH paper, contain embedded indicator dyes that yield pH-dependent color changes on contact with aqueous solutions.(credit: modification of work by Sahar Atwa)

10.2.1: Acid and Base Ionization Constants

The relative strength of an acid or base is the extent to which it ionizes when dissolved in water. If the ionization reaction is essentially complete, the acid or base is termed *strong*; if relatively little ionization occurs, the acid or base is weak. As will be evident throughout the remainder of this chapter, there are many more weak acids and bases than strong ones. The most common strong acids and bases are listed in Figure 10.2.5

6 Strong Acids		6 Strong Bases	
$HClO_4$	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$Ca(OH)_2$	calcium hydroxide
HNO_3	nitric acid	$Sr(OH)_2$	strontium hydroxide
H_2SO_4	sulfuric acid	$Ba(OH)_2$	barium hydroxide

Figure 10.2.5Some of the common strong acids and bases are listed here.

The relative strengths of acids may be quantified by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger acids ionize to a greater extent, and so yield higher concentrations of hydronium ions than do weaker acids. The equilibrium constant for an acid is called the acid-ionization constant, K_a. For the reaction of an acid HA:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O{+}}(aq) + \mathrm{A^-}(aq),$$

the acid ionization constant is written

$$K_a = \frac{[\mathrm{H_3O{+}}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

where the concentrations are those at equilibrium. Although water is a reactant in the reaction, it is the solvent as well, so we do not include [H_2O] in the equation. The larger the K_a of an acid, the larger the concentration of H_3O+ and A^- relative to the concentration of the nonionized acid, HA, in an equilibrium mixture, and the stronger the acid. An acid is classified as "strong" when it undergoes complete ionization, in which case the concentration of HA is zero and the acid ionization constant is immeasurably large ($K_a \approx \infty$). Acids that are partially ionized are called "weak," and their acid ionization constants may be experimentally measured. A table of ionization constants for weak acids is provided in Appendix H.

To illustrate this idea, three acid ionization equations and K_a values are shown below. The ionization constants increase from first to last of the listed equations, indicating the relative acid strength increases in the order $CH_3CO_2H < HNO_2 < HSO_4^-$:

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O+(aq) + CH_3CO_2{}^-(aq) \qquad K_a = 1.8 \times 10^{-5}$$

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O+(aq) + NO_2{}^-(aq) \qquad K_a = 4.6 \times 10^{-4}$$

$$HSO_4{}^-(aq) + H_2O(aq) \rightleftharpoons H_3O+(aq) + SO_4{}^2-(aq) \qquad K_a = 1.2 \times 10^{-2}$$

10.2.1.1: Link to Learning

View the simulation of strong and weak acids and bases at the molecular level.

10.2.1.2: Relative Strengths of Conjugate Acid-Base Pairs

Brønsted-Lowry acid-base chemistry is the transfer of protons; thus, logic suggests a relation between the relative strengths of conjugate acid-base pairs. The strength of an acid or base is quantified in its ionization constant, K_a or K_b, which represents the extent of the acid or base ionization reaction. For the conjugate acid-base pair HA / A^-, ionization equilibrium equations and ionization constant expressions are

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O+(aq) + A^-(aq) \qquad K_a = \frac{[H_3O+]\,[A^-]}{[HA]}$$

$$A^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HA(aq) \qquad K_b = \frac{[HA]\,[OH^-]}{[A^-]}$$

Adding these two chemical equations yields the equation for the autoionization for water:

$$\cancel{HA(aq)} + H_2O(l) + \cancel{A^-(aq)} + H_2O(l) \rightleftharpoons H_3O+(aq) + \cancel{A^-(aq)} + OH^-(aq) + \cancel{HA(aq)}$$

$$2H_2O(l) \rightleftharpoons H_3O+(aq) + OH^-(aq)$$

As discussed in another chapter on equilibrium, the equilibrium constant for a summed reaction is equal to the mathematical product of the equilibrium constants for the added reactions, and so

$$K_a \times K_b = \frac{[H_30^+]\,[A^-]}{[HA^-]} \times \frac{[HA]\,[OH^-]}{[A^-]}$$

$$\frac{[H_30^+]\,[A^-]}{[HA^-]} \times \frac{[HA]\,[OH^-]}{[A^-]} = [H_30^+]\,[OH^-]$$

$$[H_30^+]\,[OH^-] = K_w$$

This equation states the relation between ionization constants for any conjugate acid-base pair, namely, their mathematical product is equal to the ion product of water, K_w. By rearranging this equation, a reciprocal relation between the strengths of a conjugate acid-base pair becomes evident:

$$K_a = K_w/K_b \text{ or } K_b = K_w/K_a$$

The inverse proportional relation between K_a and K_b means *the stronger the acid or base, the weaker its conjugate partner*. Figure 10.2.6 illustrates this relation for several conjugate acid-base pairs.

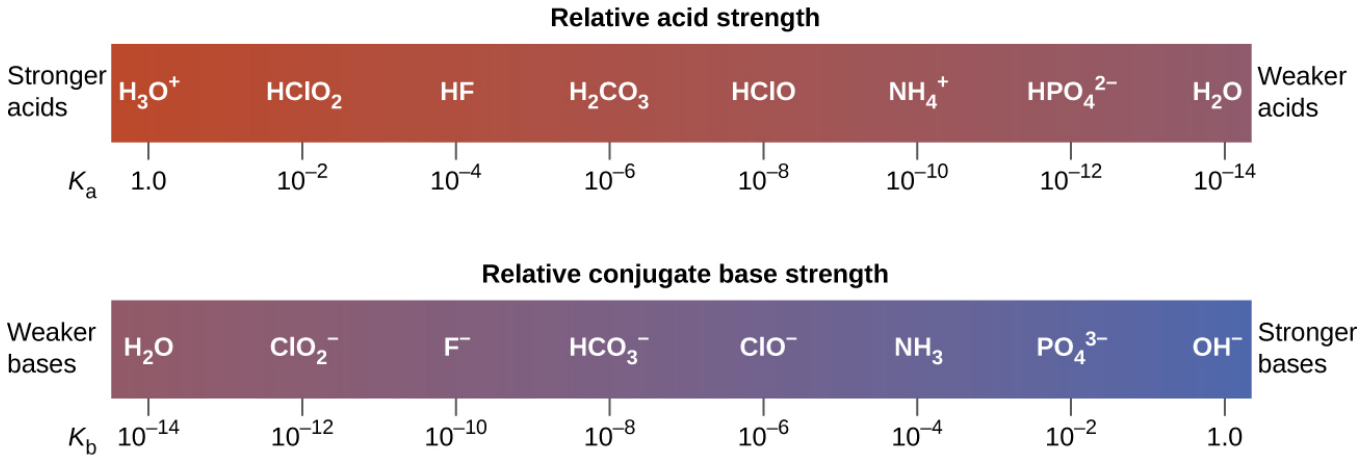


Figure 10.2.6Relative strengths of several conjugate acid-base pairs are shown.

10.2.2: Effect of Molecular Structure on Acid-Base Strength

10.2.2.0.1: Binary Acids and Bases

The acid strength of binary compounds of hydrogen with nonmetals (A) increases as the H-A bond strength decreases down a group in the periodic table. For group 17, the order of increasing acidity is HF < HCl < HBr < HI.

Across a row in the periodic table, the acid strength of binary hydrogen compounds increases with increasing electronegativity of the nonmetal atom because the polarity of the H-A bond increases. Thus, the order of increasing acidity (for removal of one proton) across the second row is $CH_4 < NH_3 < H_2O < HF$; across the third row, it is $SiH_4 < PH_3 < H_2S < HCl$ (see Figure 10.2.7).

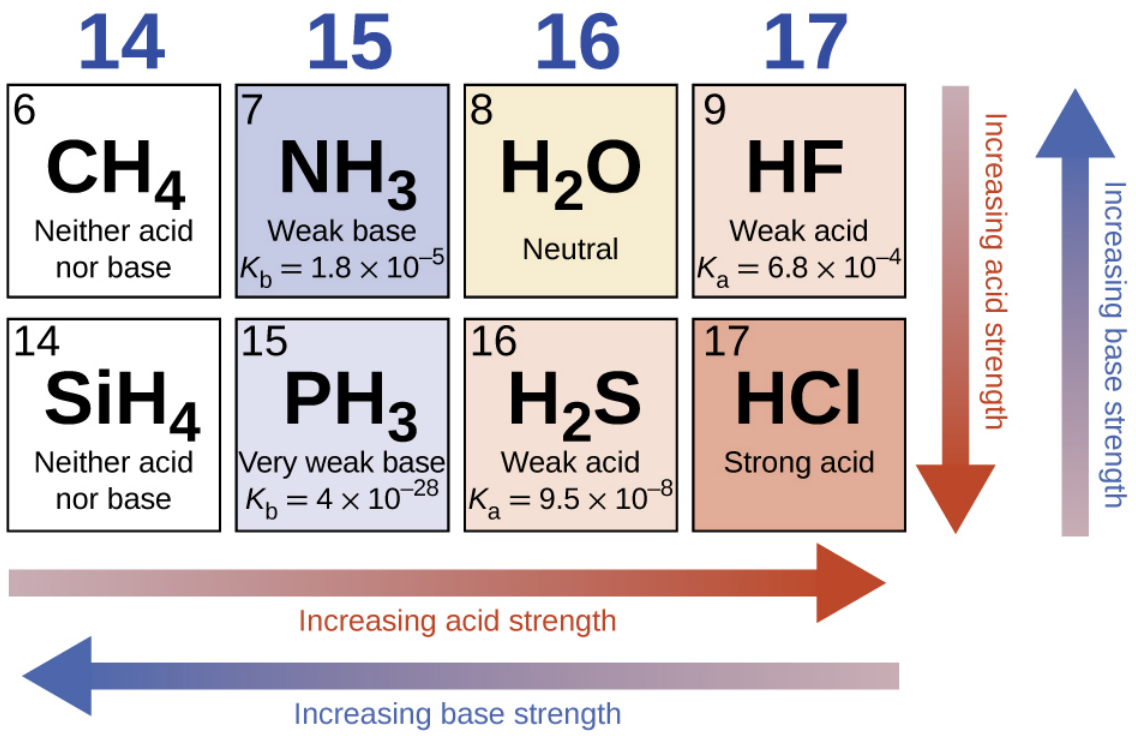


Figure 10.2.7The figure shows trends in the strengths of binary acids and bases.

10.2.2.1: Ternary Acids and Bases

Ternary compounds composed of hydrogen, oxygen, and some third element ("E") may be structured as depicted in the image below. In these compounds, the central E atom is bonded to one or more O atoms, and at least one of the O atoms is also bonded to an H atom as shown in Figure 10.2.8

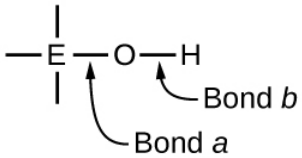


Figure 10.2.8The figure shows trends in the strengths of binary acids and bases.

If the central atom, E, has a low electronegativity, its attraction for electrons is low. Little tendency exists for the central atom to form a strong covalent bond with the oxygen atom, and bond *a* between the element and oxygen is more readily broken than bond *b* between oxygen and hydrogen. Hence bond *a* is ionic, hydroxide ions are released to the solution, and the material behaves as a base—this is the case with $Ca(OH)_2$ and KOH. Lower electronegativity is characteristic of the more metallic elements; hence, the metallic elements form ionic hydroxides that are by definition basic compounds.

If, on the other hand, the atom E has a relatively high electronegativity, it strongly attracts the electrons it shares with the oxygen atom, making bond *a* relatively strongly covalent. The oxygen-hydrogen bond, bond *b*, is thereby weakened because electrons are displaced toward E. Bond *b* is polar and readily releases hydrogen ions to the solution, so the material behaves as an acid. High electronegativities are characteristic of the more nonmetallic elements. Thus, nonmetallic elements form covalent compounds containing acidic −OH groups that are called oxyacids.

Increasing the oxidation number of the central atom E also increases the acidity of an oxyacid because this increases the attraction of E for the electrons it shares with oxygen and thereby weakens the O-H bond. Sulfuric acid, H_2SO_4, or $O_2S(OH)_2$ (with a sulfur oxidation number of +6), is more acidic than sulfurous acid, H_2SO_3, or $OS(OH)_2$ (with a sulfur oxidation number of +4). Likewise nitric acid, HNO_3, or O_2NOH (N oxidation number = +5), is more acidic than nitrous acid, HNO_2, or ONOH (N oxidation number = +3). In each of these pairs, the oxidation number of the central atom is larger for the stronger acid (Figure 10.2.9).

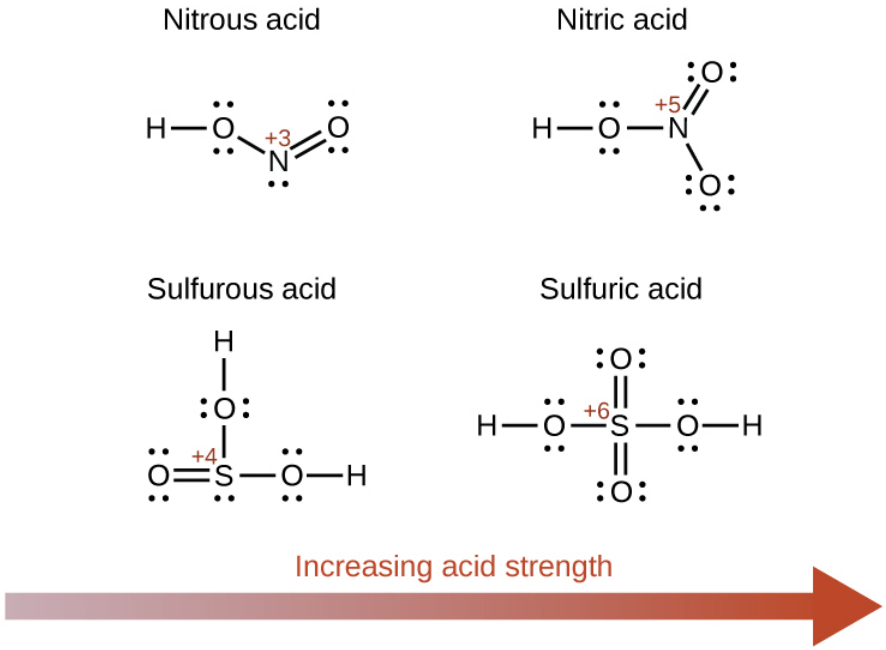


Figure 10.2.9As the oxidation number of the central atom E increases, the acidity also increases.

This page titled 10.2: pH, pOH, and Relative Strengths of Acids and Bases 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.

10.3: Hydrolysis of Salt Solutions

Learning Objectives

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

- Predict whether a salt solution will be acidic, basic, or neutral
- Calculate the concentrations of the various species in a salt solution
- Describe the acid ionization of hydrated metal ions

10.3.0.1: Salts with Acidic Ions

Salts are ionic compounds composed of cations and anions, either of which may be capable of undergoing an acid or base ionization reaction with water. Aqueous salt solutions, therefore, may be acidic, basic, or neutral, depending on the relative acid-base strengths of the salt's constituent ions. For example, dissolving ammonium chloride in water results in its dissociation, as described by the equation

$$\mathrm{NH_4Cl}(s) \rightleftharpoons \mathrm{NH_4}^+(aq) + \mathrm{Cl}^-(aq)$$

The ammonium ion is the conjugate acid of the base ammonia, NH_3; its acid ionization (or acid hydrolysis) reaction is represented by

$$\mathrm{NH_4}^+(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O}^+(aq) + \mathrm{NH_3}(aq)$$

Since ammonia is a weak base, K_b is measurable and $K_a > 0$ (ammonium ion is a weak acid).

The chloride ion is the conjugate base of hydrochloric acid, and so its base ionization (or *base hydrolysis*) reaction is represented by

$$\mathrm{Cl}^-(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HCl}(aq) + \mathrm{OH}^-(aq) \qquad K_b = K_w/K_a$$

Since HCl is a strong acid, K_a is immeasurably large and $K_b \approx 0$ (chloride ions don't undergo appreciable hydrolysis).

Thus, dissolving ammonium chloride in water yields a solution of weak acid cations ($\mathrm{NH_4}^+$) and inert anions (Cl^-), resulting in an acidic solution.

10.3.0.1: Example 14.15

10.3.0.0.1: Calculating the pH of an Acidic Salt Solution

Aniline is an amine that is used to manufacture dyes. It is isolated as anilinium chloride, $[\mathrm{C_6H_5NH_3}]\mathrm{Cl}$, a salt prepared by the reaction of the weak base aniline and hydrochloric acid. What is the pH of a 0.233 *M* solution of anilinium chloride

$$\mathrm{C_6H_5NH_3}^+(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O}^+(aq) + \mathrm{C_6H_5NH_2}(aq) \tag{10.3.1}$$

10.3.0.0.2: Solution

The K_a for anilinium ion is derived from the K_b for its conjugate base, aniline (see Appendix H):

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.3 \times 10^{-10}} = 2.3 \times 10^{-5} \tag{10.3.2}$$

Using the provided information, an Equilibrium table for this system is prepared:

	$\mathrm{C_5H_5NH_3}^+$	$\mathrm{H_2O}$	$\mathrm{C_6H_5NH_2}$	$\mathrm{H_3O}^+$
Equlibrium Concentration (M)	0.233		X	X

Substituting these equilibrium concentration terms into the K_a expression gives

$$\mathrm{K}_a = \frac{[\mathrm{C_6H_5NH_2}]\,[\mathrm{H_3O}^+]}{[\mathrm{C_6H_5NH_3^+}]} \tag{10.3.3}$$

$$2.3 \times 10^{-5} = \frac{X^2}{0.233} \tag{10.3.4}$$

X = 0.002

The ICE table defines x as the hydronium ion molarity, and so the pH is computed as

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0.0023) = 2.64$$

10.3.0.0.3: Check Your Learning

What is the hydronium ion concentration in a 0.100-*M* solution of ammonium nitrate, NH_4NO_3, a salt composed of the ions NH_4^+ and NO_3^-. Which is the stronger acid $C_6H_5NH_3^+$ or NH_4^+?

10.3.0.1: Answer:

$[H_3O^+] = 7.5 \times 10^{-6}$ *M*; $C_6H_5NH_3^+$ is the stronger acid.

10.3.0.1: Salts with Basic Ions

As another example, consider dissolving sodium acetate in water:

$$\text{NaCH}_3\text{CO}_2(s) \rightleftharpoons \text{Na}^+(aq) + \text{CH}_3\text{CO}_2{}^-(aq)$$

The sodium ion does not undergo appreciable acid or base ionization and has no effect on the solution pH. This may seem obvious from the ion's formula, which indicates no hydrogen or oxygen atoms, but some dissolved metal ions function as weak acids, as addressed later in this section.

The acetate ion, $CH_3CO_2^-$, is the conjugate base of acetic acid, CH_3CO_2H, and so its base ionization (or *base hydrolysis*) reaction is represented by

$$\text{CH}_3\text{CO}_2{}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{CO}_2\text{H}(aq) + \text{OH} - (aq) \qquad K_\text{b} = K_\text{w}/K_\text{a}$$

Because acetic acid is a weak acid, its K_a is measurable and $K_b > 0$ (acetate ion is a weak base).

Dissolving sodium acetate in water yields a solution of inert cations (Na^+) and weak base anions ($CH_3CO_2^-$), resulting in a basic solution.

10.3.0.1: Example 14.16

10.3.0.0.1: Equilibrium in a Solution of a Salt of a Weak Acid and a Strong Base

Determine the acetic acid concentration in a solution with $[CH_3CO_2^-] = 0.050$ *M* and $[OH^-] = 2.5 \times 10^{-6}$ *M* at equilibrium. The reaction is:

$$\text{NaCH}_3\text{CO}_2(s) \leftrightharpoons \text{Na}^+(aq) + \text{CH}_3\text{CO}_2{}^-(aq)$$

Solution The provided equilibrium concentrations and a value for the equilibrium constant will permit calculation of the missing equilibrium concentration. The process in question is the base ionization of acetate ion, for which

$$K_\text{b}\left(\text{CH}_3\text{CO}_2^-\right) = \frac{K_\text{w}}{K_\text{a}} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} \tag{10.3.5}$$

Substituting the available values into the K_b expression gives

$$K_\text{b} = \frac{\left[\text{CH}_3\text{CO}_2\text{H}\right]\left[\text{OH}^-\right]}{\left[\text{CH}_3\text{CO}_2^-\right]} = 5.6 \times 10^{-10}$$

$$= \frac{\left[\text{CH}_3\text{CO}_2\text{H}\right]\left(2.5 \times 10^{-6}\right)}{(0.050)} = 5.6 \times 10^{-10}$$

Solving the above equation for the acetic acid molarity yields $[CH_3CO_2H] = 1.1 \times 10^{-5}$ *M*.

10.3.0.0.2: Check Your Learning

What is the pH of a 0.083-*M* solution of NaCN?

10.3.0.1: Answer:

11.11

10.3.0.1: Salts with Acidic and Basic Ions

Some salts are composed of both acidic and basic ions, and so the pH of their solutions will depend on the relative strengths of these two species. Likewise, some salts contain a single ion that is amphiprotic, and so the relative strengths of this ion's acid and base character will determine its effect on solution pH. For both types of salts, a comparison of the K_a and K_b values allows prediction of the solution's acid-base status, as illustrated in the following example exercise.

10.3.0.1: Example 14.17

10.3.0.0.1: Determining the Acidic or Basic Nature of Salts

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

(a) KBr

(b) $NaHCO_3$

(c) Na_2HPO_4

(d) NH_4F

10.3.0.0.2: Solution

Consider each of the ions separately in terms of its effect on the pH of the solution, as shown here:

(a) The K^+ cation is inert and will not affect pH. The bromide ion is the conjugate base of a strong acid, and so it is of negligible base strength (no appreciable base ionization). The solution is neutral.

(b) The Na^+ cation is inert and will not affect the pH of the solution; while the HCO_3^- anion is amphiprotic. The K_a of HCO_3^- is 4.7×10^{-11},and its K_b is $\frac{1.0 \times 10^{-14}}{4.3 \times 10^{-7}} = 2.3 \times 10^{-8}$.

Since $K_b >> K_a$, the solution is basic.

(c) The Na^+ cation is inert and will not affect the pH of the solution, while the HPO_4^{2-} anion is amphiprotic. The K_a of HPO_4^{2-} is 4.2×10^{-13},

and its K_b is $\frac{1.0 \times 10^{-14}}{6.2 \times 10^{-8}} = 1.6 \times 10^{-7}$. Because $K_b >> K_a$, the solution is basic.

(d) The NH_4^+ ion is acidic (see above discussion) and the F^- ion is basic (conjugate base of the weak acid HF). Comparing the two ionization constants: K_a of NH_4^+ is 5.6×10^{-10} and the K_b of F^- is 1.6×10^{-11}, so the solution is acidic, since $K_a > K_b$.

10.3.0.0.3: Check Your Learning

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

(a) K_2CO_3

(b) $CaCl_2$

(c) KH_2PO_4

(d) $(NH_4)_2CO_3$

10.3.0.1: Answer:

(a) basic; (b) neutral; (c) acidic; (d) basic

This page titled 10.3: Hydrolysis of Salt Solutions 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.

10.4: Buffers

Learning Objectives

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

- Describe the composition and function of acid–base buffers
- Calculate the pH of a buffer before and after the addition of added acid or base

A solution containing appreciable amounts of a weak conjugate acid-base pair is called a buffer solution, or a buffer. Buffer solutions resist a change in pH when small amounts of a strong acid or a strong base are added (Figure 14.14). A solution of acetic acid and sodium acetate (CH_3COOH + CH_3COONa) is an example of a buffer that consists of a weak acid and its salt. An example of a buffer that consists of a weak base and its salt is a solution of ammonia and ammonium chloride ($NH_3(aq)$ + $NH_4Cl(aq)$).

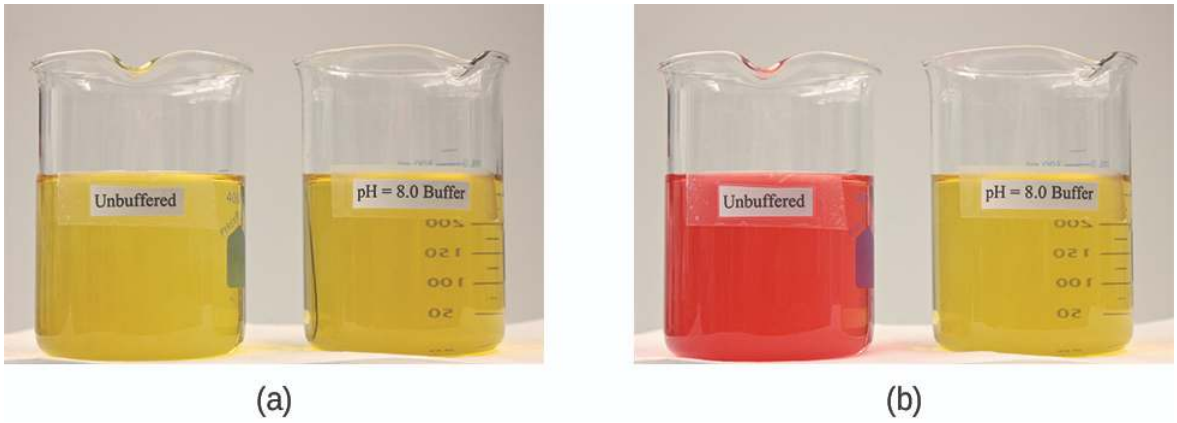


Figure 14.14 (a) The unbuffered solution on the left and the buffered solution on the right have the same pH (pH 8); they are basic, showing the yellow color of the indicator methyl orange at this pH. (b) After the addition of 1 mL of a 0.01-*M* HCl solution, the buffered solution has not detectably changed its pH but the unbuffered solution has become acidic, as indicated by the change in color of the methyl orange, which turns red at a pH of about 4. (credit: modification of work by Mark Ott)

10.4.0.1: How Buffers Work

To illustrate the function of a buffer solution, consider a mixture of roughly equal amounts of acetic acid and sodium acetate. The presence of a weak conjugate acid-base pair in the solution imparts the ability to neutralize modest amounts of added strong acid or base. For example, strong base added to this solution will neutralize hydronium ion, causing the acetic acid ionization equilibrium to shift to the right and generate additional amounts of the weak conjugate base (acetate ion):

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O{+}}(aq) + \mathrm{CH_3CO_2{}^-}(aq)$$

Likewise, strong acid added to this buffer solution will shift the above ionization equilibrium left, producing additional amounts of the weak conjugate acid (acetic acid). Figure 14.15 provides a graphical illustration of the changes in conjugate-partner concentration that occur in this buffer solution when strong acid and base are added. The buffering action of the solution is essentially a result of the added strong acid and base being converted to the weak acid and base that make up the buffer's conjugate pair. The weaker acid and base undergo only slight ionization, as compared with the complete ionization of the strong acid and base, and the solution pH, therefore, changes much less drastically than it would in an unbuffered solution.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

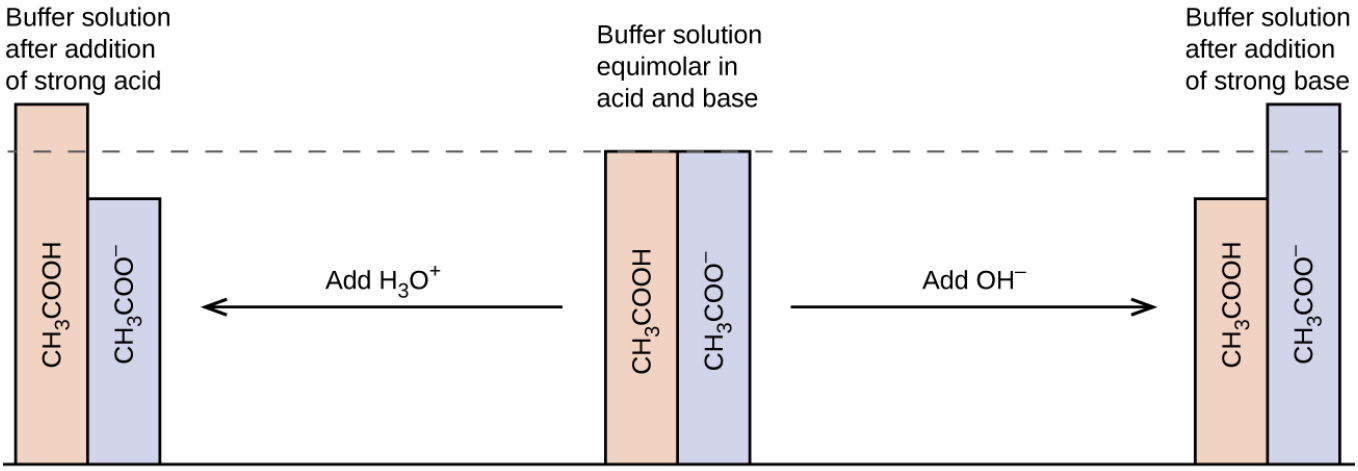


Figure 14.15 Buffering action in a mixture of acetic acid and acetate salt.

10.4.0.0.1: Example 14.20

10.4.0.0.1: pH Changes in Buffered and Unbuffered Solutions

Acetate buffers are used in biochemical studies of enzymes and other chemical components of cells to prevent pH changes that might affect the biochemical activity of these compounds.

(a) Calculate the pH of an acetate buffer that is a mixture with 0.10 *M* acetic acid and 0.10 *M* sodium acetate.

(b) Calculate the pH after adding NaOH to shift the buffer so the concentration of acetic acid is reduced to 0.05 M and the concentration of acetate ion is increased to 0.15 M.

(c) For comparison, calculate the pH after 0.05 moles of NaOH is added to 1.0 L of an unbuffered solution.

10.4.0.0.2: Solution

(a) Calculate the pH of an acetate buffer that is a mixture with 0.10 *M* acetic acid and 0.10 *M* sodium acetate.

	CH_3CO_2H	H_2O	H_3O^+	$CH_3CO_2^-$
Equlibrium Concentration (M)	0.10		X	0.10

$$K_A = \frac{\left[H_3O^+\right]\left[CH_3CO_2^-\right]}{\left[CH_3CO_2H\right]}$$
$$1.8 \times 10^{-5} = \frac{[0.10]\,[X]}{[0.10]}$$
$$\left[H_3O^+\right] = 1.8 \times 10^{-5}$$
$$pH = -log(1.8 \times 10^{-5})$$
$$pH = 4.74$$

(b) Calculate the pH after adding NaOH to shift the buffer so the concentration of acetic acid is reduced to 0.05 M and the concentration of acetate ion is increased to 0.15 M

	CH_3CO_2H	H_2O	H_3O^+	$CH_3CO_2^-$
Equlibrium Concentration (M)	0.05		X	0.15

$$K_A = \frac{\left[H_3O^+\right]\left[CH_3CO_2^-\right]}{\left[CH_3CO_2H\right]}$$
$$1.8 \times 10^{-5} = \frac{[0.15]\,[X]}{[0.05]}$$
$$\left[H_3O^+\right] = 6.0 \times 10^{-6}$$
$$pH = -log(6.0 \times 10^{-6})$$
$$pH = 5.22$$

(c) For comparison, calculate the pH after 0.05 moles of NaOH is added to 1.0 L of an unbuffered solution.

$$\left[OH^-\right] = 0.05\ M$$
$$pOH = -log(0.05)$$
$$pOH = 1.3$$
$$pH = 14 - 1.3$$
$$pH = 12.7$$

As you can see adding a comparable amout of base to an unbuffered solution causes a dramatic change in the pH.

10.4.0.0.3: Check Your Learning

Show that adding 1.0 mL of 0.10 *M* HCl changes the pH of 100 mL of a 1.8×10^{-5} *M* HCl solution from 4.74 to 3.00.

10.4.0.1: Answer:

Initial pH of 1.8×10^{-5} *M* HCl; pH = $-\log[H_3O^+] = -\log[1.8 \times 10^{-5}] = 4.74$
Moles of H_3O^+ in 100 mL 1.8×10^{-5} *M* HCl; 1.8×10^{-5} moles/L × 0.100 L = 1.8×10^{-6}
Moles of H_3O^+ added by addition of 1.0 mL of 0.10 *M* HCl: 0.10 moles/L × 0.0010 L = 1.0×10^{-4} moles; final pH after addition of 1.0 mL of 0.10 *M* HCl:

$$pH = -\log[H_3O+] = -\log\left(\frac{\text{totalmoles}\,H_3O+}{\text{total volume}}\right) = -\log\left(\frac{1.0\ \times\ 10^{-}4\,\text{mol} + 1.8\ \times\ 10^{-}}{6\,\text{mol}}\right) = 3.00$$

10.4.0.1: Buffer Capacity

Buffer solutions do not have an unlimited capacity to keep the pH relatively constant (Figure 14.16). Instead, the ability of a buffer solution to resist changes in pH relies on the presence of appreciable amounts of its conjugate weak acid-base pair. When enough strong acid or base is added to substantially lower the concentration of either member of the buffer pair, the buffering action within the solution is compromised.



Figure 14.16 The indicator color (methyl orange) shows that a small amount of acid added to a buffered solution of pH 8 (beaker on the left) has little affect on the buffered system (middle beaker). However, a large amount of acid exhausts the buffering capacity of the solution and the pH changes dramatically (beaker on the right). (credit: modification of work by Mark Ott)

The buffer capacity is the amount of acid or base that can be added to a given volume of a buffer solution before the pH changes significantly, usually by one unit. Buffer capacity depends on the amounts of the weak acid and its conjugate base that are in a buffer mixture. For example, 1 L of a solution that is 1.0 *M* in acetic acid and 1.0 *M* in sodium acetate has a greater buffer capacity than 1 L of a solution that is 0.10 *M* in acetic acid and 0.10 *M* in sodium acetate even though both solutions have the same pH. The first solution has more buffer capacity because it contains more acetic acid and acetate ion.

10.4.0.1: Selection of Suitable Buffer Mixtures

There are two useful rules of thumb for selecting buffer mixtures:

1. A good buffer mixture should have about equal concentrations of both of its components. A buffer solution has generally lost its usefulness when one component of the buffer pair is less than about 10% of the other. Figure 14.17 shows how pH changes for an acetic acid-acetate ion buffer as base is added. The initial pH is 4.74. A change of 1 pH unit occurs when the acetic acid concentration is reduced to 11% of the acetate ion concentration.

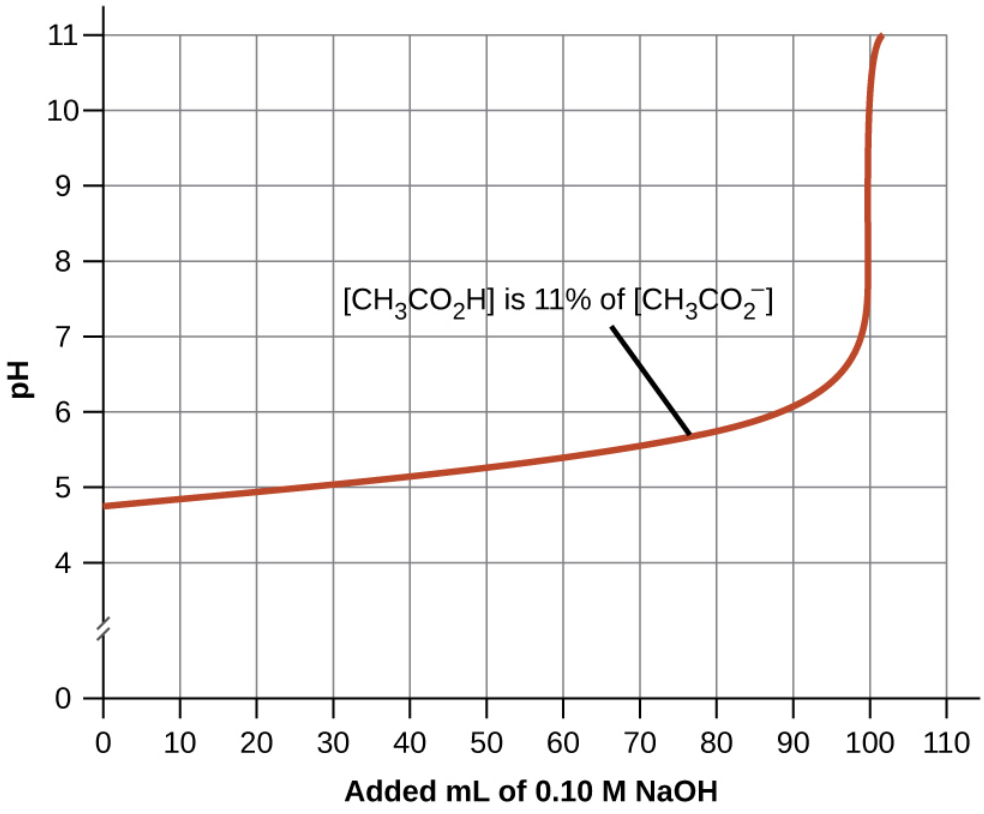

11
10
9
8
7
6
5
4
0
pH
[CH3CO2H] is 11% of [CH3CO2−]
0
10
20
30
40
50
60
70
80
90
100
110
Added mL of 0.10 M NaOH

Figure 14.17 Change in pH as an increasing amount of a 0.10-*M* NaOH solution is added to 100 mL of a buffer solution in which, initially, [CH_3CO_2H] = 0.10 *M* and $\left[CH_3CO_2^-\right] = 0.10\ M$. Note the greatly diminished buffering action occurring after the buffer capacity has been reached, resulting in drastic rises in pH on adding more strong base.

2. Weak acids and their salts are better as buffers for pH less than 7; weak bases and their salts are better as buffers for pH greater than 7.

Blood is an important example of a buffered solution, with the principal acid and ion responsible for the buffering action being carbonic acid, H_2CO_3, and the bicarbonate ion, HCO_3^-. When a hydronium ion is introduced to the blood stream, it is removed primarily by the reaction

$$H_3O^+(aq) + HCO_3^-(aq) \rightleftharpoons H_2CO_3(aq) + H_2O(l) \tag{10.4.1}$$

An added hydroxide ion is removed by the reaction:

$$OH^-(aq) + H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H_2O(l) \tag{10.4.2}$$

The added strong acid or base is thus effectively converted to the much weaker acid or base of the buffer pair (H_3O^+ is converted to H_2CO_3 and OH^- is converted to HCO_3^-). The pH of human blood thus remains very near the value determined by the buffer pairs pKa, in this case, 7.35. Normal variations in blood pH are usually less than 0.1, and pH changes of 0.4 or greater are likely to be fatal.

10.4.0.1: The Henderson-Hasselbalch Equation

The ionization-constant expression for a solution of a weak acid can be written as:

$$K_A = \frac{\left[H_3O^+\right]\left[A^-\right]}{[HA]} \tag{10.4.3}$$

Rearranging to solve for [H_3O^+] yields:

$$\left[H_3O^+\right] = K_A \times \frac{[HA]}{\left[A^-\right]} \tag{10.4.4}$$

Taking the negative logarithm of both sides of this equation gives

$$-log\left[H_3O^+\right] = -logK_A - log\frac{[HA]}{\left[A^-\right]} \tag{10.4.5}$$

which can be written as

$$pH = pK_A + log\frac{\left[A^-\right]}{[HA]} \tag{10.4.6}$$

where pK_a is the negative of the logarithm of the ionization constant of the weak acid (pK_a = −log K_a). This equation relates the pH, the ionization constant of a weak acid, and the concentrations of the weak conjugate acid-base pair in a buffered solution. Scientists often use this expression, called the Henderson-Hasselbalch equation, to calculate the pH of buffer solutions. It is important to note that the "*x* is small" assumption must be valid to use this equation.

10.4.0.1: Portrait of a Chemist

10.4.0.0.1: Lawrence Joseph Henderson and Karl Albert Hasselbalch

Lawrence Joseph Henderson (1878–1942) was an American physician, biochemist and physiologist, to name only a few of his many pursuits. He obtained a medical degree from Harvard and then spent 2 years studying in Strasbourg, then a part of Germany, before returning to take a lecturer position at Harvard. He eventually became a professor at Harvard and worked there his entire life. He discovered that the acid-base balance in human blood is regulated by a buffer system formed by the dissolved carbon dioxide in blood. He wrote an equation in 1908 to describe the carbonic acid-carbonate buffer system in blood. Henderson was broadly knowledgeable; in addition to his important research on the physiology of blood, he also wrote on the adaptations of organisms and their fit with their environments, on sociology and on university education. He also

founded the Fatigue Laboratory, at the Harvard Business School, which examined human physiology with specific focus on work in industry, exercise, and nutrition.

In 1916, Karl Albert Hasselbalch (1874–1962), a Danish physician and chemist, shared authorship in a paper with Christian Bohr in 1904 that described the Bohr effect, which showed that the ability of hemoglobin in the blood to bind with oxygen was inversely related to the acidity of the blood and the concentration of carbon dioxide. The pH scale was introduced in 1909 by another Dane, Sørensen, and in 1912, Hasselbalch published measurements of the pH of blood. In 1916, Hasselbalch expressed Henderson's equation in logarithmic terms, consistent with the logarithmic scale of pH, and thus the Henderson-Hasselbalch equation was born.

10.4.0.1: How Sciences Interconnect

10.4.0.0.2: Medicine: The Buffer System in Blood

The normal pH of human blood is about 7.4. The carbonate buffer system in the blood uses the following equilibrium reaction:

$$\mathrm{CO_2}(g) + 2\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2CO_3}(aq) \rightleftharpoons \mathrm{HCO_3}^-(aq) + \mathrm{H_3O}+(aq)$$

The concentration of carbonic acid, $\mathrm{H_2CO_3}$ is approximately 0.0012 *M*, and the concentration of the hydrogen carbonate ion, $\mathrm{HCO_3}^-$, is around 0.024 *M*. Using the Henderson-Hasselbalch equation and the pK_a of carbonic acid at body temperature, we can calculate the pH of blood:

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{base}]}{[\mathrm{acid}]} = 6.4 + \log\frac{0.024}{0.0012} = 7.7$$

The fact that the $\mathrm{H_2CO_3}$ concentration is significantly lower than that of the $\mathrm{HCO_3}^-$ ion may seem unusual, but this imbalance is due to the fact that most of the by-products of our metabolism that enter our bloodstream are acidic. Therefore, there must be a larger proportion of base than acid, so that the capacity of the buffer will not be exceeded.

Lactic acid is produced in our muscles when we exercise. As the lactic acid enters the bloodstream, it is neutralized by the $\mathrm{HCO_3}^-$ ion, producing $\mathrm{H_2CO_3}$. An enzyme then accelerates the breakdown of the excess carbonic acid to carbon dioxide and water, which can be eliminated by breathing. In fact, in addition to the regulating effects of the carbonate buffering system on the pH of blood, the body uses breathing to regulate blood pH. If the pH of the blood decreases too far, an increase in breathing removes $\mathrm{CO_2}$ from the blood through the lungs driving the equilibrium reaction such that $[\mathrm{H_3O^+}]$ is lowered. If the blood is too alkaline, a lower breath rate increases $\mathrm{CO_2}$ concentration in the blood, driving the equilibrium reaction the other way, increasing $[\mathrm{H^+}]$ and restoring an appropriate pH.

10.4.0.1: Link to Learning

View information on the buffer system encountered in natural waters.

This page titled 10.4: Buffers 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.E: Acid-Base Equilibria - Homework

10.E.1: Brønsted-Lowry Acids and Bases

1. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:
   a. H_3O^+
   b. HCl
   c. NH_3
   d. CH_3CO_2H
   e. $NH_4{}^+$
   f. $HSO_4{}^-$

   Answer

   a. $H_3O^+(aq) \longrightarrow H^+(aq) + H_2O(l)$
   b. $HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$
   c. $NH_3(aq) \longrightarrow H^+(aq) + NH_2^-(aq)$
   d. $CH_3CO_2H(aq) \longrightarrow H^+(aq) + CH_3CO_2^-(aq)$
   e. $NH_4{}^+(aq) \longrightarrow H^+(aq) + NH_3(aq)$
   f. $HSO_4^-(aq) \longrightarrow H^+(aq) + SO_4^{2-}(aq)$

2. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:
   a. (a) H_2O
   b. (b) OH^-
   c. (c) NH_3
   d. (d) CN^-

   Answer

   a. $H_2O(l) + H^+(aq) \longrightarrow H_3O^+(aq)$
   b. $OH^-(aq) + H^+(aq) \longrightarrow H_2O(l)$
   c. $NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)$
   d. $CN^-(aq) + H^+(aq) \longrightarrow HCN(aq)$

3. What is the conjugate acid of each of the following? What is the conjugate base of each?
   a. OH^-
   b. H_2O
   c. $HCO_3{}^-$
   d. NH_3

   Answer

   a. H_2O
   b. H_3O^+
   c. H_2CO_3
   d. $NH_4{}^+$

4. Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:
   a. $HNO_3 + H_2O \longrightarrow H_3O + + NO_3^-$
   b. $H_2SO_4 + Cl^- \longrightarrow HCl + HSO_4^-$
   c. $HSO_4{}^- + OH^- \longrightarrow SO_4{}^2 - + H_2O$
   d. $O^{2-} + H_2O \longrightarrow 2OH-$

   Answer

   a. HNO_3(BA), H_2O(BB), H_3O^+(CA), $NO_3{}^-$ (CB)

b. H_2SO_4(BA), Cl^-(BB), HCl(CA), HSO_4^- (CB)
c. HSO_4^- (BA), OH^-(BB), SO_4^{2-} (CB), H_2O(CA)
d. O^{2-}(BB), H_2O(BA) OH^-(CB and CA)

5. State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species.
   a. NH_3
   b. HPO_4^-
   c. Br^-

Answer

a. Acid: $HPO_4^{2-} + OH^- \longrightarrow PO_4^{3-} + H_2O$ Base: $H_2O(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
b. Acid: $HPO_4{}^{2-} + OH^- \longrightarrow PO_4{}^{3-} + H_2O$ Base: $HPO_4{}^{2-} + HClO_4 \longrightarrow H_2PO_4^- + ClO_4$
c. not amphiprotic

10.E.2: pH and pOH

1. Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:
   a. (a) 0.000259 *M* $HClO_4$
   b. (b) 0.21 *M* NaOH
   c. (c) 0.000071 *M* $Ba(OH)_2$
   d. (d) 2.5 *M* KOH

Answer

a. pH = 3.587; pOH = 10.413
b. pOH = 0.68; pH = 13.32;
c. pOH = 3.85; pH = 10.15;
d. pOH = −0.40; pH = 14.4

2. Calculate the hydronium ion concentration and the hydroxide ion concentration in lime juice from its pH. See Figure 14.2 for useful information.

Answer

$[H_3O^+] = 1 \times 10^{-2}\text{M}; [OH^-] = 1 \times 10^{-12}\text{M}$

3. The hydroxide ion concentration in household ammonia is 3.2×10^{-3} *M* at 25 °C. What is the concentration of hydronium ions in the solution?

Answer

$[OH^-] = 3.1 \times 10^{-12}\text{M}$

10.E.3: Relative Strengths of Acids and Bases

1. .The odor of vinegar is due to the presence of acetic acid, CH_3CO_2H, a weak acid. List, in order of descending concentration, all of the ionic and molecular species present in a 1-*M* aqueous solution of this acid.

Answer

$[H_2O] > [CH_3CO_2H] > [H_3O^+] \approx [CH_3CO_2^-] > [OH^-]$

2. Predict which acid in each of the following pairs is the stronger and explain your reasoning for each.
   a. H_2O or HF
   b. HSO_3^- or HSO_4^-
   c. NH_3 or H_2O
   d. NH_3 or PH_3

Answer

a. HF; Increasing acid strength to the right on the periodic table
b. HSO_4^-; increasing oxidation number of central atom
c. H_2O; NH_3 is a base, increasing acid strength to the right on the periodic table
d. PH_3; acidity increases as you go down on the periodic table

3. Rank the compounds in each of the following groups in order of increasing acidity and explain the order you assign.
   a. HOCl, HOBr, HOI
   b. HOCl, HOClO, $HOClO_2$, $HOClO_3$

Answer

a. HOI < HOBr < HOCl; in a series of the same form of oxyacids, the acidity increases as the electronegativity of the central atom increases. Cl is more electronegative than Br, and I is the least electronegative of the three.
b. HOCl < HOClO < $HOClO_2$ < $HOClO_3$; in a series of oxyacids of the same central element, the acidity increases as the number of oxygen atoms increases (or as the oxidation state of the central atom increases).

4. The active ingredient formed by aspirin in the body is salicylic acid, $C_6H_4OH(CO_2H)$. The carboxyl group ($-CO_2H$) acts as a weak acid. The phenol group (an OH group bonded to an aromatic ring) also acts as an acid but a much weaker acid. List, in order of descending concentration, all of the ionic and molecular species present in a 0.001-*M* aqueous solution of $C_6H_4OH(CO_2H)$.

Answer

$$[H_2O] > [C_6H_4OH\,(CO_2H)] > [H^+]\ 0 > [C_6H_4OH(CO_2)^-] \gg [C_6H_4O(CO_2H)^-] > [OH^-]$$

5. Why is the hydronium ion concentration in a solution that is 0.10 *M* in HCl and 0.10 *M* in HCOOH determined by the concentration of HCl?

Answer

This is a case in which the solution contains a mixture of acids of different ionization strengths. In solution, the HCO_2H exists primarily as HCO_2H molecules because the ionization of the weak acid is suppressed by the strong acid. Therefore, the HCO_2H contributes a negligible amount of hydronium ions to the solution. The stronger acid, HCl, is the dominant producer of hydronium ions because it is completely ionized. In such a solution, the stronger acid determines the concentration of hydronium ions, and the ionization of the weaker acid is fixed by the $[H_3O^+]$ produced by the stronger acid.

6. From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.
   a. ClO^-: $[OH^-] = 4.0 \times 10^{-4}$ *M*; [HClO] = 2.38×10^{-4} *M*; $[ClO^-] = 0.273$ *M*;
   b. HNO_2: $[H_3O+] = 0.011$ *M*; $[NO_2^-] = 0.0438$ *M*; $[HNO_2] = 1.07$ *M*;
   c. NH_4^+ : $[NH_4^+] = 0.100$ *M*; $[NH_3] = 7.5 \times 10^{-6}$ *M*; $[H_3O^+] = 7.5 \times 10^{-6}$ *M*

Answer

a. $K_b = 3.49 \times 10^{-7}$
b. $K_a = 4.50 \times 10^{-4}$
c. $K_a = 5.62 \times 10^{-10}$

7. Determine K_a for hydrogen sulfate ion, HSO_4^-. In a 0.10-*M* solution the acid is 29% ionized.

Answer

$$K_a = 1.2 \times 10^{-2}$$

8. Calculate the concentration of all solute species in each of the following solutions of acids or bases. Assume that the ionization of water can be neglected, and show that the change in the initial concentrations can be neglected.
   a. 0.0092 *M* HClO, a weak acid

Answer

$[H_3O^+] = [ClO^-] = 1.6 \times 10^{-5} M$

a. $[HClO^-] = 0.0092 M$

$[OH^-] = 6.1 \times 10^{-10} M$;

9. The pH of a 0.15-*M* solution of HSO_4^- is 1.43. Determine K_a for HSO_4^- from these data.

Answer

$K_a = 1.2 \times 10^{-2}$

10. Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:
    a. K_2CO_3
    b. NH_4Br
    c. $KClO_4$

Answer

a. basic
b. acidic
c. neutral

10.E.4: Buffers

1. Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the base NH_3 and a salt of its conjugate acid NH_4Cl.

Answer

If you add a small amount of base it reacts with the NH_4^+ ions in solution to make water and NH_3 - so the pH does not change. If you add a small amount of acid it reacts with the NH_3 in the solution to make NH_4^+ ions and water - so again the pH does not change.

2. What is the effect on the concentration of acetic acid, hydronium ion, and acetate ion when the following are added to an acidic buffer solution of equal concentrations of acetic acid and sodium acetate:
    a. HCl
    b. NaCl
    c. KOH
    d. CH_3CO_2H

Answer

a. The added HCl will increase the concentration of H_3O^+ slightly, which will react with $CH_3CO_2^-$ and produce CH_3CO_2H in the process. Thus, $[CH_3CO_2^-]$ decreases and $[CH_3CO_2H]$ increases.
b. The added NaCl will have no effect on the concentration of the ions.
c. The added KOH will produce OH^- ions, which will react with the H_3O^+, thus reducing $[H_3O^+]$. Some additional CH_3CO_2H will dissociate, producing $CH_3CO_2^-$ ions in the process. Thus, $[CH_3CO_2H]$ decreases slightly and $[CH_3CO_2^-]$ increases.
d. The added CH_3CO_2H will increase its concentration, causing more of it to dissociate and producing more $CH_3CO_2^-$ and H_3O^+ in the process. Thus, $[H_3O^+]$ increases slightly and $[CH_3CO_2^-]$ increases.

3. What is the effect on the concentration of ammonia, hydroxide ion, and ammonium ion when the following are added to a basic buffer solution of equal concentrations of ammonia and ammonium nitrate:
    a. KI
    b. NH_3
    c. HI
    d. NaOH
    e. NH_4Cl

Answer

a. no change in the equilibrium, since neither K+ or I- ions are in the equlibrium expression
b. Adding NH_3 will shift the equilibrium to the right, reducing the added NH_3 and increasing the NH_4^+ and OH^- concentrations.
c. Adding HI will increase the H_3O^+ concentration, which will react with the NH_3 . NH_3 will go down, NH_4^+ and OH^- will go up.
d. Adding NaOH will increase the OH- concentration. The equilibrium will respond with NH_3 going up, NH_4^+ and OH^- will go down.
e. Adding NH_4Cl will increase the NH_4^+ concentration. The equilibrium will respond with NH_3 going up, NH_4^+ and OH^- will go down.

4. A buffer solution is prepared from equal volumes of 0.200 *M* acetic acid and 0.600 *M* sodium acetate. Use 1.80×10^{-5} as K_a for acetic acid.
   a. What is the pH of the solution?
   b. Is the solution acidic or basic?
   c. What is the pH of a solution that results when 3.00 mL of 0.034 *M* HCl is added to 0.200 L of the original buffer?

Answer

a. pH = 5.222
b. The solution is acidic.
c. pH = 5.220

This page titled 10.E: Acid-Base Equilibria - Homework 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

11: Thermochemistry

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

General Chemistry

Useful forms of energy are also available from a variety of chemical reactions other than combustion. For example, the energy produced by the batteries in a cell phone, car, or flashlight results from chemical reactions. This chapter introduces many of the basic ideas necessary to explore the relationships between chemical changes and energy, with a focus on thermal energy.

11.1: Energy Basics
11.2: Calorimetry
11.3: Enthalpy- Introduction
11.4: Enthalpy- Heat of Combustion
11.5: Enthalpy- Heat of Formation
11.6: Bond Energy
11.E: Thermochemistry- Homework

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 11: Thermochemistry is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

11.1: Energy Basics

Learning Objectives

- Define energy, distinguish types of energy, and describe the nature of energy changes that accompany chemical and physical changes
- Distinguish the related properties of heat, thermal energy, and temperature
- Define and distinguish specific heat and heat capacity, and describe the physical implications of both
- Perform calculations involving heat, specific heat, and temperature change

11.1.1: Introduction

Chemical reactions, such as those that occur when you light a match, involve changes in energy as well as matter. Societies at all levels of development could not function without the energy released by chemical reactions. In 2012, about 85% of US energy consumption came from the combustion of petroleum products, coal, wood, and garbage. We use this energy to produce electricity (38%); to transport food, raw materials, manufactured goods, and people (27%); for industrial production (21%); and to heat and power our homes and businesses (10%).[1] While these combustion reactions help us meet our essential energy needs, they are also a major contributor to global climate change.



Figure 11.1.1: Sliding a match head along a rough surface initiates a combustion reaction that produces energy in the form of heat and light. (credit: modification of work by Laszlo Ilyes).

Useful forms of energy are also available from a variety of chemical reactions other than combustion. For example, the energy produced by the batteries in a cell phone, car, or flashlight results from chemical reactions. This chapter introduces many of the basic ideas necessary to explore the relationships between chemical changes and energy, with a focus on thermal energy.

Chemical changes and their accompanying changes in energy are important parts of our everyday world (Figure 11.1.2). The macronutrients in food (proteins, fats, and carbohydrates) undergo metabolic reactions that provide the energy to keep our bodies functioning. We burn a variety of fuels (gasoline, natural gas, coal) to produce energy for transportation, heating, and the generation of electricity. Industrial chemical reactions use enormous amounts of energy to produce raw materials (such as iron and aluminum). Energy is then used to manufacture those raw materials into useful products, such as cars, skyscrapers, and bridges.



Figure 11.1.2: The energy involved in chemical changes is important to our daily lives: (a) A cheeseburger for lunch provides the energy you need to get through the rest of the day; (b) the combustion of gasoline provides the energy that moves your car (and you) between home, work, and school; and (c) coke, a processed form of coal, provides the energy needed to convert iron ore into iron, which is essential for making many of the products we use daily. (credit a: modification of work by “Pink Sherbet Photography”/Flickr; credit b: modification of work by Jeffery Turner).

Over 90% of the energy we use comes originally from the sun. Every day, the sun provides the earth with almost 10,000 times the amount of energy necessary to meet all of the world’s energy needs for that day. Our challenge is to find ways to convert and store

incoming solar energy so that it can be used in reactions or chemical processes that are both convenient and nonpolluting. Plants and many bacteria capture solar energy through photosynthesis. We release the energy stored in plants when we burn wood or plant products such as ethanol. We also use this energy to fuel our bodies by eating food that comes directly from plants or from animals that got their energy by eating plants. Burning coal and petroleum also releases stored solar energy: These fuels are fossilized plant and animal matter.

This chapter will introduce the basic ideas of an important area of science concerned with the amount of heat absorbed or released during chemical and physical changes—an area called thermochemistry. The concepts introduced in this chapter are widely used in almost all scientific and technical fields. Food scientists use them to determine the energy content of foods. Biologists study the energetics of living organisms, such as the metabolic combustion of sugar into carbon dioxide and water. The oil, gas, and transportation industries, renewable energy providers, and many others endeavor to find better methods to produce energy for our commercial and personal needs. Engineers strive to improve energy efficiency, find better ways to heat and cool our homes, refrigerate our food and drinks, and meet the energy and cooling needs of computers and electronics, among other applications. Understanding thermochemical principles is essential for chemists, physicists, biologists, geologists, every type of engineer, and just about anyone who studies or does any kind of science.

Footnotes

1. US Energy Information Administration, *Primary Energy Consumption by Source and Sector, 2012*, Total Energy [www.eia.gov]. Data derived from US Energy Information Administration, *Monthly Energy Review* (January 2014).

11.1.2: Energy

Energy can be defined as the capacity to supply heat or do work. One type of work (w) is the process of causing matter to move against an opposing force. For example, we do work when we inflate a bicycle tire—we move matter (the air in the pump) against the opposing force of the air surrounding the tire.

Like matter, energy comes in different types. One scheme classifies energy into two types: potential energy, the energy an object has because of its relative position, composition, or condition, and kinetic energy, the energy that an object possesses because of its motion. Water at the top of a waterfall or dam has potential energy because of its position; when it flows downward through generators, it has kinetic energy that can be used to do work and produce electricity in a hydroelectric plant (Figure 11.1.3). A battery has potential energy because the chemicals within it can produce electricity that can do work.



(a) (b)

Figure 11.1.3: (a) Water that is higher in elevation, for example, at the top of Victoria Falls, has a higher potential energy than water at a lower elevation. As the water falls, some of its potential energy is converted into kinetic energy. (b) If the water flows through generators at the bottom of a dam, such as the Hoover Dam shown here, its kinetic energy is converted into electrical energy. (credit a: modification of work by Steve Jurvetson; credit b: modification of work by “curimedia”/Wikimedia commons).

Energy can be converted from one form into another, but all of the energy present before a change occurs always exists in some form after the change is completed. This observation is expressed in the law of conservation of energy: during a chemical or physical change, energy can be neither created nor destroyed, although it can be changed in form. (This is also one version of the first law of thermodynamics, as you will learn later.)

When one substance is converted into another, there is always an associated conversion of one form of energy into another. Heat is usually released or absorbed, but sometimes the conversion involves light, electrical energy, or some other form of energy. For example, chemical energy (a type of potential energy) is stored in the molecules that compose gasoline. When gasoline is

combusted within the cylinders of a car's engine, the rapidly expanding gaseous products of this chemical reaction generate mechanical energy (a type of kinetic energy) when they move the cylinders' pistons.

According to the law of conservation of matter (seen in an earlier chapter), there is no detectable change in the total amount of matter during a chemical change. When chemical reactions occur, the energy changes are relatively modest and the mass changes are too small to measure, so the laws of conservation of matter and energy hold well. However, in nuclear reactions, the energy changes are much larger (by factors of a million or so), the mass changes are measurable, and matter-energy conversions are significant. This will be examined in more detail in a later chapter on nuclear chemistry. To encompass both chemical and nuclear changes, we combine these laws into one statement: The total quantity of matter and energy in the universe is fixed.

11.1.3: Thermal Energy, Temperature, and Heat

Thermal energy is kinetic energy associated with the random motion of atoms and molecules. Temperature is a quantitative measure of "hot" or "cold." When the atoms and molecules in an object are moving or vibrating quickly, they have a higher average kinetic energy (KE), and we say that the object is "hot." When the atoms and molecules are moving slowly, they have lower KE, and we say that the object is "cold" (Figure 11.1.4). Assuming that no chemical reaction or phase change (such as melting or vaporizing) occurs, increasing the amount of thermal energy in a sample of matter will cause its temperature to increase. And, assuming that no chemical reaction or phase change (such as condensation or freezing) occurs, decreasing the amount of thermal energy in a sample of matter will cause its temperature to decrease.

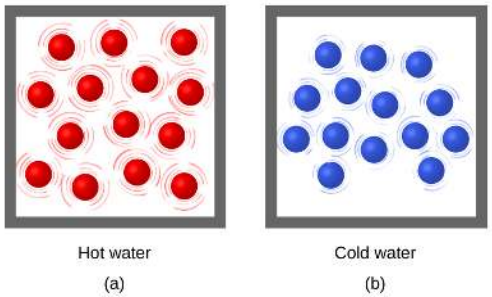


Figure 11.1.4: (a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water.

Most substances expand as their temperature increases and contract as their temperature decreases. This property can be used to measure temperature changes, as shown in Figure 11.1.5. The operation of many thermometers depends on the expansion and contraction of substances in response to temperature changes.

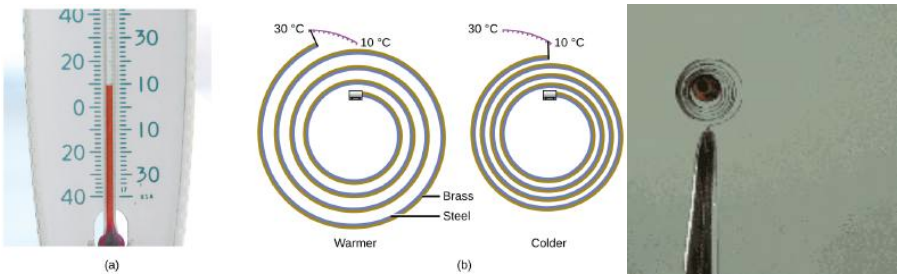


Figure 11.1.5: (a) In an alcohol or mercury thermometer, the liquid (dyed red for visibility) expands when heated and contracts when cooled, much more so than the glass tube that contains the liquid. (b) In a bimetallic thermometer, two different metals (such as brass and steel) form a two-layered strip. When heated or cooled, one of the metals (brass) expands or contracts more than the other metal (steel), causing the strip to coil or uncoil. Both types of thermometers have a calibrated scale that indicates the temperature. (credit a: modification of work by "dwstucke"/Flickr). (c) The demonstration allows one to view the effects of heating and cooling a coiled bimetallic strip.A bimetallic coil from a thermometer reacts to the heat from a lighter, by uncoiling and then coiling back up when the lighter is removed. Animation used with permission from Hustvedt (via Wikipedia).

Heat (q) is the transfer of thermal energy between two bodies at different temperatures. Heat flow increases the thermal energy of one body and decreases the thermal energy of the other. Figure 11.1.6 shows what happens when two materials at different temperatures are in contact. Initially H, the material at high temperature and high thermal energy, and L, the material at low temperature and low thermal energy, are not in contact. If H is placed in contact with L, the thermal energy flows spontaneously from substance H to substance L. The temperature of substance H will decrease, as the kinetic energy transfers to L; the temperature of substance L will increase, as it gaines kinetic energy from H. Heat flow continues until the two substances are at the same temperature (Figure 11.1.6).

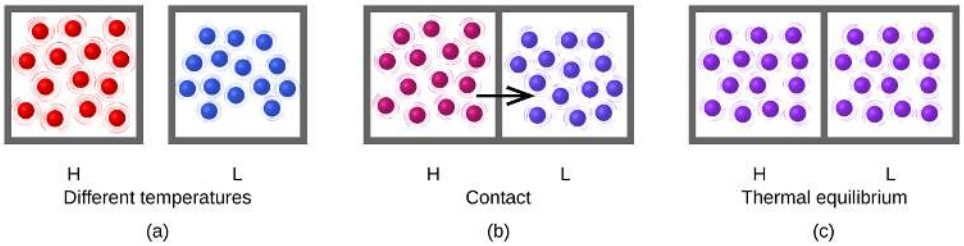


Figure 11.1.6: (a) Substances H and L are initially at different temperatures, and their atoms have different average kinetic energies. (b) When they are put into contact with each other, collisions between the molecules result in the transfer of kinetic (thermal) energy from the hotter to the cooler matter. (c) The two objects reach "thermal equilibrium" when both substances are at the same temperature, and their molecules have the same average kinetic energy.

Matter undergoing chemical reactions and physical changes can release or absorb heat. A change that releases heat is called an exothermic process. For example, the combustion reaction that occurs when using an oxyacetylene torch is an exothermic process—this process also releases energy in the form of light as evidenced by the torch's flame (Figure 11.1.7*a*). A reaction or change that absorbs heat is an endothermic process. A cold pack used to treat muscle strains provides an example of an endothermic process. When the substances in the cold pack (water and a salt like ammonium nitrate) are brought together, the resulting process absorbs heat, leading to the sensation of cold.



Figure 11.1.7: (a) An oxyacetylene torch produces heat by the combustion of acetylene in oxygen. The energy released by this exothermic reaction heats and then melts the metal being cut. The sparks are tiny bits of the molten metal flying away. (b) A cold pack uses an endothermic process to create the sensation of cold. (credit a: modification of work by "Skatebiker"/Wikimedia commons).

11.1.4: Measuring Energy and Heat Capacity

Historically, energy was measured in units of calories (cal). A calorie is the amount of energy required to raise one gram of water by 1 degree C (1 kelvin). However, this quantity depends on the atmospheric pressure and the starting temperature of the water. The ease of measurement of energy changes in calories has meant that the calorie is still frequently used. The Calorie (with a capital C), or large calorie, commonly used in quantifying food energy content, is a kilocalorie. The SI unit of heat, work, and energy is the joule. A joule (J) is defined as the amount of energy used when a force of 1 newton moves an object 1 meter. It is named in honor of the English physicist James Prescott Joule. One joule is equivalent to 1 kg m^2/s^2, which is also called 1 newton–meter. A kilojoule (kJ) is 1000 joules. To standardize its definition, 1 calorie has been set to equal 4.184 joules.

We now introduce two concepts useful in describing heat flow and temperature change. The heat capacity (C) of a body of matter is the quantity of heat (q) it absorbs or releases when it experiences a temperature change (ΔT) of 1 degree Celsius (or equivalently, 1 kelvin)

$$C = \frac{q}{\Delta T} \tag{11.1.1}$$

Heat capacity is determined by both the type and amount of substance that absorbs or releases heat. It is therefore an extensive property—its value is proportional to the amount of the substance.

For example, consider the heat capacities of two cast iron frying pans. The heat capacity of the large pan is five times greater than that of the small pan because, although both are made of the same material, the mass of the large pan is five times greater than the mass of the small pan. More mass means more atoms are present in the larger pan, so it takes more energy to make all of those

atoms vibrate faster. The heat capacity of the small cast iron frying pan is found by observing that it takes 18,150 J of energy to raise the temperature of the pan by 50.0 °C

$$C_{\text{small pan}} = \frac{18,140 \text{ J}}{50.0 \text{ }^\circ\text{C}} = 363 \text{ J/}^\circ\text{C} \tag{11.1.2}$$

The larger cast iron frying pan, while made of the same substance, requires 90,700 J of energy to raise its temperature by 50.0 °C. The larger pan has a (proportionally) larger heat capacity because the larger amount of material requires a (proportionally) larger amount of energy to yield the same temperature change:

$$C_{\text{large pan}} = \frac{90,700 \text{ J}}{50.0 \text{ }^\circ\text{C}} = 1814 \text{ J/}^\circ\text{C} \tag{11.1.3}$$

The specific heat capacity (*c*) of a substance, commonly called its "specific heat," is the quantity of heat required to raise the temperature of 1 gram of a substance by 1 degree Celsius (or 1 kelvin):

$$c = \frac{q}{\text{m}\Delta\text{T}} \tag{11.1.4}$$

Specific heat capacity depends only on the kind of substance absorbing or releasing heat. It is an intensive property—the type, but not the amount, of the substance is all that matters. For example, the small cast iron frying pan has a mass of 808 g. The specific heat of iron (the material used to make the pan) is therefore:

$$c_{\text{iron}} = \frac{18,140 \text{ J}}{(808 \text{ g})(50.0 \text{ }^\circ\text{C})} = 0.449 \text{ J/g }^\circ\text{C} \tag{11.1.5}$$

The large frying pan has a mass of 4040 g. Using the data for this pan, we can also calculate the specific heat of iron:

$$c_{\text{iron}} = \frac{90,700 \text{ J}}{(4,040 \text{ g})(50.0 \text{ }^\circ\text{C})} = 0.449 \text{ J/g }^\circ\text{C} \tag{11.1.6}$$

Although the large pan is more massive than the small pan, since both are made of the same material, they both yield the same value for specific heat (for the material of construction, iron). Note that specific heat is measured in units of energy per temperature per mass and is an intensive property, being derived from a ratio of two extensive properties (heat and mass). The molar heat capacity, also an intensive property, is the heat capacity per mole of a particular substance and has units of J/mol °C (Figure 11.1.8).



Figure 11.1.8: Due to its larger mass, a large frying pan has a larger heat capacity than a small frying pan. Because they are made of the same material, both frying pans have the same specific heat. (credit: Mark Blaser).

Liquid water has a relatively high specific heat (about 4.2 J/g °C); most metals have much lower specific heats (usually less than 1 J/g °C). The specific heat of a substance varies somewhat with temperature. However, this variation is usually small enough that we will treat specific heat as constant over the range of temperatures that will be considered in this chapter. Specific heats of some common substances are listed in Table 11.1.1.

Table 11.1.1: Specific Heats of Common Substances at 25 °C and 1 bar

Substance	Symbol (state)	Specific Heat (J/g °C)
helium	He(*g*)	5.193
water	$H_2O(l)$	4.184

Substance	Symbol (state)	Specific Heat (J/g °C)
ethanol	$C_2H_6O(l)$	2.376
ice	$H_2O(s)$	2.093 (at −10 °C)
water vapor	$H_2O(g)$	1.864
nitrogen	$N_2(g)$	1.040
aluminum	Al(s)	0.897
carbon dioxide	$CO_2(g)$	0.853
argon	Ar(g)	0.522
iron	Fe(s)	0.449
copper	Cu(s)	0.385
lead	Pb(s)	0.130
gold	Au(s)	0.129

If we know the mass of a substance and its specific heat, we can determine the amount of heat, q, entering or leaving the substance by measuring the temperature change before and after the heat is gained or lost:

$$\begin{aligned} q &= (\text{specific heat}) \times (\text{mass of substance}) \times (\text{temperature change}) \\ q &= c \times m \times \Delta T \\ &= c \times m \times (T_{\text{final}} - T_{\text{initial}}) \end{aligned}$$

In this equation, c is the specific heat of the substance, m is its mass, and ΔT (which is read “delta T”) is the temperature change, $T_{\text{final}} - T_{\text{initial}}$. If a substance gains thermal energy, its temperature increases, its final temperature is higher than its initial temperature, $T_{\text{final}} - T_{\text{initial}}$ has a positive value, and the value of q is positive. If a substance loses thermal energy, its temperature decreases, the final temperature is lower than the initial temperature, $T_{\text{final}} - T_{\text{initial}}$ has a negative value, and the value of q is negative.

Example 11.1.1: Measuring Heat

A flask containing 8.0×10^2 g of water is heated, and the temperature of the water increases from 21 °C to 85 °C. How much heat did the water absorb?

Solution

To answer this question, consider these factors:

- the specific heat of the substance being heated (in this case, water)
- the amount of substance being heated (in this case, 800 g)
- the magnitude of the temperature change (in this case, from 21 °C to 85 °C).

The specific heat of water is 4.184 J/g °C, so to heat 1 g of water by 1 °C requires 4.184 J. We note that since 4.184 J is required to heat 1 g of water by 1 °C, we will need 800 times as much to heat 800 g of water by 1 °C. Finally, we observe that since 4.184 J are required to heat 1 g of water by 1 °C, we will need 64 times as much to heat it by 64 °C (that is, from 21 °C to 85 °C).

This can be summarized using the equation:

$$\begin{aligned} q &= c \times m \times \Delta T \\ &= c \times m \times (T_{\text{final}} - T_{\text{initial}}) \\ &= (4.184 \text{ J/ } \cancel{\text{g}}^{\circ}\text{C}) \times (800 \text{ } \cancel{\text{g}}) \times (85 - 21)^{\circ}\text{C} \\ &= (4.184 \text{ J/ } \cancel{\text{g}}^{\circ} \cancel{\text{C}}) \times (800 \text{ } \cancel{\text{g}}) \times (64)^{\circ} \cancel{\text{C}} \\ &= 210,000 \text{ J} (= 210 \text{ kJ}) \end{aligned}$$

Because the temperature increased, the water absorbed heat and q is positive.

Exercise 11.1.1

How much heat, in joules, must be added to a 5.00×10^2 g iron skillet to increase its temperature from 25 °C to 250 °C? The specific heat of iron is 0.451 J/g °C.

Answer

5.05×10^4 J

Note that the relationship between heat, specific heat, mass, and temperature change can be used to determine any of these quantities (not just heat) if the other three are known or can be deduced.

Example 11.1.2: Determining Specific Heat

A piece of unknown metal weighs 348 g. When the metal piece absorbs 6.64 kJ of heat, its temperature increases from 22.4 °C to 43.6 °C. Determine the specific heat of this metal (which might provide a clue to its identity).

Solution

Since mass, heat, and temperature change are known for this metal, we can determine its specific heat using the relationship:

$$\begin{aligned} q &= c \times m \times \Delta T \\ &= c \times m \times (T_{\text{final}} - T_{\text{initial}}) \end{aligned}$$

Substituting the known values:

$$6,640 \text{ J} = c \times (348 \text{ g}) \times (43.6 - 22.4) \text{ }^{\circ}\text{C}$$

Solving:

$$c = \frac{6,640 \text{ J}}{(348 \text{ g}) \times (21.2^{\circ}\text{C})} = 0.900 \text{ J/g }^{\circ}\text{C}$$

Comparing this value with the values in Table 11.1.1, this value matches the specific heat of aluminum, which suggests that the unknown metal may be aluminum.

Exercise 11.1.2

A piece of unknown metal weighs 217 g. When the metal piece absorbs 1.43 kJ of heat, its temperature increases from 24.5 °C to 39.1 °C. Determine the specific heat of this metal, and predict its identity.

Answer

$c = 0.45$ J/g °C; the metal is likely to be iron from checking Table 11.1.1

11.1.5: Melting and Freezing

When we heat a crystalline solid, the average kinetic energy of its atoms, molecules, or ions increase and the solid gets hotter. At some point, the added energy becomes large enough to overcome the forces holding the molecules or ions of the solid in their fixed positions. At this temperature the solid begins to melt and turn into a liquid. When this happens the temperature of the solid stops rising. The additional heat continues to melt the solid. Figure 11.1.10 shows that the temperature does not change until all the solid melts and then continued heating increases the temperature of the liquid.

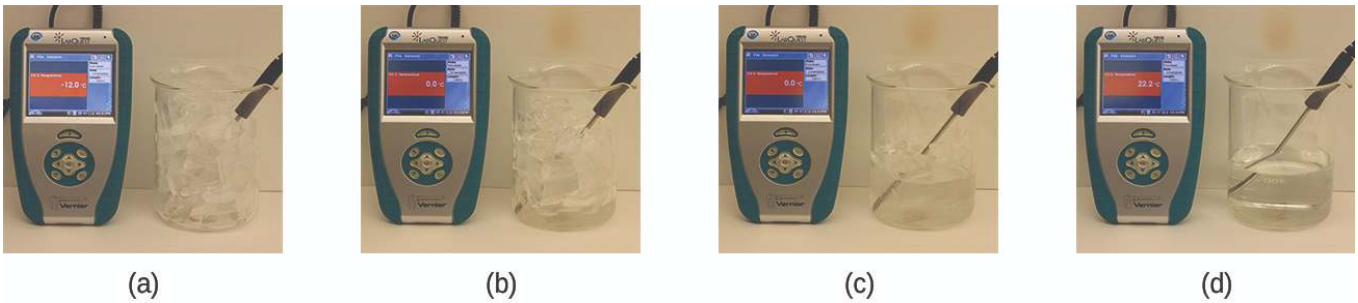


Figure 11.1.10: (a) This beaker of ice has a temperature of −12.0 °C. (b) After 10 minutes the ice has absorbed enough heat from the air to warm to 0 °C. A small amount has melted. (c) Thirty minutes later, the ice has absorbed more heat, but its temperature is still 0 °C. The ice melts without changing its temperature. (d) Only after all the ice has melted does the heat absorbed cause the temperature to increase to 22.2 °C. (credit: modification of work by Mark Ott).

If we stop heating during melting and place the mixture of solid and liquid in an insulated container the solid and liquid phases remain in equilibrium. This hapens with a mixture of ice and water in a good thermos; almost no heat gets in or out, and the mixture of solid ice and liquid water remains for hours. In a mixture of solid and liquid at equilibrium, the solid melts and the liquid freezes at the same rate, the amount of solid and liquid remains constant. The temperature with both the solid and liquid present is the melting point of the solid or the freezing point of the liquid. The terms melting or freezing depend on the direction. Solid to liquid is melting and liquid to solid is freezing).

The amount of heat required to change one mole of a substance from the solid state to the liquid state is the enthalpy of fusion, ΔH_{fus} of the substance. The enthalpy of fusion of ice is 334 J/g at 0 °C. Fusion (melting) is an endothermic process so heat must be added to cause melting:

$$\mathrm{H_2O_{(s)} \rightarrow H_2O_{(l)} \quad \Delta H_{fus} = 334\ J/g} \tag{11.1.7}$$

The reciprocal process, freezing, is an exothermic process, so heat must be removed. The amount of heat removed to freeze a gram of water is the same as the amount of heat added to melt a gram of ice. All that changes is the sign, so the enthalpy change for freezing is −334 J/g at 0 °C:

$$\mathrm{H_2O_{(l)} \rightarrow H_2O_{(s)} \quad \Delta H_{frz} = -\Delta H_{fus} = -334\ J/g} \tag{11.1.8}$$

The enthalpy of fusion and the melting point of a crystalline solid depend on the strength of the attractive forces between the units present in the crystal. Molecules with weak attractive forces form crystals with low melting points. Crystals consisting of particles with stronger attractive forces melt at higher temperatures.

11.1.6: Enthalpy of Vaporization

Vaporization, when a liquid changes into a gas, is an endothermic process that requires heat. This causes the cooling effect when you leave a swimming pool or a shower and the water on your skin evaporates. When the water evaporates, it removes heat from your skin and causes you to feel cold. The energy change associated with the vaporization process is the enthalpy of vaporization, ΔH_{vap}. The vaporization of water at standard temperature is represented by:

$$\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(g) \quad \Delta H_{vap} = 2260\ \mathrm{J/g}$$

As described in the chapter on thermochemistry, the reverse of an endothermic process is exothermic. And so, the condensation of a gas releases heat:

$$\mathrm{H_2O}(g) \longrightarrow \mathrm{H_2O}(l) \quad \Delta H_{con} = -\Delta H_{vap} = -2260\ \mathrm{J/g}$$

The enthalpy of vaporization is also the energy required when a liquid at the boiling point changes into a gas. As with melting, when you add heat to a liquid the temperature will rise until the liquid reaches a specific temperature - the boiling point. At this temperature any additional heat does not change the temperature of the liquid, instead it causes the liquid to change into a gas. If a system goes in the other direction and a gas condenses to a liquid, energy must be released for the phase change to occur.

Example 11.1.3: Using Enthalpy of Vaporization

One way our body is cooled is by evaporation of the water in sweat (Figure 11.1.9). In very hot climates, we can lose as much as 1.5 L of sweat per day. Although sweat is not pure water, we can get an approximate value of the amount of heat removed by evaporation by assuming that it is. How much heat is required to evaporate 1.5 L of water (1.5 kg) at T = 37 °C (normal body temperature); $\Delta H_{vap} = 2260\ J/g$ at 37 °C.



Figure 11.1.9: Evaporation of sweat helps cool the body. (credit: “Kullez”/Flickr)

Solution We start with the known volume of sweat (approximated as just water) and use the given information to convert to the amount of heat needed:

$$1.5\ \cancel{\text{L}} \times \frac{1000\ \cancel{\text{g}}}{1\ \cancel{\text{L}}} \times \frac{2260\ \text{J}}{1\ \cancel{\text{g}}} = 3.6 \times 10^6\ \text{J}$$

Thus, 3600 kJ of heat are removed by the evaporation of 1.5 L of water.

Exercise 11.1.3: Boiling Ammonia

How much heat is required to evaporate 100.0 g of liquid ammonia, NH_3, at its boiling point if its enthalpy of vaporization is 4.8 kJ/mol?

Answer

28 kJ

11.1.7: Heating and Cooling Curves

The heat required to change temperature, melt, and evaporate a sample can be combined into a heating curve like the one shown in Figure 11.1.11. The relation between the amount of heat absorbed or related by a substance, q, and its accompanying temperature change, ΔT, is:

$$q = mc\Delta T$$

Where m is the mass of the substance and c is its specific heat. The relation applies to matter being heated or cooled but not undergoing a change in state. These temperature changes are shown in Figure 11.1.11for water as a solid, liquid, and gas.

When a substance being heated or cooled reaches a temperature corresponding to one of its phase transitions, the melting or boiling points, additional heat is used to overcome intermolecular attractions, not to changing the kinetic energies or temperature. While a

substance is undergoing a change in state the temperature remains constant, as shown in the horizontal regions of Figure 11.1.11 where the solid melts and the liquid evaporates.

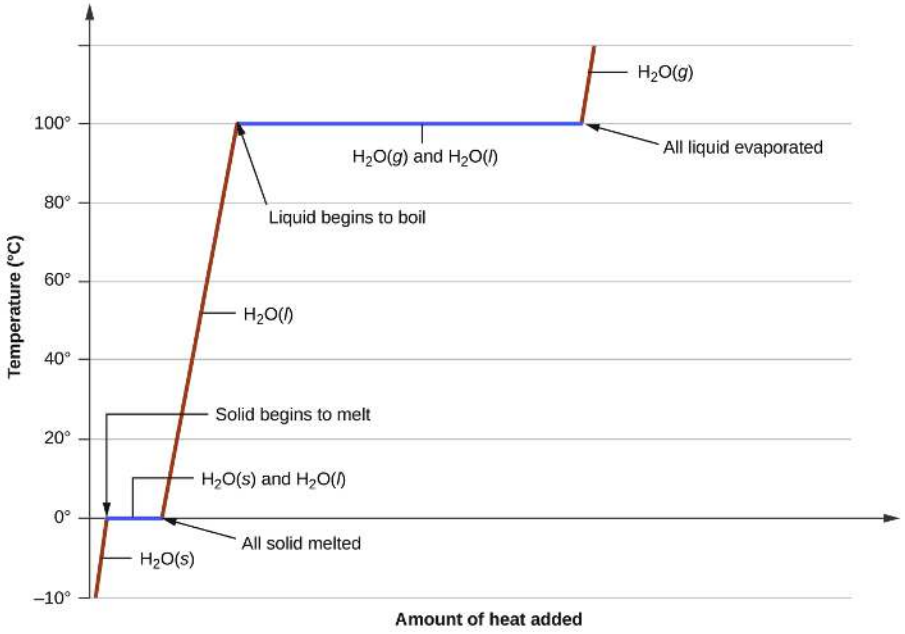


Figure 11.1.11: A typical heating curve for a substance depicts changes in temperature that result as the substance absorbs increasing amounts of heat. Plateaus in the curve (regions of constant temperature) are exhibited when the substance undergoes phase transitions.

Consider the example of heating a pot of water to boiling. A stove burner will supply heat at a roughly constant rate; initially, this heat serves to increase the water's temperature. When the water reaches its boiling point, the temperature remains constant despite the continued input of heat from the stove burner. This same temperature is maintained by the water as long as it is boiling. If the burner setting is increased to provide heat at a greater rate, the water temperature does not rise, but instead the boiling becomes more vigorous (rapid). This behavior is observed for other phase transitions as well: Figure 11.1.10shows the temperature remains constant while the ice melts.

Example 11.1.4: Total Heat Needed to Change Temperature and Phase for a Substance

How much heat is required to convert 135 g of ice at −15 °C into water vapor at 120 °C?

Solution

The transition described involves the following steps:

1. Heat ice from −15 °C to 0 °C
2. Melt ice
3. Heat water from 0 °C to 100 °C
4. Boil water
5. Heat steam from 100 °C to 120 °C

The heat needed to change the temperature of a given substance (with no change in phase) is: $q = m \times c \times \Delta T$ (see previous chapter on thermochemistry). The heat needed to induce a given change in phase is given by $q = n \times \Delta H$.

Using these equations with the appropriate values for specific heat of ice, water, and steam, and enthalpies of fusion and vaporization, we have:

$$
\begin{aligned}
q_{\text{total}} &= (m \cdot c \cdot \Delta T)_{\text{ice}} + n \cdot \Delta H_{\text{fus}} + (m \cdot c \cdot \Delta T)_{\text{water}} + n \cdot \Delta H_{\text{vap}} + (m \cdot c \cdot \Delta T)_{\text{steam}} \\
&= (135\ \text{g} \cdot 2.09\ \text{J/g} \cdot {}^\circ\text{C} \cdot 15\,{}^\circ\text{C}) + (135\ \text{g} \cdot 334\ \text{J/g}) \\
&+ (135\ \text{g} \cdot 4.18\ \text{J/g} \cdot {}^\circ\text{C} \cdot 100\,{}^\circ\text{C}) + (135\ \text{g} \cdot 2260\ \text{J/g}) \\
&+ (135\ \text{g} \cdot 1.84\ \text{J/g} \cdot {}^\circ\text{C} \cdot 20\,{}^\circ\text{C}) \\
&= 4230\ \text{J} + 45.0\ \text{kJ} + 56,500\ \text{J} + 305\ \text{kJ} + 4970\ \text{J}
\end{aligned}
$$

Converting the quantities in J to kJ for convenience and adding the steps gives the total heat required:

$$= 4.23\ \text{kJ} + 45.0\ \text{kJ} + 56.5\ \text{kJ} + 305\ \text{kJ} + 4.97\ \text{kJ} = 416\ \text{kJ}$$

? Exercise 11.1.4

What is the total amount of heat released when 94.0 g water at 80.0 °C cools to form ice at −30.0 °C?

Answer

40.5 kJ

11.1.8: Conservation of Energy Calcualtions - Video

Video Topics

The Law of conservation of energy says that the total energy between a system and its surroundings must remain constant. This means heat lost by a system is gained by its surroundings and vice versa. This idea is expressed by the equation q of the system = - q of the surroundings. Using this equation the moment of heat between two different bodies can be calculated. Also the final temperature of the combination can be found. This video contains a sample problem, which involves these concepts.

Link to Video

Conservation of Energy: The Movement of Heat between Substances: https://youtu.be/pGEYy-pNHBg



- Prof. Steven Farmer (Sonoma State University)

11.1.9: Solar Thermal Energy Power Plants

The sunlight that reaches the earth contains thousands of times more energy than we presently capture. Solar thermal systems provide one possible solution to the problem of converting energy from the sun into energy we can use. Large-scale solar thermal

plants have different design specifics, but all concentrate sunlight to heat some substance; the heat “stored” in that substance is then converted into electricity.

The Solana Generating Station in Arizona’s Sonora Desert produces 280 megawatts of electrical power. It uses parabolic mirrors that focus sunlight on pipes filled with a heat transfer fluid (HTF) (Figure 11.1.12). The HTF then does two things: It turns water into steam, which spins turbines, which in turn produces electricity, and it melts and heats a mixture of salts, which functions as a thermal energy storage system. After the sun goes down, the molten salt mixture can then release enough of its stored heat to produce steam to run the turbines for 6 hours. Molten salts are used because they possess a number of beneficial properties, including high heat capacities and thermal conductivities.

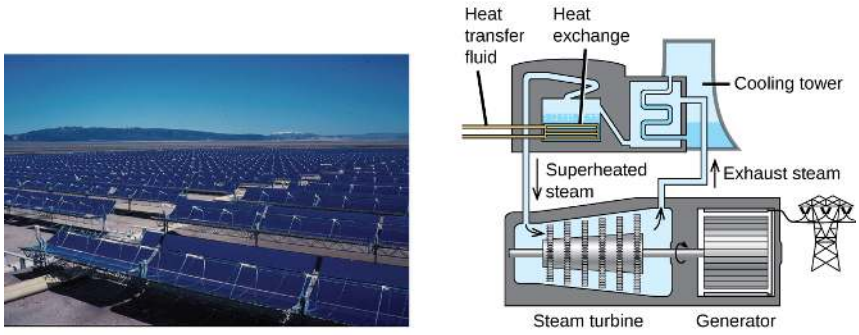


Figure 11.1.12: This solar thermal plant uses parabolic trough mirrors to concentrate sunlight. (credit a: modification of work by Bureau of Land Management)

The 377-megawatt Ivanpah Solar Generating System, located in the Mojave Desert in California, is the largest solar thermal power plant in the world (Figure 11.1.13). Its 170,000 mirrors focus huge amounts of sunlight on three water-filled towers, producing steam at over 538 °C that drives electricity-producing turbines. It produces enough energy to power 140,000 homes. Water is used as the working fluid because of its large heat capacity and heat of vaporization.



Figure 11.1.13: (a) The Ivanpah solar thermal plant uses 170,000 mirrors to concentrate sunlight on water-filled towers. (b) It covers 4000 acres of public land near the Mojave Desert and the California-Nevada border. (credit a: modification of work by Craig Dietrich; credit b: modification of work by “USFWS Pacific Southwest Region”/Flickr)

11.1.10: Summary

Energy is the capacity to do work (applying a force to move matter). Kinetic energy (KE) is the energy of motion; potential energy is energy due to relative position, composition, or condition. When energy is converted from one form into another, energy is neither created nor destroyed (law of conservation of energy or first law of thermodynamics). Matter has thermal energy due to the KE of its molecules and temperature that corresponds to the average KE of its molecules. Heat is energy that is transferred between objects at different temperatures; it flows from a high to a low temperature. Chemical and physical processes can absorb heat (endothermic) or release heat (exothermic). The SI unit of energy, heat, and work is the joule (J). Specific heat and heat capacity are measures of the energy needed to change the temperature of a substance or object. The amount of heat absorbed or released by a substance depends directly on the type of substance, its mass, and the temperature change it undergoes.

11.1.11: Key Equations

- $q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$

Glossary

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

endothermic process
chemical reaction or physical change that absorbs heat

energy
capacity to supply heat or do work

exothermic process
chemical reaction or physical change that releases heat

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)

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

kinetic energy
energy of a moving body, in joules, equal to $\frac{1}{2}mv^2$ (where m = mass and v = velocity)

potential energy
energy of a particle or system of particles derived from relative position, composition, or condition

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)

temperature
intensive property of matter that is a quantitative measure of “hotness” and “coldness”

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

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

---

This page titled 11.1: Energy Basics is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

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

- **5.1: Prelude to Thermochemistry** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.
- **10.4: Phase Transitions** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

11.2: Calorimetry

Learning Objectives

- Explain the technique of calorimetry
- Calculate and interpret heat and related properties using typical calorimetry data

One technique we can use to measure the amount of heat involved in a chemical or physical process is known as calorimetry. Calorimetry is used to measure amounts of heat transferred to or from a substance. To do so, the heat is exchanged with a calibrated object (calorimeter). The change in temperature of the measuring part of the calorimeter is converted into the amount of heat (since the previous calibration was used to establish its heat capacity). The measurement of heat transfer using this approach requires the definition of a system (the substance or substances undergoing the chemical or physical change) and its surroundings (the other components of the measurement apparatus that serve to either provide heat to the system or absorb heat from the system). Knowledge of the heat capacity of the surroundings, and careful measurements of the masses of the system and surroundings and their temperatures before and after the process allows one to calculate the heat transferred as described in this section.

A calorimeter is a device used to measure the amount of heat involved in a chemical or physical process. For example, when an exothermic reaction occurs in solution in a calorimeter, the heat produced by the reaction is absorbed by the solution, which increases its temperature. When an endothermic reaction occurs, the heat required is absorbed from the thermal energy of the solution, which decreases its temperature (Figure 11.2.1). The temperature change, along with the specific heat and mass of the solution, can then be used to calculate the amount of heat involved in either case.

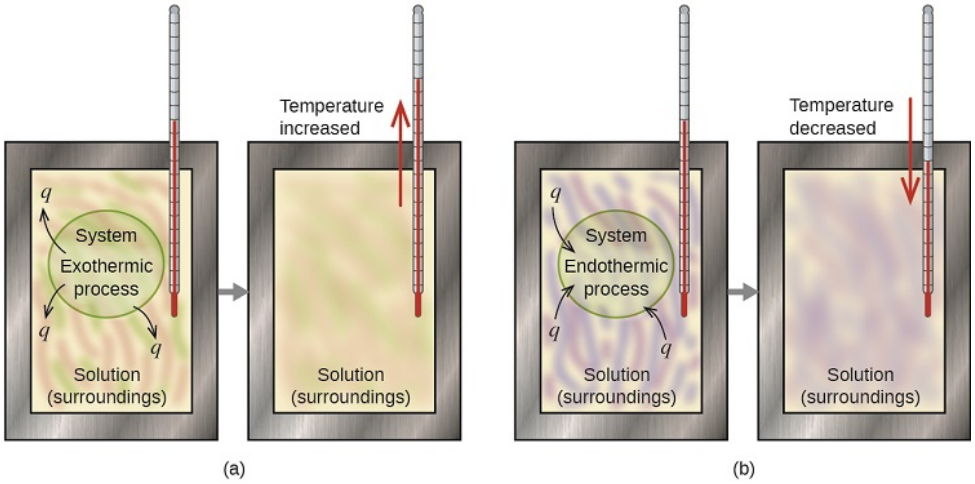


Figure 11.2.1: In a calorimetric determination, either (a) an exothermic process occurs and heat, q, is negative, indicating that thermal energy is transferred from the system to its surroundings, or (b) an endothermic process occurs and heat, q, is positive, indicating that thermal energy is transferred from the surroundings to the system.

By convention, q is given a negative (-) sign when the system releases heat to the surroundings (exothermic); q is given a positive (+) sign when the system absorbs heat from the surroundings (endothermic).

Scientists use well-insulated calorimeters that minimize the transfer of heat between the calorimeter and its environment. This enables the accurate determination of the heat involved in chemical processes, the energy content of foods, and so on. General chemistry students often use simple calorimeters constructed from polystyrene cups (Figure 11.2.2). These easy-to-use “coffee cup” calorimeters allow more heat exchange with their surroundings, and therefore produce less accurate energy values.

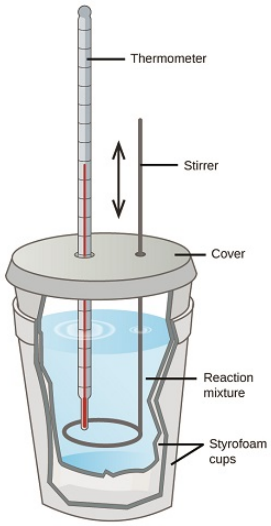


Figure 11.2.2: A simple calorimeter can be constructed from two polystyrene cups. A thermometer and stirrer extend through the cover into the reaction mixture.

Commercial solution calorimeters are also available. More expensive calorimeters used for industry and research typically have a well-insulated, fully enclosed reaction vessel, motorized stirring mechanism, and a more accurate temperature sensor as shown in Figure 11.2.3.

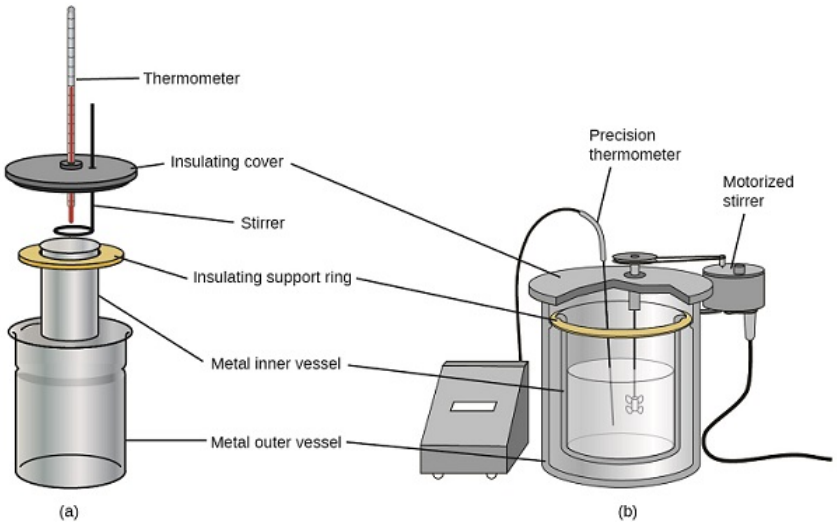


Figure 11.2.3: Commercial solution calorimeters range from (a) simple, inexpensive models for student use to (b) expensive, more accurate models for industry and research.

Before we practice calorimetry problems involving chemical reactions, consider a simple example that illustrates the core idea behind calorimetry. Suppose we initially have a high-temperature substance, such as a hot piece of metal and a low-temperature substance, such as cool water. If we place the metal in the water, heat will flow from the metal to the water. The temperature of the metal will decrease, and the temperature of the water will increase, until the two substances have the same temperature—that is, when they reach thermal equilibrium (Figure 11.2.4). If this occurs in a calorimeter, ideally all of this heat transfer occurs between the two substances, with no heat gained or lost by either the calorimeter or the calorimeter's surroundings. Under these ideal circumstances, the net heat change is zero:

$$q_{\text{metal}} + q_{\text{water}} = 0 \tag{11.2.1}$$

This relationship can be rearranged to show that the heat gained by substance metal is equal to the heat lost by substance W:

$$q_{\text{metal}} = -q_{\text{water}} \tag{11.2.2}$$

The magnitude of the heat (change) is therefore the same for both substances, and the negative sign merely shows that q_{metal} and q_{water} are opposite in direction of heat flow (gain or loss) but does not indicate the arithmetic sign of either q value (that is determined by whether the matter in question gains or loses heat, per definition). In the specific situation described, q_{metal} is a negative value and q_{water} is positive, since heat is transferred from the metal to the water.

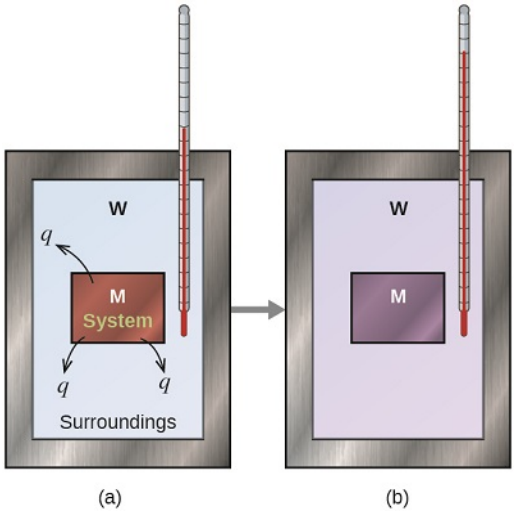


Figure 11.2.4: In a simple calorimetry process, (a) heat, q, is transferred from the hot metal, M, to the cool water, W, until (b) both are at the same temperature.

Example 11.2.1: Heat Transfer between Substances at Different Temperatures

A hot 360-g piece of rebar (a steel rod used for reinforcing concrete) is dropped into 425 mL of water at 24.0 °C. The final temperature of the water is measured as 42.7 °C. Calculate the initial temperature of the piece of rebar. Assume the specific heat of steel is approximately the same as that for iron (Table T4), and that all heat transfer occurs between the rebar and the water (there is no heat exchange with the surroundings).

Solution

The temperature of the water increases from 24.0 °C to 42.7 °C, so the water absorbs heat. That heat came from the piece of rebar, which initially was at a higher temperature. Assuming that all heat transfer was between the rebar and the water, with no heat "lost" to the surroundings, then heat given off by rebar = − heat taken in by water, or:

$$q_{\text{rebar}} = -q_{\text{water}}$$

Since we know how heat is related to other measurable quantities, we have:

$$(c \times m \times \Delta T)_{\text{rebar}} = -(c \times m \times \Delta T)_{\text{water}}$$

Letting f = final and i = initial, in expanded form, this becomes:

$$c_{\text{rebar}} \times m_{\text{rebar}} \times (T_{\text{f,rebar}} - T_{\text{i,rebar}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{\text{f,water}} - T_{\text{i,water}})$$

The density of water is 1.0 g/mL, so 425 mL of water = 425 g. Noting that the final temperature of both the rebar and water is 42.7 °C, substituting known values yields:

$$(0.449\ \text{J/g}\ ^\circ\text{C})(360\text{g})(42.7^\circ\text{C} - T_{\text{i,rebar}}) = -(4.184\ \text{J/g}\ ^\circ\text{C})(425\ \text{g})(42.7^\circ\text{C} - 24.0^\circ\text{C})$$

$$T_{\text{i,rebar}} = \frac{(4.184\ \text{J/g}\ ^\circ\text{C})(425\ \text{g})(42.7^\circ\text{C} - 24.0^\circ\text{C})}{(0.449\ \text{J/g}\ ^\circ\text{C})(360\ \text{g})} + 42.7^\circ\text{C}$$

Solving this gives Ti,rebar= 248 °C, so the initial temperature of the rebar was 248 °C.

Exercise 11.2.1A

A 248-g piece of copper is dropped into 390 mL of water at 22.6 °C. The final temperature of the water was measured as 39.9 °C. Calculate the initial temperature of the piece of copper. Assume that all heat transfer occurs between the copper and the water.

Answer

The initial temperature of the copper was 335.6 °C.

Exercise 11.2.1B

A 248-g piece of copper initially at 314 °C is dropped into 390 mL of water initially at 22.6 °C. Assuming that all heat transfer occurs between the copper and the water, calculate the final temperature.

Answer

The final temperature (reached by both copper and water) is 38.7 °C.

This method can also be used to determine other quantities, such as the specific heat of an unknown metal.

When we use calorimetry to determine the heat involved in a chemical reaction, the same principles we have been discussing apply. Because energy is neither created nor destroyed during a chemical reaction, there is no overall energy change during the reaction. The heat produced or consumed in the reaction (the "system"), q_{reaction}, plus the heat absorbed or lost by the solution (the "surroundings"), $q_{solution}$, must add up to zero:

$$q_{\text{reaction}} + q_{\text{solution}} = 0 \tag{11.2.3}$$

This means that the amount of heat produced or consumed in the reaction equals the amount of heat absorbed or lost by the solution:

$$q_{\text{reaction}} = -q_{\text{solution}} \tag{11.2.4}$$

This concept lies at the heart of all calorimetry problems and calculations.

Example 11.2.2: Heat Produced by an Exothermic Reaction

When 50.0 mL of 0.10 M HCl(*aq*) and 50.0 mL of 1.00 M NaOH(*aq*), both at 22.0 °C, are added to a coffee cup calorimeter, the temperature of the mixture reaches a maximum of 28.9 °C. What is the approximate amount of heat produced by this reaction?

$$\text{HCl}(aq) + \text{NaOH}(aq) \longrightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$$

Solution

To visualize what is going on, imagine that you could combine the two solutions so quickly that no reaction took place while they mixed; then after mixing, the reaction took place. At the instant of mixing, you have 100.0 mL of a mixture of HCl and NaOH at 22.0 °C. The HCl and NaOH then react until the solution temperature reaches 28.9 °C.

The heat given off by the reaction is equal to that taken in by the solution. Therefore:

$$q_{\text{reaction}} = -q_{\text{solution}}$$

(It is important to remember that this relationship only holds if the calorimeter does not absorb any heat from the reaction, and there is no heat exchange between the calorimeter and its surroundings.)

Next, we know that the heat absorbed by the solution depends on its specific heat, mass, and temperature change:

$$q_{\text{solution}} = (c \times m \times \Delta T)_{\text{solution}}$$

To proceed with this calculation, we need to make a few more reasonable assumptions or approximations. Since the solution is aqueous, we can proceed as if it were water in terms of its specific heat and mass values. The density of water is approximately

1.0 g/mL, so 100.0 mL has a mass of about 1.0×10^2 g (two significant figures). The specific heat of water is approximately 4.18 J/g °C, so we use that for the specific heat of the solution. Substituting these values gives:

$$q_{\text{solution}} = (4.184\ \text{J/g}\ ^\circ\text{C})(1.0 \times 10^2\ \text{g})(28.9^\circ\text{C} - 22.0^\circ\text{C}) = 2.89 \times 10^3\ \text{J} \tag{11.2.5}$$

Finally, since we are trying to find the heat of the reaction, we have:

$$q_{\text{reaction}} = -q_{\text{solution}} = -2.89 \times 10^3\ J$$

The negative sign indicates that the reaction is exothermic. It produces 2.89 kJ of heat.

Exercise 11.2.2

When 100 mL of 0.200 M NaCl(*aq*) and 100 mL of 0.200 M $AgNO_3$(*aq*), both at 21.9 °C, are mixed in a coffee cup calorimeter, the temperature increases to 23.5 °C as solid AgCl forms. How much heat is produced by this precipitation reaction? What assumptions did you make to determine your value?

Answer

$1.34 \times 10^3\ J$; assume no heat is absorbed by the calorimeter, no heat is exchanged between the calorimeter and its surroundings, and that the specific heat and mass of the solution are the same as those for water

Thermochemistry of Hand Warmers

When working or playing outdoors on a cold day, you might use a hand warmer to warm your hands (Figure 11.2.5). A common reusable hand warmer contains a supersaturated solution of $NaC_2H_3O_2$ (sodium acetate) and a metal disc. Bending the disk creates nucleation sites around which the metastable $NaC_2H_3O_2$ quickly crystallizes (a later chapter on solutions will investigate saturation and supersaturation in more detail).

The process $\text{NaC}_2\text{H}_3\text{O}_2(aq) \longrightarrow \text{NaC}_2\text{H}_3\text{O}_2(s)$ is exothermic, and the heat produced by this process is absorbed by your hands, thereby warming them (at least for a while). If the hand warmer is reheated, the $NaC_2H_3O_2$ redissolves and can be reused.



Figure 11.2.5: Chemical hand warmers produce heat that warms your hand on a cold day. In this one, you can see the metal disc that initiates the exothermic precipitation reaction. (credit: modification of work by Science Buddies TV/YouTube)

Another common hand warmer produces heat when it is ripped open, exposing iron and water in the hand warmer to oxygen in the air. One simplified version of this exothermic reaction is

$$2\,\text{Fe(s)} + \tfrac{3}{2}\text{O}_2\text{(g)} \longrightarrow \text{Fe}_2\text{O}_3\text{(s)}$$

Salt in the hand warmer catalyzes the reaction, so it produces heat more rapidly; cellulose, vermiculite, and activated carbon help distribute the heat evenly. Other types of hand warmers use lighter fluid (a platinum catalyst helps lighter fluid oxidize exothermically), charcoal (charcoal oxidizes in a special case), or electrical units that produce heat by passing an electrical current from a battery through resistive wires.

11.2.1: Calorimetry Calculations - Video

Link to Video

Conservation of Energy: Coffee Cup Calorimetry: https://youtu.be/FwQcc17PN0k



11.2.2: Attribution

- Prof. Steven Farmer (Sonoma State University)

11.2.3: Summary

Calorimetry is used to measure the amount of thermal energy transferred in a chemical or physical process. This requires careful measurement of the temperature change that occurs during the process and the masses of the system and surroundings. These measured quantities are then used to compute the amount of heat produced or consumed in the process using known mathematical relations. Calorimeters are designed to minimize energy exchange between the system being studied and its surroundings. They range from simple coffee cup calorimeters used by introductory chemistry students to sophisticated bomb calorimeters used to determine the energy content of food.

Glossary

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

nutritional calorie (Calorie)

unit used for quantifying energy provided by digestion of foods, defined as 1000 cal or 1 kcal

surroundings

all matter other than the system being studied

system

portion of matter undergoing a chemical or physical change being studied

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 11.2: Calorimetry is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

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

11.3: Enthalpy- Introduction

Learning Objectives

- State the first law of thermodynamics
- Define enthalpy and explain its classification as a state function
- Write and balance thermochemical equations
- Calculate enthalpy changes for various chemical reactions
- Explain Hess's law and use it to compute reaction enthalpies

Thermochemistry is a branch of chemical thermodynamics, the science that deals with the relationships between heat, work, and other forms of energy in the context of chemical and physical processes. As we concentrate on thermochemistry in this chapter, we need to consider some widely used concepts of thermodynamics.

Substances act as reservoirs of energy, meaning that energy can be added to them or removed from them. Energy is stored in a substance when the kinetic energy of its atoms or molecules is raised. The greater kinetic energy may be in the form of increased translations (travel or straight-line motions), vibrations, or rotations of the atoms or molecules. When thermal energy is lost, the intensities of these motions decrease and the kinetic energy falls. The total of all possible kinds of energy present in a substance is called the internal energy (U), sometimes symbolized as E.

As a system undergoes a change, its internal energy can change, and energy can be transferred from the system to the surroundings, or from the surroundings to the system. Energy is transferred into a system when it absorbs heat (q) from the surroundings or when the surroundings do work (w) on the system. For example, energy is transferred into room-temperature metal wire if it is immersed in hot water (the wire absorbs heat from the water), or if you rapidly bend the wire back and forth (the wire becomes warmer because of the work done on it). Both processes increase the internal energy of the wire, which is reflected in an increase in the wire's temperature. Conversely, energy is transferred out of a system when heat is lost from the system, or when the system does work on the surroundings.

The relationship between internal energy, heat, and work can be represented by the equation:

$$\Delta U = q + w \tag{11.3.1}$$

as shown in Figure 11.3.1. This is one version of the first law of thermodynamics, and it shows that the internal energy of a system changes through heat flow into or out of the system (positive q is heat flow in; negative q is heat flow out) or work done on or by the system. The work, w, is positive if it is done on the system and negative if it is done by the system.

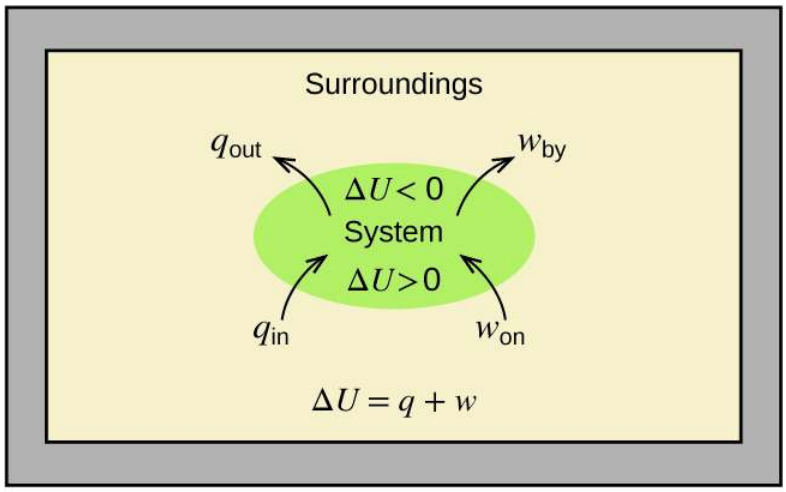


Figure 11.3.1: The internal energy, U, of a system can be changed by heat flow and work. If heat flows into the system, q_{in}, or work is done on the system, w_{on}, its internal energy increases, $\Delta U > 0$. If heat flows out of the system, q_{out}, or work is done by the system, w_{by}, its internal energy decreases, $\Delta U < 0$.

A type of work called expansion work (or pressure-volume work) occurs when a system pushes back the surroundings against a restraining pressure, or when the surroundings compress the system. An example of this occurs during the operation of an internal combustion engine. The reaction of gasoline and oxygen is exothermic. Some of this energy is given off as heat, and some does work pushing the piston in the cylinder. The substances involved in the reaction are the system, and the engine and the rest of the universe are the surroundings. The system loses energy by both heating and doing work on the surroundings, and its internal energy decreases. (The engine is able to keep the car moving because this process is repeated many times per second while the engine is running.) We will consider how to determine the amount of work involved in a chemical or physical change in the chapter on thermodynamics.

As discussed, the relationship between internal energy, heat, and work can be represented as $\Delta U = q + w$. Internal energy is a type of quantity known as a state function (or state variable), whereas heat and work are not state functions. The value of a state function depends only on the state that a system is in, and not on how that state is reached. If a quantity is not a state function, then its value *does* depend on how the state is reached. An example of a state function is altitude or elevation. If you stand on the summit of Mt. Kilimanjaro, you are at an altitude of 5895 m, and it does not matter whether you hiked there or parachuted there. The distance you traveled to the top of Kilimanjaro, however, is not a state function. You could climb to the summit by a direct route or by a more roundabout, circuitous path (Figure 11.3.2). The distances traveled would differ (distance is not a state function) but the elevation reached would be the same (altitude is a state function).

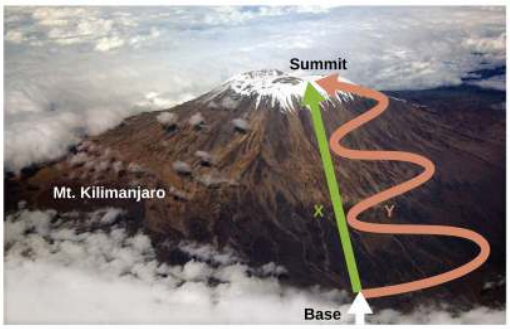


Figure 11.3.2: Paths X and Y represent two different routes to the summit of Mt. Kilimanjaro. Both have the same change in elevation (altitude or elevation on a mountain is a state function; it does not depend on path), but they have very different distances traveled (distance walked is not a state function; it depends on the path). (credit: modification of work by Paul Shaffner)

11.3.1: Enthalpy

Chemists ordinarily use a property known as enthalpy (H) to describe the thermodynamics of chemical and physical processes. Enthalpy is defined as the sum of a system's internal energy (U) and the mathematical product of its pressure (P) and volume (V):

$$H = U + PV \tag{11.3.2}$$

Since it is derived from three state functions (U, P, and V), enthalpy is also a state function. Enthalpy values for specific substances cannot be measured directly; only enthalpy changes for chemical or physical processes can be determined. For processes that take place at constant pressure (a common condition for many chemical and physical changes), the enthalpy change (ΔH) is:

$$\Delta H = \Delta U + P\Delta V \tag{11.3.3}$$

The mathematical product $P\Delta V$ represents work (w), namely, expansion or pressure-volume work as noted. By their definitions, the arithmetic signs of ΔV and w will always be opposite:

$$P\Delta V = -w \tag{11.3.4}$$

Combining these equations yields:

$$\Delta H = \Delta U + P\Delta V \tag{11.3.5}$$

$$= q_\text{p} + \cancel{w} - \cancel{w} \tag{11.3.6}$$

$$= q_\text{p} \tag{11.3.7}$$

where q_p is the heat of reaction under conditions of constant pressure.

And so, if a chemical or physical process is carried out at constant pressure with the only work done caused by expansion or contraction, then the heat flow (q_p) and enthalpy change (ΔH) for the process are equal.

The heat given off when you operate a Bunsen burner is equal to the enthalpy change of the methane combustion reaction that takes place, since it occurs at the essentially constant pressure of the atmosphere. On the other hand, the heat produced by a reaction measured in a bomb calorimeter is not equal to ΔH because the closed, constant-volume metal container prevents expansion work from occurring. Chemists usually perform experiments under normal atmospheric conditions, at constant external pressure with $q = \Delta H$, which makes enthalpy the most convenient choice for determining heat.

11.3.2: Using Enthalpy

The following conventions apply when we use ΔH:

1. Chemists use a thermochemical equation to represent the changes in both matter and energy. In a thermochemical equation, the enthalpy change of a reaction is shown as a Δ*H* value following the equation for the reaction. This ΔH value indicates the amount of heat associated with the reaction involving the number of moles of reactants and products as shown in the chemical equation. For example, consider this equation:

   $$\mathrm{H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l)} \quad \Delta H = -286\ \mathrm{kJ} \tag{11.3.8}$$

   This equation indicates that when 1 mole of hydrogen gas and 12 mole of oxygen gas at some temperature and pressure change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released to the surroundings. If the coefficients of the chemical equation are multiplied by some factor, the enthalpy change must be multiplied by that same factor (ΔH is an extensive property).

   $$\begin{array}{l}\text{(two-fold increase in amounts)} \\ \mathrm{2\,H_2}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{2\,H_2O}(l) \quad \Delta H = 2 \times (-286\ \mathrm{kJ}) = -572\ \mathrm{kJ} \\ \text{(two-fold decrease in amounts)} \\ \mathrm{\frac{1}{2}H_2}(g) + \mathrm{\frac{1}{4}O_2}(g) \longrightarrow \mathrm{\frac{1}{2}H_2O}(l) \quad \Delta H = \frac{1}{2} \times (-286\ \mathrm{kJ}) = -143\ \mathrm{kJ}\end{array}$$

2. The enthalpy change of a reaction depends on the physical state of the reactants and products of the reaction (whether we have gases, liquids, solids, or aqueous solutions), so these must be shown. For example, when 1 mole of hydrogen gas and 12 mole of oxygen gas change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released. If gaseous water forms, only 242 kJ of heat are released.

   $$\mathrm{H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g)} \quad \Delta H = -242\ \mathrm{kJ} \tag{11.3.9}$$

3. A negative value of an enthalpy change, Δ*H*, indicates an exothermic reaction; a positive value of Δ*H* indicates an endothermic reaction. If the direction of a chemical equation is reversed, the arithmetic sign of its Δ*H* is changed (a process that is

endothermic in one direction is exothermic in the opposite direction).

Example 11.3.1: Measurement of an Enthalpy Change

When 0.0500 mol of HCl(*aq*) reacts with 0.0500 mol of NaOH(*aq*) to form 0.0500 mol of NaCl(*aq*), 2.9 kJ of heat are produced. What is ΔH, the enthalpy change, per mole of acid reacting, for the acid-base reaction run under the conditions described ?

$$\mathrm{HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)}$$

Solution

For the reaction of 0.0500 mol acid (HCl), q = −2.9 kJ. This ratio

$$\frac{-2.9\ \mathrm{kJ}}{0.0500\ \mathrm{mol\ HCl}}$$

can be used as a conversion factor to find the heat produced when 1 mole of HCl reacts:

$$\Delta H = 1\ \ \mathrm{mol\ \cancel{HCl}} \times \frac{-2.9\ \mathrm{kJ}}{0.0500\ \ \mathrm{mol\ \cancel{HCl}}} = -58\ \mathrm{kJ}$$

The enthalpy change when 1 mole of HCl reacts is −58 kJ. Since that is the number of moles in the chemical equation, we write the thermochemical equation as:

$$\mathrm{HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)} \quad \Delta H = -58\ kJ}$$

Exercise 11.3.1

When 1.34 g Zn(s) reacts with 60.0 mL of 0.750 M HCl(aq), 3.14 kJ of heat are produced. Determine the enthalpy change per mole of zinc reacting for the reaction:

$$\mathrm{Zn_{(s)} + 2\,HCl_{(aq)} \longrightarrow ZnCl_{(aq)} + H_{2(g)}}$$

Answer

ΔH = −153 kJ

11.3.3: $\Delta H^\circ_{combustion}$, $\Delta H^\circ_{formation}$, ΔH°_{fusion}, $\Delta H^\circ_{vaporization}$

Be sure to take both stoichiometry and limiting reactants into account when determining the Δ*H* for a chemical reaction.

Enthalpy changes are tabulated for a variety of different processes including combustion, formation, fusion, and vaporization. For these tabulated values the reactions are under a standard set of conditions. The IUPAC standard state is for materials at a pressure of 1 bar and solutions at a concentration of 1 M. Many thermochemical tables list values at a pressure of 1 atm, which was previously used as the standard state. Fortunately Δ*H* values do not change much with pressure and the new standard is close to 1 atm (1 bar = 0.987 atm). The superscripted “o” in the enthalpy change symbol designates that the value is at standard conditions.

The enthalpy changes for many types of chemical and physical processes are available in the reference literature, including those for combustion reactions, phase transitions, and formation reactions. As we discuss these quantities, it is important to remember enthalpy is an extensive property - the amount of material matters. The tabulated enthalpy values are typically listed per-mole or per-gram. You must take this into account for any calculations. For enthalpy calculations with chemical reactions you must also take the stoichiometry and limiting reactants into account for Δ*H* calculations.

11.3.4: Summary

If a chemical change is carried out at constant pressure and the only work done is caused by expansion or contraction, *q* for the change is called the enthalpy change with the symbol Δ*H*, or ΔH° for reactions occurring under standard state conditions. The value of Δ*H* for a reaction in one direction is equal in magnitude, but opposite in sign, to Δ*H* for the reaction in the opposite direction. And Δ*H* is directly proportional to the quantity of reactants and products.

Key Equations

- $\Delta U = q + w$
- $\Delta H^\circ_{\text{reaction}} = \sum n \times \Delta H^\circ_{\text{f}}(\text{products}) - \sum n \times \Delta H^\circ_{\text{f}}(\text{reactants})$

Glossary

chemical thermodynamics
area of science that deals with the relationships between heat, work, and all forms of energy associated with chemical and physical processes

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

expansion work (pressure-volume work)
work done as a system expands or contracts against external pressure

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

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

hydrocarbon
compound composed only of hydrogen and carbon; the major component of fossil fuels

internal energy (*U*)
total of all possible kinds of energy present in a substance or substances

standard enthalpy of combustion ($\Delta H^\circ_{\text{c}}$)
heat released when one mole of a compound undergoes complete combustion under standard conditions

standard enthalpy of formation ($\Delta H^\circ_{\text{f}}$)
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 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

state function
property depending only on the state of a system, and not the path taken to reach that state

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 11.3: Enthalpy- Introduction is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

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

11.4: Enthalpy- Heat of Combustion

Learning Objectives

- State the first law of thermodynamics
- Define enthalpy and explain its classification as a state function
- Write and balance thermochemical equations
- Calculate enthalpy changes for various chemical reactions
- Explain Hess's law and use it to compute reaction enthalpies

Standard enthalpy of combustion (ΔH_C°) is the enthalpy change when 1 mole of a substance burns (combines vigorously with oxygen) under standard state conditions; it is sometimes called "heat of combustion." For example, the enthalpy of combustion of ethanol, −1366.8 kJ/mol, is the amount of heat produced when one mole of ethanol undergoes complete combustion at 25 °C and 1 atmosphere pressure, yielding products also at 25 °C and 1 atm.

$$\mathrm{C_2H_5OH}(l) + 3\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{CO_2} + 3\,\mathrm{H_2O}(l) \quad \Delta H_{298}^\circ = -1366.8\ \mathrm{kJ} \tag{11.4.1}$$

Enthalpies of combustion for many substances have been measured; a few of these are listed in Table 11.4.1. Many readily available substances with large enthalpies of combustion are used as fuels. These include hydrogen; carbon as coal or charcoal; and hydrocarbons like methane, propane, and the major components of gasoline.

Table 11.4.1: Standard Molar Enthalpies of Combustion

Substance	Combustion Reaction	Enthalpy of Combustion ΔH_c° $\left(\frac{\mathrm{kJ}}{\mathrm{mol}}\ \text{at}\ 25^\circ\mathrm{C}\right)$
carbon	$\mathrm{C}(s) + \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g)$	−393.5
hydrogen	$\mathrm{H_2}(g) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{H_2O}(l)$	−285.8

Substance	Combustion Reaction	Enthalpy of Combustion $\Delta H_c^\circ \left(\frac{\text{kJ}}{\text{mol}} \text{ at } 25^\circ\text{C}\right)$
magnesium	$\text{Mg}(s) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{MgO}(s)$	−601.6
methane	$\text{CH}_4(g) + 2\,\text{O}_2(g) \longrightarrow \text{CO}_2(g) + 2\,\text{H}_2\text{O}(l)$	−890.8
ethanol	$\text{C}_2\text{H}_5\text{OH}(l) + 3\,\text{O}_2(g) \longrightarrow \text{CO}_2(g) + 3\,\text{H}_2\text{O}(l)$	−1366.8
isooctane	$\text{C}_8\text{H}_{18}(l) + \frac{25}{2}\text{O}_2(g) \longrightarrow 8\,\text{CO}_2(g) + 9\,\text{H}_2\text{O}(l)$	−5461
glucose	$\text{C}_6\text{H}_{12}\text{O}_6(s) + \frac{6}{2}\text{O}_2(g) \longrightarrow 6\,\text{CO}_2(g) + 6\,\text{H}_2\text{O}(l)$	-2813

Example 11.4.1: Using Enthalpy of Combustion

As Figure 11.4.1 suggests, the combustion of gasoline is a highly exothermic process. Let us determine the approximate amount of heat produced by burning 1.00 L of gasoline, assuming the enthalpy of combustion of gasoline is the same as that of isooctane, a common component of gasoline. The density of isooctane is 0.692 g/mL.



Figure 11.4.1: The combustion of gasoline is very exothermic. (credit: modification of work by “AlexEagle”/Flickr)

Solution

Starting with a known amount (1.00 L of isooctane), we can perform conversions between units until we arrive at the desired amount of heat or energy. The enthalpy of combustion of isooctane provides one of the necessary conversions. Table 11.4.1 gives this value as −5460 kJ per 1 mole of isooctane (C_8H_{18}).

Using these data,

$$1.00\ \cancel{\text{L C}_8\text{H}_{18}} \times \frac{1000\ \cancel{\text{mL C}_8\text{H}_{18}}}{1\ \cancel{\text{L C}_8\text{H}_{18}}} \times \frac{0.692\ \cancel{\text{g C}_8\text{H}_{18}}}{1\ \cancel{\text{mL C}_8\text{H}_{18}}} \times \frac{1\ \cancel{\text{mol C}_8\text{H}_{18}}}{114\ \cancel{\text{g C}_8\text{H}_{18}}} \times \frac{-5460\ \text{kJ}}{1\ \cancel{\text{mol C}_8\text{H}_{18}}} = -3.31 \times 10^4\ \text{kJ}$$

The combustion of 1.00 L of isooctane produces 33,100 kJ of heat. (This amount of energy is enough to melt 99.2 kg, or about 218 lbs, of ice.)

Note: If you do this calculation one step at a time, you would find:

$$1.00\ \text{L C}_8\text{H}_{18} \longrightarrow 1.00 \times 10^3\ \text{mL C}_8\text{H}_{18}$$
$$1.00 \times 10^3\ \text{mL C}_8\text{H}_{18} \longrightarrow 692\ \text{g C}_8\text{H}_{18}$$
$$692\ \text{g C}_8\text{H}_{18} \longrightarrow 6.07\ \text{mol C}_8\text{H}_{18}$$
$$692\ \text{g C}_8\text{H}_{18} \longrightarrow -3.31 \times 10^4\ \text{kJ}$$

Exercise 11.4.1a

How much heat is produced by the combustion of 125 g of acetylene?

Answer

6.25×10^3 kJ

Exercise 11.4.1b

How much heat is produced by the combustion of 125 g of glucose?

Answer

1.95×10^3 kJ

Emerging Algae-Based Energy Technologies (Biofuels)

As reserves of fossil fuels diminish and become more costly to extract, the search is ongoing for replacement fuel sources for the future. Among the most promising biofuels are those derived from algae (Figure 11.4.2). The species of algae used are nontoxic, biodegradable, and among the world's fastest growing organisms. About 50% of algal weight is oil, which can be readily converted into fuel such as biodiesel. Algae can yield 26,000 gallons of biofuel per hectare—much more energy per acre than other crops. Some strains of algae can flourish in brackish water that is not usable for growing other crops. Algae can produce biodiesel, biogasoline, ethanol, butanol, methane, and even jet fuel.



Figure 11.4.2: (a) Tiny algal organisms can be (b) grown in large quantities and eventually (c) turned into a useful fuel such as biodiesel. (credit a: modification of work by Micah Sittig; credit b: modification of work by Robert Kerton; credit c: modification of work by John F. Williams)

According to the US Department of Energy, only 39,000 square kilometers (about 0.4% of the land mass of the US or less than $\frac{1}{7}$ of the area used to grow corn) can produce enough algal fuel to replace all the petroleum-based fuel used in the US. The cost of algal fuels is becoming more competitive—for instance, the US Air Force is producing jet fuel from algae at a total cost of under $5 per gallon. The process used to produce algal fuel is as follows: grow the algae (which use sunlight as their energy source and CO_2 as a raw material); harvest the algae; extract the fuel compounds (or precursor compounds); process as necessary (e.g., perform a transesterification reaction to make biodiesel); purify; and distribute (Figure 11.4.3).

Footnotes

1. 1 For more on algal fuel, see www.theguardian.com/environme...n-fuel-problem.

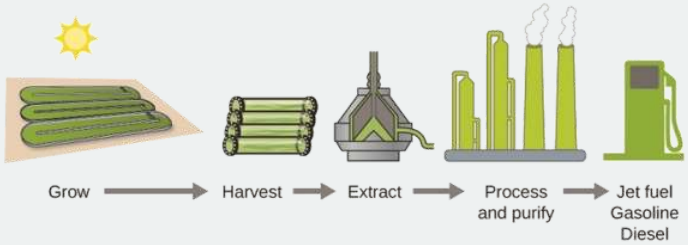


Figure 11.4.3: Algae convert sunlight and carbon dioxide into oil that is harvested, extracted, purified, and transformed into a variety of renewable fuels.

Summary

If a chemical change is carried out at constant pressure and the only work done is caused by expansion or contraction, the heat produced or required for the change is called the enthalpy change with the symbol ΔH, or ΔH° for reactions occurring under standard state conditions. The value of ΔH for a reaction in one direction is equal in magnitude, but opposite in sign, to ΔH for the reaction in the opposite direction, and ΔH is directly proportional to the quantity of reactants and products. Examples of enthalpy changes include enthalpy of combustion, enthalpy of fusion, enthalpy of vaporization, and standard enthalpy of formation. The standard enthalpy of formation, ΔH_f°, is the enthalpy change accompanying the formation of 1 mole of a substance from the elements in their most stable states at 1 bar (standard state). Many of the processes are carried out at 298.15 K. If the enthalpies of formation are available for the reactants and products of a reaction, the enthalpy change can be calculated using Hess's law: If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps.

11.4.1: Key Equations

- $\Delta U = q + w$
- $\Delta H^\circ_{\text{reaction}} = \sum n \times \Delta H^\circ_{\text{f}}(\text{products}) - \sum n \times \Delta H^\circ_{\text{f}}(\text{reactants})$

11.4.2: Footnotes

1. 1 For more on algal fuel, see www.theguardian.com/environme...n-fuel-problem.

Glossary

enthalpy (*H*)

sum of a system's internal energy and the mathematical product of its pressure and volume

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

hydrocarbon

compound composed only of hydrogen and carbon; the major component of fossil fuels

standard enthalpy of combustion (ΔH°_c)

heat released when one mole of a compound undergoes complete combustion under standard conditions

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 11.4: Enthalpy- Heat of Combustion is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

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

11.5: Enthalpy- Heat of Formation

Learning Objectives

- State the first law of thermodynamics
- Define enthalpy and explain its classification as a state function
- Write and balance thermochemical equations
- Calculate enthalpy changes for various chemical reactions
- Explain Hess's law and use it to compute reaction enthalpies

11.5.1: Standard Enthalpy of Formation

A standard enthalpy of formation ΔH_f° is an enthalpy change for a reaction in which exactly 1 mole of a pure substance is formed from free elements in their most stable states under standard state conditions. These values are especially useful for computing or predicting enthalpy changes for chemical reactions that are impractical or dangerous to carry out, or for processes for which it is difficult to make measurements. If we have values for the appropriate standard enthalpies of formation, we can determine the enthalpy change for any reaction, which we will practice in the next section on Hess's law.

The standard enthalpy of formation of $CO_2(g)$ is −393.5 kJ/mol. This is the enthalpy change for the exothermic reaction:

$$\mathrm{C}(s) + \mathrm{O}_2(g) \longrightarrow \mathrm{CO}_2(g) \quad \Delta H_f^\circ = \Delta H_{298}^\circ = -393.5 \text{ kJ} \tag{11.5.1}$$

starting with the reactants at a pressure of 1 atm and 25 °C (with the carbon present as graphite, the most stable form of carbon under these conditions) and ending with one mole of CO_2, also at 1 atm and 25 °C. For nitrogen dioxide, $NO_{2(g)}$, ΔH_f° is 33.2 kJ/mol. This is the enthalpy change for the reaction:

$$\frac{1}{2}\mathrm{N}_2(g) + \mathrm{O}_2(g) \longrightarrow \mathrm{NO}_2(g) \quad \Delta H_f^\circ = \Delta H_{298}^\circ = +33.2 \text{ kJ} \tag{11.5.2}$$

A reaction equation with $\frac{1}{2}$ mole of N_2 and 1 mole of O_2 is correct in this case because the standard enthalpy of formation always refers to 1 mole of product, $NO_2(g)$.

You will find a table of standard enthalpies of formation of many common substances in Table 11.5.1. These values indicate that formation reactions range from highly exothermic (such as −2984 kJ/mol for the formation of P_4O_{10}) to strongly endothermic (such as +226.7 kJ/mol for the formation of acetylene, C_2H_2). By definition, the standard enthalpy of formation of an element in its most stable form is equal to zero under standard conditions, which is 1 atm for gases and 1 M for solutions.

Table 11.5.1: Heat of Formation (kJ/Mole) from NIST Webbok (https://webbook.nist.gov/)

Formula	Name	ΔH_f (kJ/mol)		Formula	Name	ΔH_f (kJ/mol)
CH_4(g)	methane	-74.87		C_5H_8(g)	Isoprene	75.7
C_2H_2(g)	acetylene	226.73		C_2H_5OH(l)	ethanol	-276.
C_2H_4(g)	etylene	52.47		CCl_4(l)	carbon tetrachloride	-128.1
C_2H_6(g)	ethane	-84.		CO(g)	carbon monoxiode	-110.53
C_3H_6(g)	propene	20.41		CO_2(g)	carbon dioxide	-393.51
C_3H_8(g)	propane	-104.7		H_2O(g)	water	-241.83
C_4H_8(g)	1-butene	-0.63		H_2O(l)	water	-285.83
C_4H_8(g)	2-butene	-10.8		SO_2(g)	sulfur dioxide	-296.81
C_4H_{10}(g)	butane	-125.6		SO_3(g)	sulfur trioxide	-395.77
C_4H_{10}(g)	isobutane	-134.2		H_2S(g)	dihydrogen sufide	-20.6

Formula	Name	ΔH_f (kJ/mol)	Formula	Name	ΔH_f (kJ/mol)
$C_8H_{18}(g)$	octane	-208.7	HF(g)	hydrogen fluoride	-273.30
$C_8H_{18}(l)$	octane	-250.3	HCl(g)	hydrogen chloride	-92.31
$C_6H_6(l)$	benzene	49.	HBr(g)	hydrogen bromide	-36.29
$C_8H_{12}O_6(s)$	fructose	-1265.6	HI(g)	hydrogen iodide	26.5
$C_8H_{12}O_6(s)$	glucose	-1263.4	NO(g)	nitrogen monoxide	90.29
$C_{12}H_{22}O_{11}(s)$	Sucrose	-2221.2	$NO_2(g)$	nitrogen dioxide	33.10
$CH_3OH(l)$	methanol	-238.4	$HNO_3(aq)$	nitric acid	-207.4

Example 11.5.1: Evaluating an Enthalpy of Formation

Ozone, $O_3(g)$, forms from oxygen, $O_2(g)$, by an endothermic process. Ultraviolet radiation is the source of the energy that drives this reaction in the upper atmosphere. Assuming that both the reactants and products of the reaction are in their standard states, determine the standard enthalpy of formation, ΔH_f° of ozone from the following information:

$$3\,O_2(g) \longrightarrow 2\,O_3(g) \qquad \Delta H_{298}^\circ = +286\text{ kJ}$$

Solution ΔH_f° is the enthalpy change for the formation of one mole of a substance in its standard state from the elements in their standard states. Thus, ΔH_f° for $O_3(g)$ is the enthalpy change for the reaction:

$$\frac{3}{2}O_2(g) \longrightarrow O_3(g)$$

For the formation of 2 mol of $O_3(g)$, $\Delta H_{298}^\circ = +286$ kJ. This ratio, $\left(\dfrac{286\text{ kJ}}{2\text{ mol }O_3}\right)$, can be used as a conversion factor to find the heat produced when 1 mole of $O_3(g)$ is formed, which is the enthalpy of formation for $O_3(g)$:

$$\Delta H^\circ \text{ for 1 mole of } O_3(g) = 1\ \cancel{\text{mol } O_3} \times \frac{286\text{ kJ}}{2\ \cancel{\text{mol } O_3}} = 143\text{ kJ}$$

Therefore, $\Delta H_f^\circ[O_3(g)] = +143\text{ kJ/mol}$.

Exercise 11.5.1

Hydrogen gas, H_2, reacts explosively with gaseous chlorine, Cl_2, to form hydrogen chloride, HCl(g). What is the enthalpy change for the reaction of 1 mole of $H_2(g)$ with 1 mole of $Cl_2(g)$ if both the reactants and products are at standard state conditions? The standard enthalpy of formation of HCl(g) is −92.3 kJ/mol.

Answer

For the reaction

$$H_2(g) + Cl_2(g) \longrightarrow 2\,HCl(g) \qquad \Delta H_{298}^\circ = -184.6\text{ kJ}$$

Example 11.5.2: Writing Reaction Equations for ΔH_f°

Write the heat of formation reaction equations for:

a. $C_2H_5OH_{(l)}$
b. $Ca_3(PO_4)_{2(s)}$

Solution

Remembering that ΔH_f° reaction equations are for forming 1 mole of the compound from its constituent elements under standard conditions, we have:

a. $2\,C(s,\ \text{graphite}) + 3\,H_2(g) + \frac{1}{2}O_2(g) \longrightarrow C_2H_5OH(l)$
b. $3\,Ca(s) + \frac{1}{2}P_4(s) + 4\,O_2(g) \longrightarrow Ca_3(PO_4)_2(s)$

Note: The standard state of carbon is graphite, and phosphorus exists as P_4.

? Exercise 11.5.2

Write the heat of formation reaction equations for:

a. $C_2H_5OC_2H_{5(l)}$
b. $Na_2CO_{3(s)}$

Answer a

$$4\,C(s,\ \text{graphite}) + 5\,H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow C_2H_5OC_2H_5(l)\ ;$$

Answer b

$$2\,Na(s) + C(s,\ \text{graphite}) + \frac{3}{2}O_2(g) \longrightarrow Na_2CO_3(s)$$

11.5.2: Hess's Law

There are two ways to determine the amount of heat involved in a chemical change: measure it experimentally, or calculate it from other experimentally determined enthalpy changes. Some reactions are difficult, if not impossible, to investigate and make accurate measurements for experimentally. And even when a reaction is not hard to perform or measure, it is convenient to be able to determine the heat involved in a reaction without having to perform an experiment.

This type of calculation usually involves the use of Hess's law, which states: If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps. Hess's law is valid because enthalpy is a state function: Enthalpy changes depend only on where a chemical process starts and ends, but not on the path it takes from start to finish. For example, we can think of the reaction of carbon with oxygen to form carbon dioxide as occurring either directly or by a two-step process. The direct process is written:

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \quad \Delta H^\circ_{298} = -394\ \text{kJ} \tag{11.5.3}$$

In the two-step process, first carbon monoxide is formed:

$$C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)} \quad \Delta H^\circ_{298} = -111\ \text{kJ} \tag{11.5.4}$$

Then, carbon monoxide reacts further to form carbon dioxide:

$$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g) \quad \Delta H^\circ_{298} = -283\ \text{kJ} \tag{11.5.5}$$

The equation describing the overall reaction is the sum of these two chemical changes:

$$\begin{aligned} &\text{Step 1: } C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) \\ &\text{Step 2: } CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g) \\ \hline &\text{Sum: } C(s) + \frac{1}{2}O_2(g) + CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO(g) + CO_2(g) \end{aligned}$$

Because the CO produced in Step 1 is consumed in Step 2, the net change is:

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \tag{11.5.6}$$

According to Hess's law, the enthalpy change of the reaction will equal the sum of the enthalpy changes of the steps. We can apply the data from the experimental enthalpies of combustion in Table 11.5.1 to find the enthalpy change of the entire reaction from its two steps:

$$\begin{aligned} &\mathrm{C}(s)+\frac{1}{2}\mathrm{O_2}(g)\longrightarrow \mathrm{CO}(g) && \Delta H^\circ_{298}=-111\ \mathrm{kJ}\\ &\mathrm{CO}(g)+\frac{1}{2}\mathrm{O_2}(g)\longrightarrow \mathrm{CO_2}(g) && \Delta H^\circ_{298}=-283\ \mathrm{kJ}\\ \hline &\mathrm{C}(s)+\mathrm{O_2}(g)\longrightarrow \mathrm{CO_2}(g) && \Delta H^\circ_{298}=-394\ \mathrm{kJ} \end{aligned}$$

The result is shown in Figure 11.5.6. We see that ΔH of the overall reaction is the same whether it occurs in one step or two. This finding (overall ΔH for the reaction = sum of Δ*H* values for reaction "steps" in the overall reaction) is true in general for chemical and physical processes.

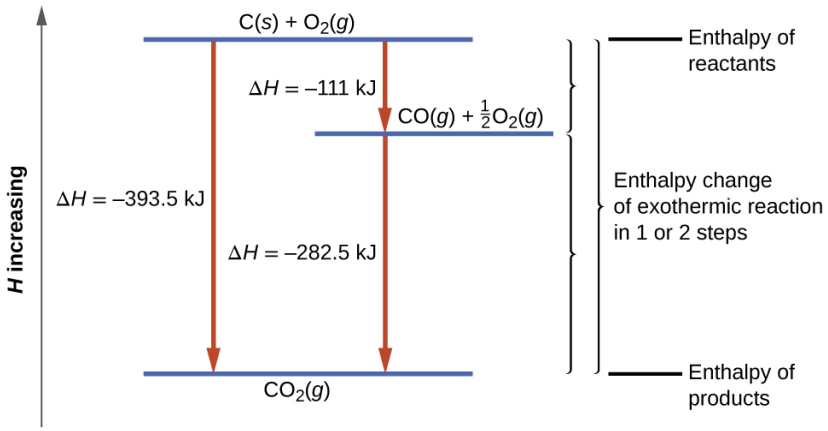


Figure 11.5.6: The formation of CO_2(g) from its elements can be thought of as occurring in two steps, which sum to the overall reaction, as described by Hess's law. The horizontal blue lines represent enthalpies. For an exothermic process, the products are at lower enthalpy than are the reactants.

Before we further practice using Hess's law, let us recall two important features of Δ*H*.

1. Δ*H* is directly proportional to the quantities of reactants or products. For example, the enthalpy change for the reaction forming 1 mole of $NO_2(g)$ is +33.2 kJ:

$$\frac{1}{2}\mathrm{N_2}(g)+\mathrm{O_2}(g)\longrightarrow \mathrm{NO_2}(g)\quad \Delta H=+33.2\ \mathrm{kJ} \tag{11.5.7}$$

   When 2 moles of NO_2 (twice as much) are formed, the Δ*H* will be twice as large:

$$\mathrm{N_2}(g)+2\,\mathrm{O_2}(g)\longrightarrow 2\,\mathrm{NO_2}(g)\quad \Delta H=+66.4\ \mathrm{kJ} \tag{11.5.8}$$

   In general, if we multiply or divide an equation by a number, then the enthalpy change should also be multiplied or divided by the same number.

2. Δ*H* for a reaction in one direction is equal in magnitude and opposite in sign to Δ*H* for the reaction in the reverse direction. For example, given that:

$$\mathrm{H_2}(g)+\mathrm{Cl_2}(g)\longrightarrow 2\,\mathrm{HCl}(g)\quad \Delta H=-184.6\ \mathrm{kJ} \tag{11.5.9}$$

   Then, for the "reverse" reaction, the enthalpy change is also "reversed":

$$2\,\mathrm{HCl}(g)\longrightarrow \mathrm{H_2}(g)+\mathrm{Cl_2}(g)\quad \Delta H=+184.6\ \mathrm{kJ} \tag{11.5.10}$$

Here is a less straightforward example that illustrates the thought process involved in solving many Hess's law problems. It shows how we can find many standard enthalpies of formation (and other values of Δ*H*) if they are difficult to determine experimentally.

Example 11.5.3: Stepwise Calculation of ΔH_f°

Using Hess's Law Determine the enthalpy of formation, ΔH_f°, of $FeCl_3$(s) from the enthalpy changes of the following two-step process that occurs under standard state conditions:

$$Fe(s) + Cl_2(g) \longrightarrow FeCl_2(s) \quad \Delta H^\circ = -341.8 \text{ kJ}$$

$$FeCl_2(s) + \frac{1}{2}Cl_2(g) \longrightarrow FeCl_3(s) \quad \Delta H^\circ = -57.7\ kJ$$

Solution

We are trying to find the standard enthalpy of formation of FeCl3(s), which is equal to ΔH° for the reaction:

$$Fe(s) + \frac{3}{2}Cl_2(g) \longrightarrow FeCl_3(s) \quad \Delta H_f^\circ = ?$$

Looking at the reactions, we see that the reaction for which we want to find Δ*H*° is the sum of the two reactions with known Δ*H* values, so we must sum their Δ*H*s:

$$\begin{aligned} Fe(s) + Cl_2(g) &\longrightarrow FeCl_2(s) && \Delta H^\circ = -341.8 \text{ kJ} \\ FeCl_2(s) + \frac{1}{2}Cl_2(g) &\longrightarrow FeCl_3(s) && \Delta H^\circ = -57.7 \text{ kJ} \\ \hline Fe(s) + \frac{1}{2}Cl_2(g) &\longrightarrow FeCl_3(s) && \Delta H^\circ = -399.5 \text{ kJ} \end{aligned}$$

The enthalpy of formation, ΔH_f°, of $FeCl_3$(s) is −399.5 kJ/mol.

Exercise 11.5.3

Calculate ΔH for the process:

$$N_2(g) + 2\,O_2(g) \longrightarrow 2\,NO_2(g)$$

from the following information:

$$N_2(g) + O_2(g) \longrightarrow 2\,NO(g) \quad \Delta H = 180.5 \text{ kJ}$$

$$NO(g) + \frac{1}{2}O_2(g) \longrightarrow NO_2(g) \quad \Delta H = -57.06 \text{ kJ}$$

Answer

66.4 kJ

11.5.3: Hess's Law and Heat of Formation

We also can use Hess's law to determine the enthalpy change of any reaction if the corresponding enthalpies of formation of the reactants and products are available. The stepwise reactions we consider are: (i) decompositions of the reactants into their component elements (for which the enthalpy changes are proportional to the negative of the enthalpies of formation of the reactants), followed by (ii) re-combinations of the elements to give the products (with the enthalpy changes proportional to the enthalpies of formation of the products).

Example 11.5.4: Using Hess's Law

What is the standard enthalpy change for the reaction:

$$3\,NO_2(g) + H_2O(l) \longrightarrow 2\,HNO_3(aq) + NO(g) \quad \Delta H^\circ = ?$$

Solving with Hess's Law and Heat of Formation

We can write this reaction as the sum of the decompositions of $3NO_2(g)$ and $1H_2O(l)$ into their constituent elements, and the formation of 2 $HNO_3(aq)$ and 1 $NO(g)$ from their constituent elements. Writing out these reactions, and noting their relationships to the ΔH_f° values for these compounds (from Tables T1 and T2), we have:

$$3\,NO_2(g) \longrightarrow \frac{3}{2}N_2(g) + 3O_2(g) \quad \Delta H_1^\circ = -99.6\text{ kJ}$$

$$H_2O(l) \longrightarrow H_2(g) + \frac{1}{2}O_2(g) \quad \Delta H_2^\circ = +285.8\text{ kJ } [-1 \times \Delta H_f^\circ(H_2O)]$$

$$H_2(g) + N_2(g) + 3O_2(g) \longrightarrow 2\,HNO_3(aq) \quad \Delta H_3^\circ = -414.8\ kJ\ [2 \times \Delta H_f^\circ(HNO_3)]$$

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(g) \quad \Delta H_4^\circ = +90.2\text{ kJ } [1 \times (NO)]$$

Summing these reaction equations gives the reaction we are interested in:

$$3\,NO_2(g) + H_2O(l) \longrightarrow 2\,HNO_3(aq) + NO(g)$$

Summing their enthalpy changes gives the value we want to determine:

$$\begin{aligned}\Delta H_{rxn}^\circ &= \Delta H_1^\circ + \Delta H_2^\circ + \Delta H_3^\circ + \Delta H_4^\circ = (-99.6\text{ kJ}) + (+285.8\text{ kJ}) + (-414.8\text{ kJ}) + (+90.2\text{ kJ}) \\ &= -138.4\text{ kJ}\end{aligned}$$

So the standard enthalpy change for this reaction is $\Delta H°$ = −138.4 kJ.

Note that this result was obtained by:

1. multiplying the ΔH_f° of each product by its stoichiometric coefficient and summing those values,
2. multiplying the ΔH_f° of each reactant by its stoichiometric coefficient and summing those values, and then
3. subtracting the result found in step 2 from the result found in step 1.

Setting up Hess's Law Problems using a Reaction Table.

An easy way to set up these problems is with a reaction table. Below each reactant and product write the ΔH^\circ_\ce{f} value from the table above. In the next row change the sign of ΔH^\circ_\ce{f} value each reactant, since you are decomposing the reactants NOT forming them. And multiply the ΔH^\circ_\ce{f} value by the stoichiometric coefficent to account for the number of moles for each reactant and product.

	$3\,NO_2(g)$	$H_2O(l)$	$\longrightarrow$	$2\,HNO_3(aq)$	$NO(g)$
$\Delta H_f^\circ(kJ)$	33.2	-285.83		-207.4	90.2
$\Delta H_{rxn}^\circ(kJ)$	-99.6	+285.83		-414.8	90.2

After the table is set up, just combine the values in the last row to find $\Delta H_{rxn}^\circ = -138.4kJ$

Setting up Hess's Law Problems using the sums equation.

The standard enthalpy change of the overall reaction is therefore equal to: (ii) the sum of the standard enthalpies of formation of all the products plus (i) the sum of the negatives of the standard enthalpies of formation of the reactants. This is usually rearranged slightly to be written as follows, with $\sum$ representing "the sum of" and *n* standing for the stoichiometric coefficients:

$$\Delta H_{reaction}^\circ = \sum n \times \Delta H_f^\circ(\text{products}) - \sum n \times \Delta H_f^\circ(\text{reactants}) \tag{11.5.11}$$

The following example shows in detail why this equation is valid, and how to use it to calculate the enthalpy change for a reaction of interest.

The solution to this is as follows:

$$\Delta H_{reaction}^\circ = \sum n \times \Delta H_f^\circ(\text{products}) - \sum n \times \Delta H_f^\circ(\text{reactants})$$

$$= \left[2 \text{ mol } \cancel{HNO_3} \times \frac{-207.4 \text{ kJ}}{\text{mol } \cancel{HNO_3\ (aq)}} + 1 \text{ mol } \cancel{NO\ (g)} \times \frac{+90.2 \text{ kJ}}{\text{mol } \cancel{NO\ (g)}} \right]$$

$$- \left[3 \text{ mol } \cancel{NO_2\ (g)} \times \frac{+33.2 \text{ kJ}}{\text{mol } \cancel{NO_2\ (g)}} + 1 \text{ mol } \cancel{H_2O\ (l)} \times \frac{-285.8 \text{ kJ}}{\text{mol } \cancel{H_2O\ (l)}} \right]$$

$$= 2(-207.4 \text{ kJ}) + 1(+90.2 \text{ kJ}) - 3(+33.2 \text{ kJ}) - 1(-285.8 \text{ kJ})$$

$$= -138.4 \text{ kJ}$$

? Exercise 11.5.4

Calculate the heat of combustion of 1 mole of ethanol, $C_2H_5OH(l)$, when $H_2O(l)$ and $CO_2(g)$ are formed. Use the following enthalpies of formation: $C_2H_5OH(l)$, −278 kJ/mol; $H_2O(l)$, −286 kJ/mol; and $CO_2(g)$, −394 kJ/mol.

Answer

−1368 kJ/mol

This project was preformed to supply **Libretext Authors** with videos on General Chemistry topics which can be used to enhance their projects. Also, these videos are meant to act as a learning resource for **all General Chemistry students**.

Video Topics

The enthalpy of an unknown reaction can be found using the equation: ΔH° = Sum of VΔHf°(product) - Sum of VΔHf° (reactants). ΔHf is the enthalpy of formation for a given species. V is the stoichiometric coefficient of the species from the balanced reaction. Remember that ΔHf° = 0 for elements in their reference states. This video contains a sample problem, which involves these concepts.

Link to Video

Calculating H° using Hf°: https://youtu.be/Y3aJJno9W2c



11.5.4: Attribution

- Prof. Steven Farmer (Sonoma State University)

11.5.5: Summary

If a chemical change is carried out at constant pressure and the only work done is caused by expansion or contraction, *q* for the change is called the enthalpy change with the symbol ΔH, or ΔH°_{298} for reactions occurring under standard state conditions. The value of ΔH for a reaction in one direction is equal in magnitude, but opposite in sign, to ΔH for the reaction in the opposite direction, and ΔH is directly proportional to the quantity of reactants and products. Examples of enthalpy changes include enthalpy of combustion, enthalpy of fusion, enthalpy of vaporization, and standard enthalpy of formation. The standard enthalpy of formation, ΔH°_f, is the enthalpy change accompanying the formation of 1 mole of a substance from the elements in their most stable states at 1 bar (standard state). Many of the processes are carried out at 298.15 K. If the enthalpies of formation are available for the reactants and products of a reaction, the enthalpy change can be calculated using Hess's law: If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps.

11.5.6: Glossary

enthalpy (*H*)
sum of a system's internal energy and the mathematical product of its pressure and volume

enthalpy change (ΔH)
heat released or absorbed by a system under constant pressure during a chemical or physical process

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

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

hydrocarbon
compound composed only of hydrogen and carbon; the major component of fossil fuels

internal energy (*U*)
total of all possible kinds of energy present in a substance or substances

standard enthalpy of formation (ΔH°_f)
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 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

state function
property depending only on the state of a system, and not the path taken to reach that state

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 11.5: Enthalpy- Heat of Formation is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

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

11.6: Bond Energy

Bond Strength: Covalent Bonds

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.

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:

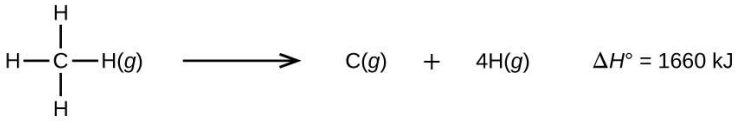
$$XY_{(g)} \longrightarrow X_{(g)} + Y_{(g)} \quad D_{X-Y} = \Delta H^\circ \tag{11.6.1}$$

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:

$$H_{2(g)} \longrightarrow 2H_{(g)} \quad D_{H-H} = \Delta H^\circ = 436kJ \tag{11.6.2}$$

> *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:



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. The 415 kJ/mol average value for a C-H bond is listed in Table 11.6.1.

The strength of a bond between two atoms increases as the number of electron pairs in the bond increases. Table 11.6.1 shows bond energies for common double and triple bonds. Also notice that bond strength typically decreases going down a group in the periodic table. For example; C–F is 439 kJ/mol, C–Cl is 330 kJ/mol, and C–Br is 275 kJ/mol.

Table 11.6.1: Bond Energies (kJ/mol)

	H	C	N	O	F	Cl	Br
H	436	415	390	464	569	432	370
C		345 (C-C) 611 (C=C) 837 (C≡C)	290 (C-N) 615 (C=N) 891 (C≡N)	350 (C-O) 741 (C=O) 1080 (C≡O)	439	330	275
N			160 (N-N) 418 (N=N) 946 (N≡)	200	270	200	245
O				140 (O-O) 498 (O=O)	160	205	
F					160	255	235
Cl						243	220

	H	C	N	O	F	Cl	Br
Br							190

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:

$$\Delta H = \sum BondEnergy_{\text{bonds broken}} - \sum BondEnergy_{\text{bonds formed}} \tag{11.6.3}$$

In this expression, the symbol Σ means "the sum of" and the bond energy from Table $11.6.1$ is in kilojoules per mole, which is always a positive number. The bond energy is for a type of bond, single, double, or triple, between to specific atoms. Enthalpies calculated this way must include all bonds broke and created in a chemical reaction. Because bond energy values are averages for one type of bond in many different molecules, these calculations provide an estimate for the enthalpy of reaction.

Consider the following reaction:

$$\mathrm{H_{2\,(g)} + Cl_{2\,(g)} \longrightarrow 2\,HCl_{(g)}} \tag{11.6.4}$$

or

$$\mathrm{H\text{–}H_{(g)} + Cl\text{–}Cl_{(g)} \longrightarrow 2\,H\text{–}Cl_{(g)}} \tag{11.6.5}$$

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 form (bond energy = 432 kJ/mol) to release 2 × 432 kJ; or 864 kJ of energy.

$$\begin{aligned}\Delta H &= \sum \mathrm{D_{bonds\ broken}} - \sum \mathrm{D_{bonds\ formed}} \\ &= [\mathrm{D_{H-H}} + \mathrm{D_{Cl-Cl}}] - 2\mathrm{D_{H-Cl}} \\ &= [436 + 243] - 2(432) = -185\ \mathrm{kJ}\end{aligned}$$

This excess energy is released as heat, so the reaction is exothermic. The value calculated -864 kJ is for the formation of 2 moles of HCl, so this compares with two times the standard molar enthalpy of formation of HCl(g), ΔH_f°. –92.3 kJ/mol x 2 mol = –184.6 kJ, which agrees with found using bond energies.

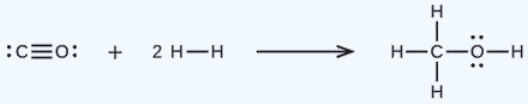
Example 11.6.4: Using Bond Energies to Approximate Enthalpy Changes

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 $11.6.1$, calculate the approximate enthalpy change, ΔH, for the reaction here:

$$CO_{(g)} + 2H2_{(g)} \longrightarrow CH_3OH_{(g)} \tag{11.6.6}$$

Solution

First, we need to write the Lewis structures of the reactants and the products:



From this, we see that Δ*H* 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 ???):

$$\begin{aligned}\Delta H &= \sum D_{bonds\ broken} - \sum D_{bonds\ formed} \\ \Delta H &= [\mathrm{D_{C\equiv O} + 2(D_{H-H})}] - [\mathrm{3(D_{C-H}) + D_{C-O} + D_{O-H}}]\end{aligned}$$

Using the bond energy values in Table 11.6.1, we obtain:

$$\begin{aligned}\Delta H &= [1080 + 2(436)] - [3(415) + 350 + 464] \\ &= -107\ \mathrm{kJ}\end{aligned}$$

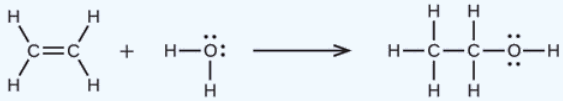
We can compare this value to the value calculated based on ΔH_f° data from Appendix G:

$$\begin{aligned}\Delta H &= [\Delta H_f^\circ \mathrm{CH_3OH}(g)] - [\Delta H_f^\circ \mathrm{CO}(g) + 2 \times \Delta H_f^\circ \mathrm{H_2}] \\ &= [-201.0] - [-110.52 + 2 \times 0] \\ &= -90.5\ \mathrm{kJ}\end{aligned}$$

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 11.6.4

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:



Using the bond energies in Table 11.6.1, calculate an approximate enthalpy change, Δ*H*, for this reaction.

Answer

–35 kJ

11.6: Bond Energy is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **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.

11.E: Thermochemistry- Homework

11.E.1: Turn in your answers for the following questions - show your work

1. An electric stove has a 1200 watt heating element. If it takes 5 minutes for a teakettle to come to a boil, how much energy (in joules) is required?

2. A piece of titanium metal (mass 452.398 g) is placed in boiling water (100.00 °C). After 20 minutes it is removed from the boiling water and placed in a 1.000 liter container of water at 20.00 °C. The temperature of the water increases to 24.28 °C. What is the specific heat of titanium? How does this compare to the value given in the CRC Handbook of Chemistry and Physics?

3. Next the same piece of titanium is heated in an acetylene flame (like that used for welding) to an unknown temperature. When the piece of titanium is placed in a 10.000 liter container of water at 20.00 °C the final temperature is now 30.72 °C. What is the temperature of the flame (assuming that the piece of titanium was at equilibrium)? At what temperature does titanium melt?

4. Balance the following reactions, calculate [delta]H_{rxn}, calculate the energy released (or required) for the combustion of 10.00 grams of fuel (H_2, CH_4 (methane), or C_4H_{10} (butane)) in each reaction, and compare the energetics for the reactions (which is the best fuel).
   a. H_2 (g) + O_2 (g) --> H_2O (g)
   b. CH_4 (g) + O_2 (g) --> CO_2 (g) + H_2O (g)
   c. C_4H_{10} (g) + O_2 (g) --> CO_2 (g) + H_2O (g)

11.E.2: The Following Questions are for your practice - Do Not Turn In. They include answers so you can check your work

1. How much heat, in joules and in calories, must be added to a 75.0–g iron block with a specific heat of 0.449 J/g °C to increase its temperature from 25 °C to its melting temperature of 1535 °C?

   answer

   $$q = mC\Delta^\circ T$$

   $$q = (75.0g) \times (\frac{0.449\ J}{g\ ^\circ C}) \times (1,510^\circ K) = 50,800J$$

   50,800J ; 12,200cal

2. How much would the temperature of 275 g of water increase if 36.5 kJ of heat were added?

   answer

   ΔT° = 31.7° C

11.E.2.1: Calorimetry

1. How much will the temperature of a cup (180 g) of coffee at 95 °C be reduced when a 45 g silver spoon (specific heat 0.24 J/g °C) at 25 °C is placed in the coffee and the two are allowed to reach the same temperature? Assume that the coffee has the same density and specific heat as water.

   answer

   The temperature of the coffee will drop 1 degree.

2. If a reaction produces 1.506 kJ of heat, which is trapped in 30.0 g of water initially at 26.5 °C in a calorimeter like that in Figure, what is the resulting temperature of the water?

   answer

   38.5 °C

11.E.2.2: Enthalpy

1. When 2.50 g of methane burns in oxygen, 125 kJ of heat is produced. What is the enthalpy of combustion per mole of methane under these conditions?

   answer

   802 kJ mol^{-1}

2. Calculate the standard molar enthalpy of formation of NO(g) from the following data:

$$N_2(g) + 2\,O_2 \longrightarrow 2\,NO_2(g) \quad \Delta H^\circ_{298} = 66.4\ \text{kJ}$$

$$2\,NO(g) + O_2 \longrightarrow 2\,NO_2(g) \quad \Delta H^\circ_{298} = -114.1\ \text{kJ}$$

   answer

   90.3 mol^{-1} of NO

3. The decomposition of hydrogen peroxide, H_2O_2, has been used to provide thrust in the control jets of various space vehicles. Using the data in Appendix G, determine how much heat is produced by the decomposition of exactly 1 mole of H_2O_2 under standard conditions.

$$2\,H_2O_2(l) \longrightarrow 2\,H_2O(g) + O_2(g)$$

   answer

   −54.04 kJ mol^{-1}

4. Propane, C_3H_8, is a hydrocarbon that is commonly used as a fuel.
   a. Write a balanced equation for the complete combustion of propane gas.
   b. Assuming that all of the heat released in burning 25.0 grams of propane is transferred to 4.00 kilograms of water, calculate the increase in temperature of the water.

   answer

   a. $C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(l)$;
   b. 75.4 °C

This page titled 11.E: Thermochemistry- Homework is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

CHAPTER OVERVIEW

12: Thermodynamics

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

General Chemistry

Among the many capabilities of chemistry is its ability to predict if a process will occur under specified conditions. Thermodynamics, the study of relationships between the energy and work associated with chemical and physical processes, provides this predictive ability. Previous chapters in this text have described various applications of thermochemistry, an important aspect of thermodynamics concerned with the heat flow accompanying chemical reactions and phase transitions. This chapter will introduce additional thermodynamic concepts, including those that enable the prediction of any chemical or physical changes under a given set of conditions.

12.1: Introduction to Spontaneity and Entropy

12.2: The Second and Third Laws of Thermodynamics

12.3: Free Energy

12.E: Thermodynamics - Homework

This page titled 12: Thermodynamics 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.

12.1: Introduction to Spontaneity and Entropy



Figure 16.1 Geysers are a dramatic display of thermodynamic principles in nature. Water deep within the underground channels of the geyser is under high pressure and heated to high temperature by magma. When a pocket of water near the surface reaches boiling point and is expelled, the resulting drop in pressure causes larger volumes of water to flash boil, forcefully ejecting steam and water in an impressive eruption. (credit: modification of work by Yellowstone National Park)

Chapter Outline

16.1 Spontaneity
16.2 Entropy
16.3 The Second and Third Laws of Thermodynamics
16.4 Free Energy

Among the many capabilities of chemistry is its ability to predict if a process will occur under specified conditions. Thermodynamics, the study of relationships between the energy and work associated with chemical and physical processes, provides this predictive ability. Previous chapters in this text have described various applications of thermochemistry, an important aspect of thermodynamics concerned with the heat flow accompanying chemical reactions and phase transitions. This chapter will introduce additional thermodynamic concepts, including those that enable the prediction of any chemical or physical changes under a given set of conditions.

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

- Distinguish between spontaneous and nonspontaneous processes
- Describe the dispersal of matter and energy that accompanies certain spontaneous processes

Processes have a natural tendency to occur in one direction under a given set of conditions. Water will naturally flow downhill, but uphill flow requires outside intervention such as the use of a pump. Iron exposed to the earth's atmosphere will corrode, but rust is not converted to iron without intentional chemical treatment. A spontaneous process is one that occurs naturally under certain conditions. A nonspontaneous process, on the other hand, will not take place unless it is "driven" by the continual input of energy from an external source. A process that is spontaneous in one direction under a particular set of conditions is nonspontaneous in the reverse direction. At room temperature and typical atmospheric pressure, for example, ice will spontaneously melt, but water will not spontaneously freeze.

The spontaneity of a process is *not* correlated to the speed of the process. A spontaneous change may be so rapid that it is essentially instantaneous or so slow that it cannot be observed over any practical period of time. To illustrate this concept, consider the decay of radioactive isotopes, a topic more thoroughly treated in the chapter on nuclear chemistry. Radioactive decay is by definition a spontaneous process in which the nuclei of unstable isotopes emit radiation as they are converted to more stable nuclei.

All the decay processes occur spontaneously, but the rates at which different isotopes decay vary widely. Technetium-99m is a popular radioisotope for medical imaging studies that undergoes relatively rapid decay and exhibits a half-life of about six hours. Uranium-238 is the most abundant isotope of uranium, and its decay occurs much more slowly, exhibiting a half-life of more than four billion years (Figure 16.2).

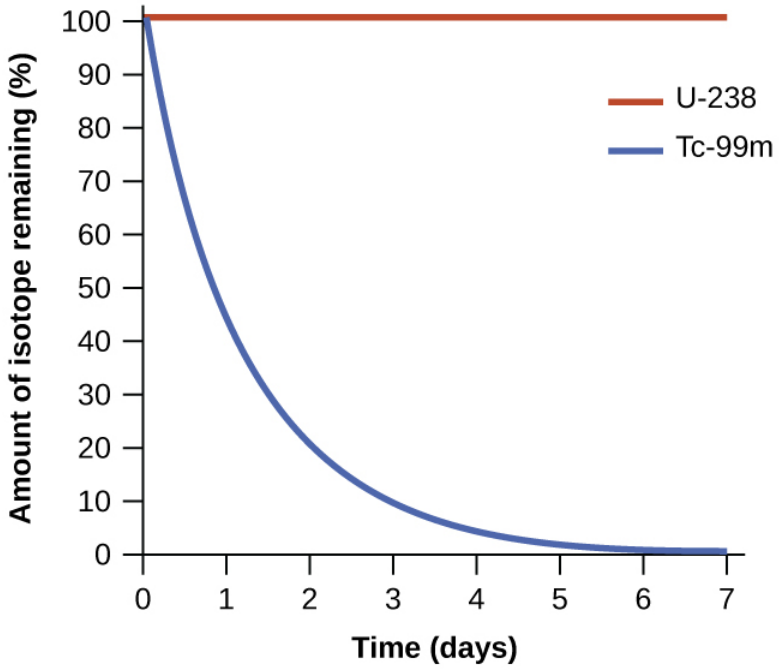


Figure 16.2 Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed.

As another example, consider the conversion of diamond into graphite (Figure 16.3).

$$\mathrm{C}(s,\ \text{diamond}) \longrightarrow \mathrm{C}(s,\ \text{graphite})$$

The phase diagram for carbon indicates that graphite is the stable form of this element under ambient atmospheric pressure, while diamond is the stable allotrope at very high pressures, such as those present during its geologic formation. Thermodynamic calculations of the sort described in the last section of this chapter indicate that the conversion of diamond to graphite at ambient pressure occurs spontaneously, yet diamonds are observed to exist, and persist, under these conditions. Though the process is spontaneous under typical ambient conditions, its rate is extremely slow; so, for all practical purposes diamonds are indeed "forever." Situations such as these emphasize the important distinction between the thermodynamic and the kinetic aspects of a process. In this particular case, diamonds are said to be *thermodynamically unstable* but *kinetically stable* under ambient conditions.

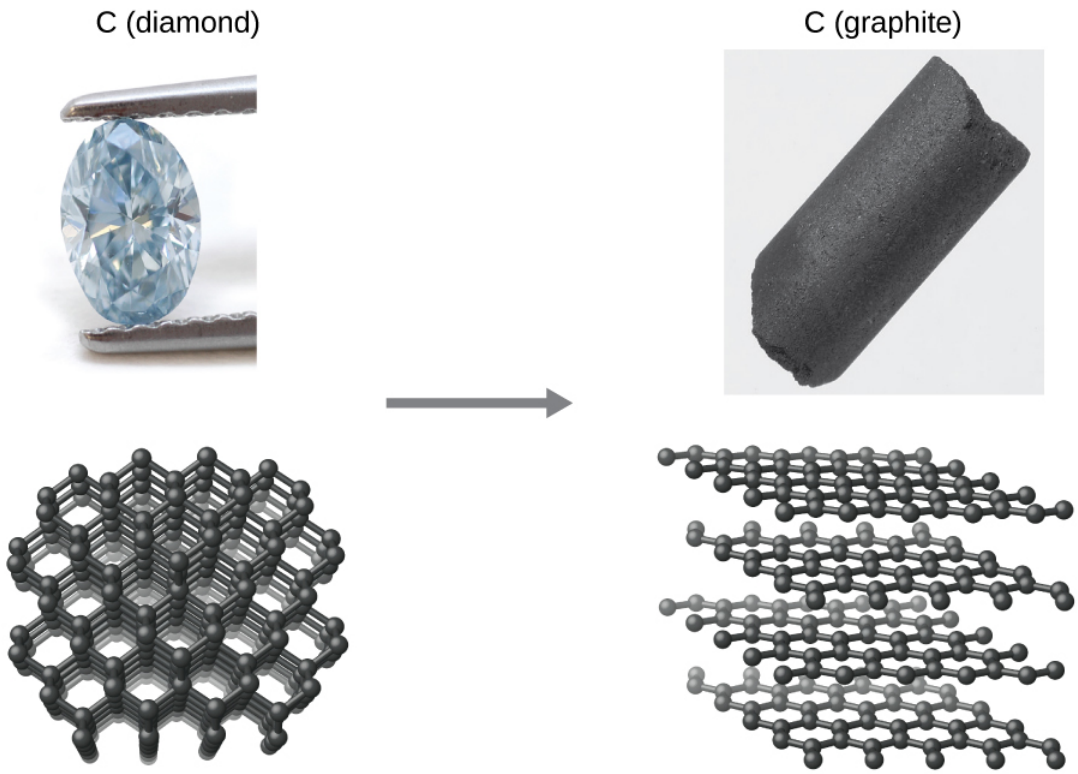


Figure 16.3 The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as *graphitization*, and its rate can be increased to easily measurable values at temperatures in the 1000–2000 K range. (credit "diamond" photo: modification of work by "Fancy Diamonds"/Flickr; credit "graphite" photo: modification of work by images-of-elements.com/carbon.php)

Dispersal of Matter and Energy

Extending the discussion of thermodynamic concepts toward the objective of predicting spontaneity, consider now an isolated system consisting of two flasks connected with a closed valve. Initially there is an ideal gas in one flask and the other flask is empty (P = 0). (Figure 16.4). When the valve is opened, the gas spontaneously expands to fill both flasks equally. Recalling the definition of pressure-volume work from the chapter on thermochemistry, note that no work has been done because the pressure in a vacuum is zero.

$$w = -P\Delta V = 0 \qquad (P = 0 \text{ in a vacuum})$$

Note as well that since the system is isolated, no heat has been exchanged with the surroundings (q = 0). The *first law of thermodynamics* confirms that there has been no change in the system's internal energy as a result of this process.

$$\Delta U = q + w = 0 + 0 =$$

The spontaneity of this process is therefore not a consequence of any change in energy that accompanies the process. Instead, the driving force appears to be related to the *greater, more uniform dispersal of matter* that results when the gas is allowed to expand. Initially, the system was comprised of one flask containing matter and another flask containing nothing. After the spontaneous expansion took place, the matter was distributed both more widely (occupying twice its original volume) and more uniformly (present in equal amounts in each flask).

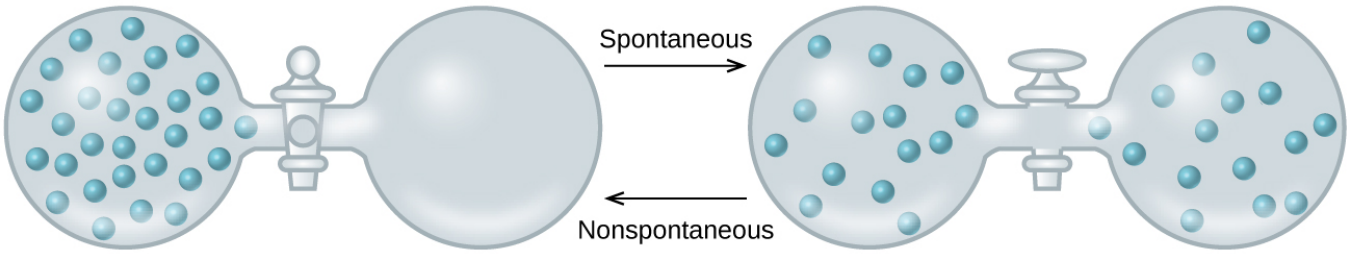


Figure 16.4 An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.

Now consider two objects at different temperatures: object X at temperature T_X and object Y at temperature T_Y, with $T_X > T_Y$ (Figure 16.5). When these objects come into contact, heat spontaneously flows from the hotter object (X) to the colder one (Y). This corresponds to a loss of thermal energy by X and a gain of thermal energy by Y.

$$q_X < 0 \qquad \text{and} \qquad q_Y = -q_X >$$

From the perspective of this two-object system, there was no net gain or loss of thermal energy, rather the available thermal energy was redistributed among the two objects. This spontaneous process resulted in a *more uniform dispersal of energy*.



Figure 16.5 When two objects at different temperatures come in contact, heat spontaneously flows from the hotter to the colder object.

As illustrated by the two processes described, an important factor in determining the spontaneity of a process is the extent to which it changes the dispersal or distribution of matter and/or energy. In each case, a spontaneous process took place that resulted in a more uniform distribution of matter or energy.

Example 16.1

Redistribution of Matter during a Spontaneous Process

Describe how matter is redistributed when the following spontaneous processes take place:

(a) A solid sublimes.

(b) A gas condenses.

(c) A drop of food coloring added to a glass of water forms a solution with uniform color.

Solution

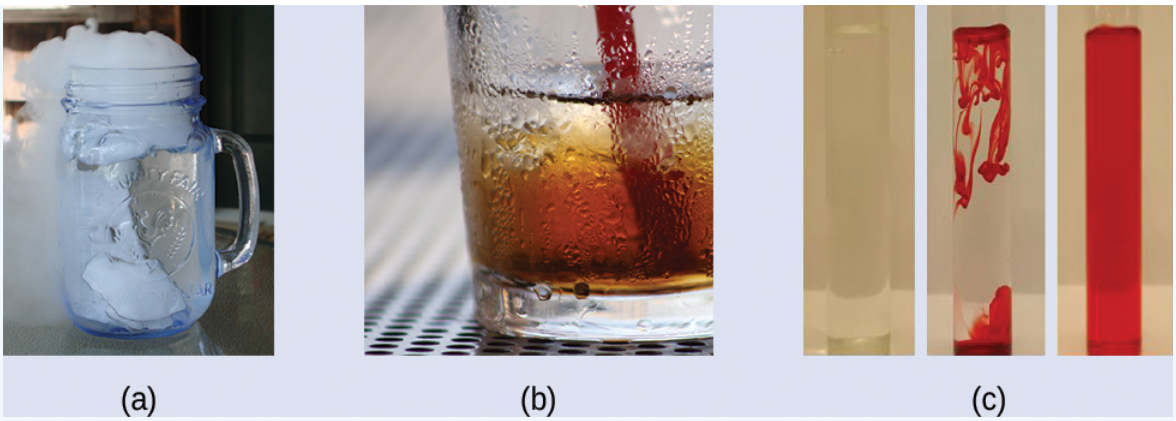


Figure 16.6 (credit a: modification of work by Jenny Downing; credit b: modification of work by “Fuzzy Gerdes”/Flickr; credit c: modification of work by Paul A. Flowers)

(a) Sublimation is the conversion of a solid (relatively high density) to a gas (much lesser density). This process yields a much greater dispersal of matter, since the molecules will occupy a much greater volume after the solid-to-gas transition.

(b) Condensation is the conversion of a gas (relatively low density) to a liquid (much greater density). This process yields a much lesser dispersal of matter, since the molecules will occupy a much lesser volume after the gas-to-liquid transition.

(c) The process in question is diffusion. This process yields a more uniform dispersal of matter, since the initial state of the system involves two regions of different dye concentrations (high in the drop of dye, zero in the water), and the final state of the system contains a single dye concentration throughout.

Check Your Learning

Describe how energy is redistributed when a spoon at room temperature is placed in a cup of hot coffee.

Answer:

Heat will spontaneously flow from the hotter object (coffee) to the colder object (spoon), resulting in a more uniform distribution of thermal energy as the spoon warms and the coffee cools.

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

- Define entropy
- Explain the relationship between entropy and the number of microstates
- Predict the sign of the entropy change for chemical and physical processes

In 1824, at the age of 28, Nicolas Léonard Sadi Carnot (Figure 16.7) published the results of an extensive study regarding the efficiency of steam heat engines. A later review of Carnot’s findings by Rudolf Clausius introduced a new thermodynamic property that relates the spontaneous heat flow accompanying a process to the temperature at which the process takes place. This new property was expressed as the ratio of the *reversible* heat (q_{rev}) and the kelvin temperature (T). In thermodynamics, a reversible process is one that takes place at such a slow rate that it is always at equilibrium and its direction can be changed (it can be “reversed”) by an infinitesimally small change in some condition. Note that the idea of a reversible process is a formalism required to support the development of various thermodynamic concepts; no real processes are truly reversible, rather they are classified as *irreversible*.



Figure 16.7 (a) Nicholas Léonard Sadi Carnot's research into steam-powered machinery and (b) Rudolf Clausius's later study of those findings led to groundbreaking discoveries about spontaneous heat flow processes.

Similar to other thermodynamic properties, this new quantity is a state function, so its change depends only upon the initial and final states of a system. In 1865, Clausius named this property entropy (*S*) and defined its change for any process as the following:

$$\Delta S = \frac{q_{rev}}{T} \tag{12.1.1}$$

The entropy change for a real, irreversible process is then equal to that for the theoretical reversible process that involves the same initial and final states.

Entropy and Microstates

Following the work of Carnot and Clausius, Ludwig Boltzmann developed a molecular-scale statistical model that related the entropy of a system to the *number of microstates* (*W*) possible for the system. A microstate is a specific configuration of all the locations and energies of the atoms or molecules that make up a system. The relation between a system's entropy and the number of possible microstates is

$$S = k \ln W S \tag{12.1.2}$$

where *k* is the Boltzmann constant, 1.38×10^{-23} J/K.

As for other state functions, the change in entropy for a process is the difference between its final (S_f) and initial (S_i) values:

$$\Delta S = S_f - S_i = k \ln W_f - k \ln W_i = k \ln \frac{W_f}{W_i} \tag{12.1.3}$$

For processes involving an increase in the number of microstates, $W_f > W_i$, the entropy of the system increases and $\Delta S > 0$. Conversely, processes that reduce the number of microstates, $W_f < W_i$, yield a decrease in system entropy, $\Delta S < 0$. This molecular-scale interpretation of entropy provides a link to the probability that a process will occur as illustrated in the next paragraphs.

Consider the general case of a system comprised of N particles distributed among n boxes. The number of microstates possible for such a system is n^N. For example, distributing four particles among two boxes will result in $2^4 = 16$ different microstates as illustrated in Figure 16.8. Microstates with equivalent particle arrangements (not considering individual particle identities) are grouped together and are called *distributions*. The probability that a system will exist with its components in a given distribution is proportional to the number of microstates within the distribution. Since entropy increases logarithmically with the number of microstates, *the most probable distribution is therefore the one of greatest entropy*.

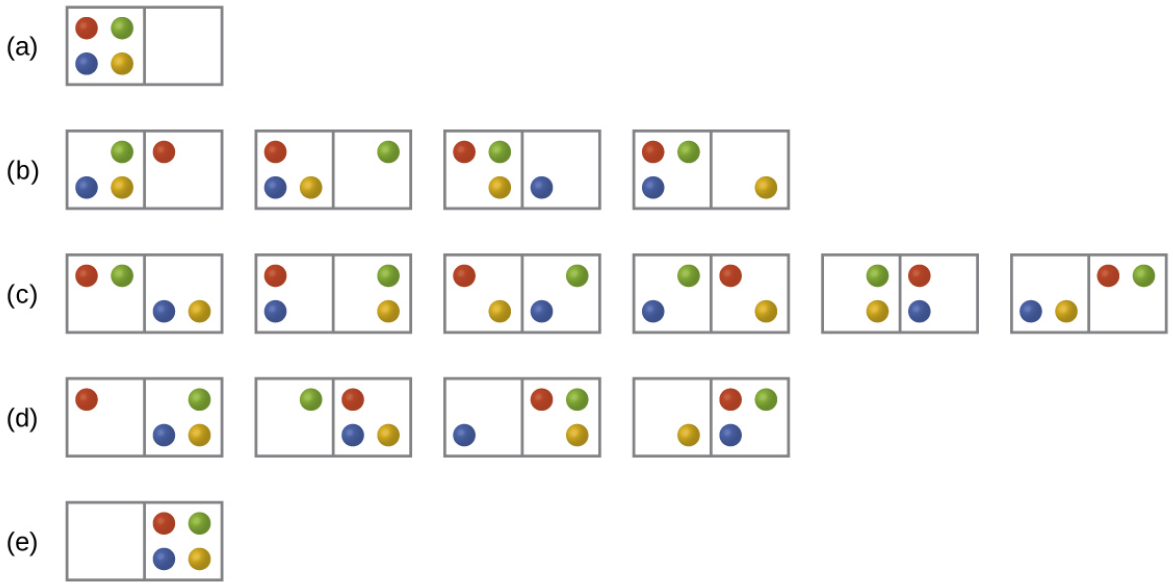


Figure 16.8 The sixteen microstates associated with placing four particles in two boxes are shown. The microstates are collected into five distributions—(a), (b), (c), (d), and (e)—based on the numbers of particles in each box.

For this system, the most probable configuration is one of the six microstates associated with distribution (c) where the particles are evenly distributed between the boxes, that is, a configuration of two particles in each box. The probability of finding the system in this configuration is $\frac{6}{16}$ or $\frac{3}{8}$. The least probable configuration of the system is one in which all four particles are in one box, corresponding to distributions (a) and (e), each with a probability of $\frac{1}{16}$. The probability of finding all particles in only one box (either the left box or right box) is then $\left(\frac{1}{16} + \frac{1}{16}\right) = \frac{2}{16}$ or $\frac{1}{8}$.

As you add more particles to the system, the number of possible microstates increases exponentially (2^N). A macroscopic (laboratory-sized) system would typically consist of moles of particles ($N \sim 10^{23}$), and the corresponding number of microstates would be staggeringly huge. Regardless of the number of particles in the system, however, the distributions in which roughly equal numbers of particles are found in each box are always the most probable configurations.

This matter dispersal model of entropy is often described qualitatively in terms of the *disorder* of the system. By this description, microstates in which all the particles are in a single box are the most ordered, thus possessing the least entropy. Microstates in which the particles are more evenly distributed among the boxes are more disordered, possessing greater entropy.

The previous description of an ideal gas expanding into a vacuum (Figure 16.4) is a macroscopic example of this particle-in-a-box model. For this system, the most probable distribution is confirmed to be the one in which the matter is most uniformly dispersed or distributed between the two flasks. Initially, the gas molecules are confined to just one of the two flasks. Opening the valve between the flasks increases the volume available to the gas molecules and, correspondingly, the number of microstates possible for the system. Since $W_f > W_i$, the expansion process involves an increase in entropy ($\Delta S > 0$) and is spontaneous.

A similar approach may be used to describe the spontaneous flow of heat. Consider a system consisting of two objects, each containing two particles, and two units of thermal energy (represented as "*") in Figure 16.9. The hot object is comprised of particles **A** and **B** and initially contains both energy units. The cold object is comprised of particles **C** and **D**, which initially has no energy units. Distribution (a) shows the three microstates possible for the initial state of the system, with both units of energy contained within the hot object. If one of the two energy units is transferred, the result is distribution (b) consisting of four microstates. If both energy units are transferred, the result is distribution (c) consisting of three microstates. Thus, we may describe this system by a total of ten microstates. The probability that the heat does not flow when the two objects are brought into contact,

that is, that the system remains in distribution (a), is $\frac{3}{10}$. More likely is the flow of heat to yield one of the other two distribution, the combined probability being $\frac{7}{10}$. The most likely result is the flow of heat to yield the uniform dispersal of energy represented by distribution (b), the probability of this configuration being $\frac{4}{10}$. This supports the common observation that placing hot and cold objects in contact results in spontaneous heat flow that ultimately equalizes the objects' temperatures. And, again, this spontaneous process is also characterized by an increase in system entropy.

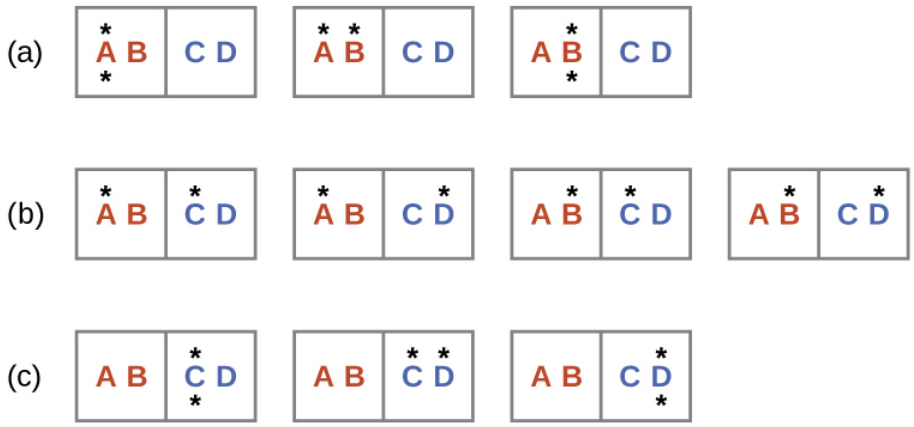
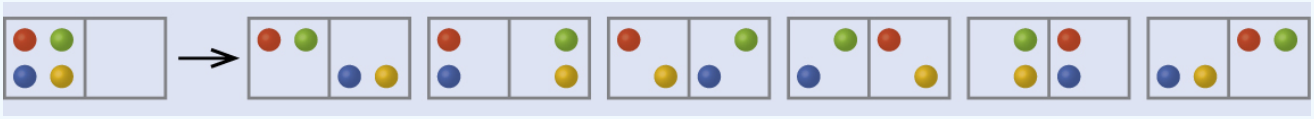


Figure 16.9 This shows a microstate model describing the flow of heat from a hot object to a cold object. (a) Before the heat flow occurs, the object comprised of particles **A** and **B** contains both units of energy and as represented by a distribution of three microstates. (b) If the heat flow results in an even dispersal of energy (one energy unit transferred), a distribution of four microstates results. (c) If both energy units are transferred, the resulting distribution has three microstates.

Example 16.2

Determination of ΔS

Calculate the change in entropy for the process depicted below.



Solution

The initial number of microstates is one, the final six:

$$\Delta S = k \ln \frac{W_c}{W_a} = 1.38 \times 10^{-}23\,\text{J/K} \times \ln \frac{6}{1} = 2.47 \times 10^{-}23\,\text{J/}$$

The sign of this result is consistent with expectation; since there are more microstates possible for the final state than for the initial state, the change in entropy should be positive.

Check Your Learning

Consider the system shown in Figure 16.9. What is the change in entropy for the process where *all* the energy is transferred from the hot object (**AB**) to the cold object (**CD**)?

Answer:

0 J/K

Predicting the Sign of ΔS

The relationships between entropy, microstates, and matter/energy dispersal described previously allow us to make generalizations regarding the relative entropies of substances and to predict the sign of entropy changes for chemical and physical processes. Consider the phase changes illustrated in Figure 16.10. In the solid phase, the atoms or molecules are restricted to nearly fixed positions with respect to each other and are capable of only modest oscillations about these positions. With essentially fixed

locations for the system's component particles, the number of microstates is relatively small. In the liquid phase, the atoms or molecules are free to move over and around each other, though they remain in relatively close proximity to one another. This increased freedom of motion results in a greater variation in possible particle locations, so the number of microstates is correspondingly greater than for the solid. As a result, $S_{liquid} > S_{solid}$ and the process of converting a substance from solid to liquid (melting) is characterized by an increase in entropy, $\Delta S > 0$. By the same logic, the reciprocal process (freezing) exhibits a decrease in entropy, $\Delta S < 0$.

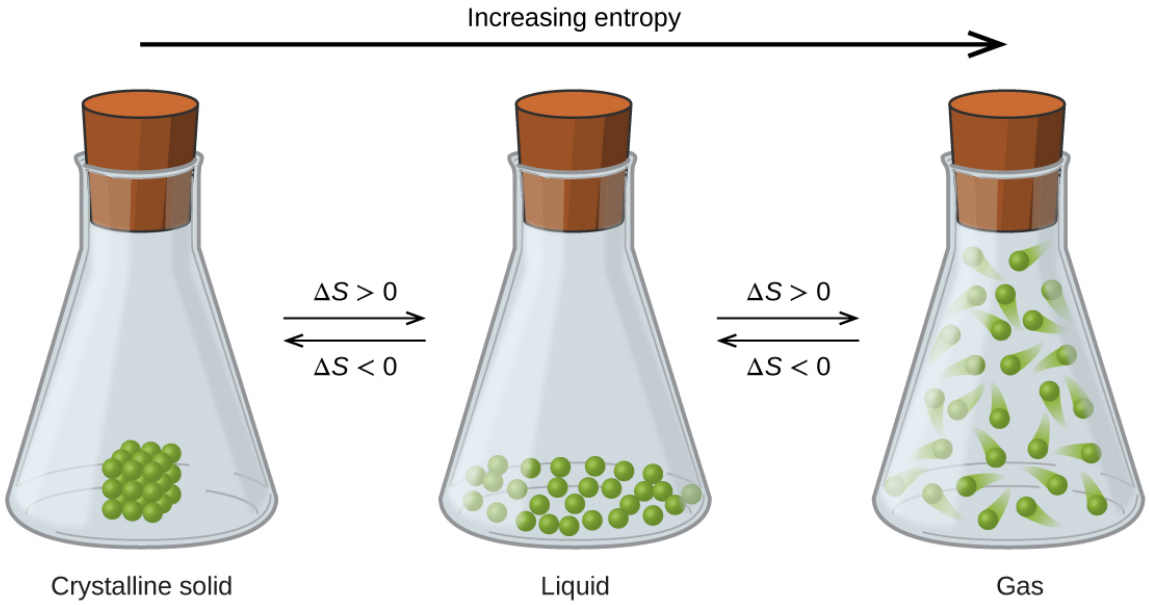


Figure 16.10 The entropy of a substance increases ($\Delta S > 0$) as it transforms from a relatively ordered solid, to a less-ordered liquid, and then to a still less-ordered gas. The entropy decreases ($\Delta S < 0$) as the substance transforms from a gas to a liquid and then to a solid.

Now consider the gaseous phase, in which a given number of atoms or molecules occupy a *much* greater volume than in the liquid phase. Each atom or molecule can be found in many more locations, corresponding to a much greater number of microstates. Consequently, for any substance, $S_{gas} > S_{liquid} > S_{solid}$, and the processes of vaporization and sublimation likewise involve increases in entropy, $\Delta S > 0$. Likewise, the reciprocal phase transitions, condensation and deposition, involve decreases in entropy, $\Delta S < 0$.

According to kinetic-molecular theory, the temperature of a substance is proportional to the average kinetic energy of its particles. Raising the temperature of a substance will result in more extensive vibrations of the particles in solids and more rapid translations of the particles in liquids and gases. At higher temperatures, the distribution of kinetic energies among the atoms or molecules of the substance is also broader (more dispersed) than at lower temperatures. Thus, the entropy for any substance increases with temperature (Figure 16.11).

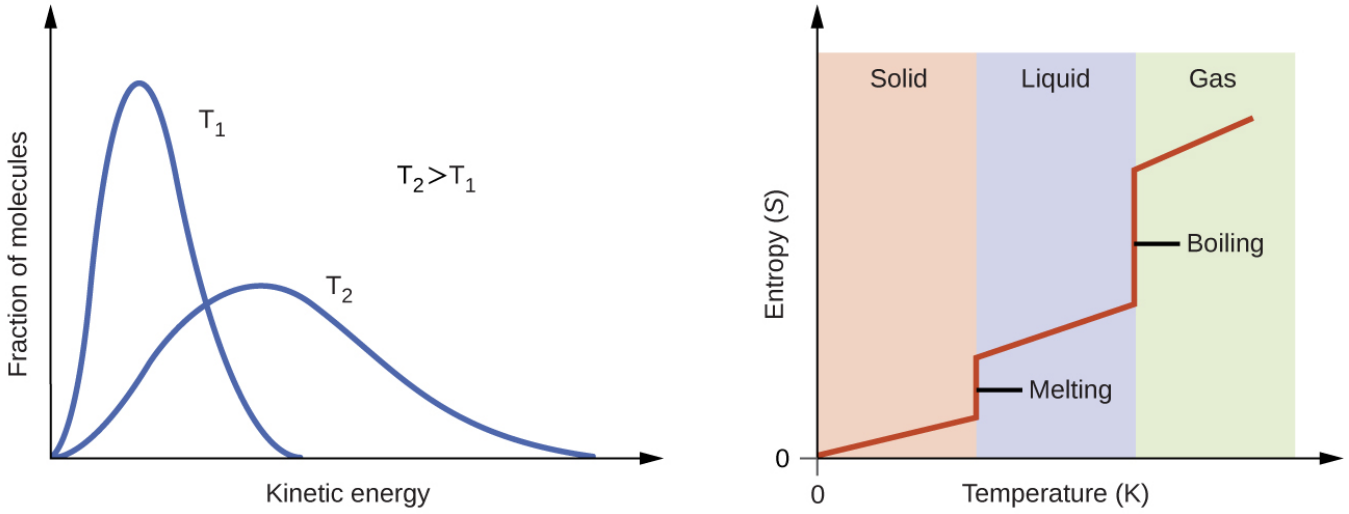


Figure 16.11 Entropy increases as the temperature of a substance is raised, which corresponds to the greater spread of kinetic energies. When a substance undergoes a phase transition, its entropy changes significantly.

Link to Learning

Try this simulator with interactive visualization of the dependence of particle location and freedom of motion on physical state and temperature.

The entropy of a substance is influenced by the structure of the particles (atoms or molecules) that comprise the substance. With regard to atomic substances, heavier atoms possess greater entropy at a given temperature than lighter atoms, which is a consequence of the relation between a particle's mass and the spacing of quantized translational energy levels (a topic beyond the scope of this text). For molecules, greater numbers of atoms increase the number of ways in which the molecules can vibrate and thus the number of possible microstates and the entropy of the system.

Finally, variations in the types of particles affects the entropy of a system. Compared to a pure substance, in which all particles are identical, the entropy of a mixture of two or more different particle types is greater. This is because of the additional orientations and interactions that are possible in a system comprised of nonidentical components. For example, when a solid dissolves in a liquid, the particles of the solid experience both a greater freedom of motion and additional interactions with the solvent particles. This corresponds to a more uniform dispersal of matter and energy and a greater number of microstates. The process of dissolution therefore involves an increase in entropy, $\Delta S > 0$.

Considering the various factors that affect entropy allows us to make informed predictions of the sign of ΔS for various chemical and physical processes as illustrated in Example 16.3.

Example 16.3

Predicting the Sign of ΔS

Predict the sign of the entropy change for the following processes. Indicate the reason for each of your predictions.

(a) One mole liquid water at room temperature $\longrightarrow$ one mole liquid water at 50 °C

(b) $\mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq) \longrightarrow \mathrm{AgCl}(s)$

(c) $\mathrm{C_6H_6}(l) + \frac{15}{2}\mathrm{O_2}(g) \longrightarrow 6\mathrm{CO_2}(g) + 3\mathrm{H_2O}(l)$

(d) $\mathrm{NH_3}(s) \longrightarrow \mathrm{NH_3}(l)$

Solution

(a) positive, temperature increases

(b) negative, reduction in the number of ions (particles) in solution, decreased dispersal of matter

(c) negative, net decrease in the amount of gaseous species

(d) positive, phase transition from solid to liquid, net increase in dispersal of matter

Check Your Learning

Predict the sign of the entropy change for the following processes. Give a reason for your prediction.

(a) $\mathrm{NaNO_3}(s) \longrightarrow \mathrm{Na}+(aq) + \mathrm{NO_3}^-(aq)$

(b) the freezing of liquid water

(c) $\mathrm{CO_2}(s) \longrightarrow \mathrm{CO_2}(g)$

(d) $\mathrm{CaCO_3}(s) \longrightarrow \mathrm{CaO}(s) + \mathrm{CO_2}(g)$

Answer:

(a) Positive; The solid dissolves to give an increase of mobile ions in solution. (b) Negative; The liquid becomes a more ordered solid. (c) Positive; The relatively ordered solid becomes a gas. (d) Positive; There

12.1: Introduction to Spontaneity and Entropy is shared under a CC BY license and was authored, remixed, and/or curated by LibreTexts.

12.2: The Second and Third Laws of Thermodynamics

Learning Objectives

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

- State and explain the second and third laws of thermodynamics
- Calculate entropy changes for phase transitions and chemical reactions under standard conditions

12.2.0.1: The Second Law of Thermodynamics

In the quest to identify a property that may reliably predict the spontaneity of a process, a promising candidate has been identified: entropy. Processes that involve an increase in entropy *of the system* ($\Delta S > 0$) are very often spontaneous; however, examples to the contrary are plentiful. By expanding consideration of entropy changes to include *the surroundings*, we may reach a significant conclusion regarding the relation between this property and spontaneity. In thermodynamic models, the system and surroundings comprise everything, that is, the universe, and so the following is true

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \tag{12.2.1}$$

To illustrate this relation, consider again the process of heat flow between two objects, one identified as the system and the other as the surroundings. There are three possibilities for such a process:

1. The objects are at different temperatures, and heat flows from the hotter to the cooler object. *This is always observed to occur spontaneously.* Designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{\text{sys}} = \frac{-q_{\text{rev}}}{T_{\text{sys}}} \text{ and } \Delta S_{\text{surr}} = \frac{q_{\text{rev}}}{T_{\text{surr}}} \tag{12.2.2}$$

The magnitudes of $-q_{\text{rev}}$ and q_{rev} are equal, their opposite arithmetic signs denoting loss of heat by the system and gain of heat by the surroundings. Since $T_{\text{sys}} > T_{\text{surr}}$ in this scenario, the entropy *decrease* of the system will be less than the entropy *increase* of the surroundings, and so *the entropy of the universe will increase*:

$$\begin{aligned} |\Delta S_{\text{sys}}| &< |\Delta S_{\text{surr}}| \\ \Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \end{aligned}$$

2. The objects are at different temperatures, and heat flows from the cooler to the hotter object. *This is never observed to occur spontaneously.* Again designating the hotter object as the system and invoking the definition of entropy yields the following

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T_{\text{sys}}} \text{ and } \Delta S_{\text{surr}} = \frac{-q_{\text{rev}}}{T_{\text{surr}}} \tag{12.2.3}$$

The arithmetic signs of q_{rev} denote the gain of heat by the system and the loss of heat by the surroundings. The magnitude of the entropy change for the surroundings will again be greater than that for the system, but in this case, the signs of the heat changes (that is, *the direction of the heat flow*) will yield a negative value for ΔS_{univ}. *This process involves a decrease in the entropy of the universe.*

3. The objects are at essentially the same temperature, $T_{\text{sys}} \approx T_{\text{surr}}$, and so the magnitudes of the entropy changes are essentially the same for both the system and the surroundings. In this case, the entropy change of the universe is zero, and the system is *at equilibrium*.

$$\begin{aligned} |\Delta S_{\text{sys}}| &\approx |\Delta S_{\text{surr}}| \\ \Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0 \end{aligned}$$

These results lead to a profound statement regarding the relation between entropy and spontaneity known as the second law of thermodynamics: *all spontaneous changes cause an increase in the entropy of the universe.* A summary of these three relations is provided in Table 16.1.

The Second Law of Thermodynamics

$\Delta S_{univ} > 0$	spontaneous
$\Delta S_{univ} < 0$	nonspontaneous (spontaneous in opposite direction)
$\Delta S_{univ} = 0$	at equilibrium

Table 16.1

For many realistic applications, the surroundings are vast in comparison to the system. In such cases, the heat gained or lost by the surroundings as a result of some process represents a very small, nearly infinitesimal, fraction of its total thermal energy. For example, combustion of a fuel in air involves transfer of heat from a system (the fuel and oxygen molecules undergoing reaction) to surroundings that are infinitely more massive (the earth's atmosphere). As a result, q_{surr} is a good approximation of q_{rev}, and the second law may be stated as the following:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \tag{12.2.4}$$

We may use this equation to predict the spontaneity of a process as illustrated in Example 16.4.

12.2.0.1: Example 16.4

12.2.0.0.1: Will Ice Spontaneously Melt?

The entropy change for the process

$$\mathrm{H_2O}(s) \longrightarrow \mathrm{H_2O}(l)$$

is 22.1 J/K and requires that the surroundings transfer 6.00 kJ of heat to the system. Is the process spontaneous at −10.00 °C? Is it spontaneous at +10.00 °C?

12.2.0.0.2: Solution

We can assess the spontaneity of the process by calculating the entropy change of the universe. If ΔS_{univ} is positive, then the process is spontaneous. At both temperatures, ΔS_{sys} = 22.1 J/K and q_{surr} = −6.00 kJ.

At −10.00 °C (263.15 K), the following is true:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \tfrac{q_{\text{surr}}}{T} \\ &= 22.1\ \text{J/K} + \tfrac{-6.00 \times 10^3\ \text{J}}{263.15\ \text{K}} = -0.7\ \text{J/}\end{aligned}$$

S_{univ} < 0, so melting is nonspontaneous (*not* spontaneous) at −10.0 °C.

At 10.00 °C (283.15 K), the following is true:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \tfrac{q_{\text{surr}}}{T}$$

$$= 22.1\ \text{J/K} + \frac{-6.00 \times 10^3\ \text{J}}{283.15\ \text{K}} = +0.9\ \text{J/}$$

S_{univ} > 0, so melting *is* spontaneous at 10.00 °C.

12.2.0.0.3: Check Your Learning

Using this information, determine if liquid water will spontaneously freeze at the same temperatures. What can you say about the values of S_{univ}?

12.2.0.1: Answer:

Entropy is a state function, so $\Delta S_{freezing} = -\Delta S_{melting}$ = −22.1 J/K and q_{surr} = +6.00 kJ. At −10.00 °C spontaneous, +0.7 J/K; at +10.00 °C nonspontaneous, −0.9 J/K.

This page titled 12.2: The Second and Third Laws of Thermodynamics 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.

12.3: Free Energy

Learning Objectives

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

- Define Gibbs free energy, and describe its relation to spontaneity
- Calculate free energy change for a process using free energies of formation for its reactants and products
- Calculate free energy change for a process using enthalpies of formation and the entropies for its reactants and products
- Explain how temperature affects the spontaneity of some processes
- Relate standard free energy changes to equilibrium constants

One of the challenges of using the second law of thermodynamics to determine if a process is spontaneous is that it requires measurements of the entropy change for the system *and* the entropy change for the surroundings. An alternative approach involving a new thermodynamic property defined in terms of system properties only was introduced in the late nineteenth century by American mathematician Josiah Willard Gibbs. This new property is called the Gibbs free energy (G) (or simply the *free energy*), and it is defined in terms of a system's enthalpy and entropy as the following:

$$G = H - TS \tag{12.3.1}$$

Free energy is a state function, and at constant temperature and pressure, the free energy change (ΔG) may be expressed as the following:

$$\Delta G = \Delta H - T\Delta S \tag{12.3.2}$$

(For simplicity's sake, the subscript "sys" will be omitted henceforth.)

The relationship between this system property and the spontaneity of a process may be understood by recalling the previously derived second law expression:

$$\Delta S_{\text{univ}} = \Delta S + \frac{q_{\text{surr}}}{T} \tag{12.3.3}$$

The first law requires that $q_{\text{surr}} = -q_{\text{sys}}$, and at constant pressure $q_{\text{sys}} = \Delta H$, so this expression may be rewritten as:

$$\Delta S_{\text{univ}} = \Delta S - \frac{\Delta H}{T} \tag{12.3.4}$$

Multiplying both sides of this equation by $-T$, and rearranging yields the following:

$$-T\Delta S_{\text{univ}} = \Delta H - T\Delta S \tag{12.3.5}$$

Comparing this equation to the previous one for free energy change shows the following relation

$$\Delta G = -T\Delta S_{\text{univ}} \tag{12.3.6}$$

The free energy change is therefore a reliable indicator of the spontaneity of a process, being directly related to the previously identified spontaneity indicator, ΔS_{univ}. Table 16.3 summarizes the relation between the spontaneity of a process and the arithmetic signs of these indicators.

Relation between Process Spontaneity and Signs of Thermodynamic Properties

$\Delta S_{\text{univ}} > 0$	$\Delta G < 0$	spontaneous
$\Delta S_{\text{univ}} < 0$	$\Delta G > 0$	nonspontaneous
$\Delta S_{\text{univ}} = 0$	$\Delta G = 0$	at equilibrium

Table 16.3

12.3.0.1: What's "Free" about ΔG?

In addition to indicating spontaneity, the free energy change also provides information regarding the amount of useful work (w) that may be accomplished by a spontaneous process. Although a rigorous treatment of this subject is beyond the scope of an

introductory chemistry text, a brief discussion is helpful for gaining a better perspective on this important thermodynamic property.

For this purpose, consider a spontaneous, exothermic process that involves a decrease in entropy. The free energy, as defined by

$$\Delta G = \Delta H - T\Delta S \tag{12.3.7}$$

may be interpreted as representing the difference between the energy produced by the process, ΔH, and the energy lost to the surroundings, $T\Delta S$. The difference between the energy produced and the energy lost is the energy available (or "free") to do useful work by the process, ΔG. If the process somehow could be made to take place under conditions of thermodynamic reversibility, the amount of work that could be done would be maximal:

$$\Delta G = w_{\text{max}} \tag{12.3.8}$$

where w_{max} refers to all types of work except expansion (pressure-volume) work.

However, as noted previously in this chapter, such conditions are not realistic. In addition, the technologies used to extract work from a spontaneous process (e.g., batteries) are never 100% efficient, and so the work done by these processes is always less than the theoretical maximum. Similar reasoning may be applied to a nonspontaneous process, for which the free energy change represents the *minimum* amount of work that must be done *on* the system to carry out the process.

12.3.0.1: Calculating Free Energy Change

Free energy is a state function, so its value depends only on the conditions of the initial and final states of the system. A convenient and common approach to the calculation of free energy changes for physical and chemical reactions is by use of widely available compilations of standard state thermodynamic data. One method involves the use of standard enthalpies and entropies to compute standard free energy changes, $\Delta G°$, according to the following relation.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

12.3.0.1: Example 16.7

12.3.0.0.1: Using Standard Enthalpy and Entropy Changes to Calculate $\Delta G°$

Use standard enthalpy and entropy data from Appendix G to calculate the standard free energy change for the vaporization of water at room temperature (298 K). What does the computed value for $\Delta G°$ say about the spontaneity of this process?

12.3.0.0.2: Solution

The process of interest is the following:

$$\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(g)$$

The standard change in free energy may be calculated using the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

From Appendix G:

Substance	$\Delta H_\mathrm{f}^\circ\,(\mathrm{kJ/mol})$	$S^\circ\,(\mathrm{J/K{\cdot}mol})$
$\mathrm{H_2O}(l)$	−285.83	70.0
$\mathrm{H_2O}(g)$	−241.82	188.8

Using the appendix data to calculate the standard enthalpy and entropy changes yields:

$$\begin{aligned}\Delta H^\circ &= \Delta H_\mathrm{f}^\circ\left(\mathrm{H_2O}(g)\right) - \Delta H_\mathrm{f}^\circ\left(\mathrm{H_2O}(l)\right)\\ &= [-241.82\ \mathrm{kJ/mol} - (-285.83)]\ \mathrm{kJ/mol} = 44.01\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= 1\ \mathrm{mol} \times S^\circ\left(\mathrm{H_2O}(g)\right) - 1\ \mathrm{mol} \times S^\circ\left(\mathrm{H_2O}(l)\right)\\ &= (1\ \mathrm{mol})188.8\ \mathrm{J/mol{\cdot}K} - (1\ \mathrm{mol})70.0\ \mathrm{J/mol\ K} = 118.8\ \mathrm{J/}\end{aligned}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Substitution into the standard free energy equation yields:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= 44.01\ \text{kJ} - (298\ \text{K} \times 118.8\ \text{J/K}) \times \tfrac{1}{\text{kJ}}$$

$$44.01\ \text{kJ} - 35.4\ \text{kJ} = 8.6\ \text{kJ}$$

At 298 K (25 °C) $\Delta G^\circ > 0$, so boiling is nonspontaneous (*not* spontaneous).

12.3.0.0.3: Check Your Learning

Use standard enthalpy and entropy data from Appendix G to calculate the standard free energy change for the reaction shown here (298 K). What does the computed value for Δ*G*° say about the spontaneity of this process?

$$\text{C}_2\text{H}_6(g) \longrightarrow \text{H}_2(g) + \text{C}_2\text{H}_4(g)$$

12.3.0.1: Answer:

$\Delta G^\circ = 102.0\ \text{kJ/mol}$; the reaction is nonspontaneous (*not* spontaneous) at 25 °C.

12.3.0.1: Temperature Dependence of Spontaneity

As was previously demonstrated in this chapter's section on entropy, the spontaneity of a process may depend upon the temperature of the system. Phase transitions, for example, will proceed spontaneously in one direction or the other depending upon the temperature of the substance in question. Likewise, some chemical reactions can also exhibit temperature dependent spontaneities. To illustrate this concept, the equation relating free energy change to the enthalpy and entropy changes for the process is considered:

$$\Delta G = \Delta H - T\Delta S \tag{12.3.9}$$

The spontaneity of a process, as reflected in the arithmetic sign of its free energy change, is then determined by the signs of the enthalpy and entropy changes and, in some cases, the absolute temperature. Since *T* is the absolute (kelvin) temperature, it can only have positive values. Four possibilities therefore exist with regard to the signs of the enthalpy and entropy changes:

1. **Both Δ*H* and Δ*S* are positive.** This condition describes an endothermic process that involves an increase in system entropy. In this case, Δ*G* will be negative if the magnitude of the *T*Δ*S* term is greater than Δ*H*. If the *T*Δ*S* term is less than Δ*H*, the free energy change will be positive. Such a process is *spontaneous at high temperatures and nonspontaneous at low temperatures.*
2. **Both Δ*H* and Δ*S* are negative.** This condition describes an exothermic process that involves a decrease in system entropy. In this case, Δ*G* will be negative if the magnitude of the *T*Δ*S* term is less than Δ*H*. If the *T*Δ*S* term's magnitude is greater than Δ*H*, the free energy change will be positive. Such a process is *spontaneous at low temperatures and nonspontaneous at high temperatures.*
3. **Δ*H* is positive and Δ*S* is negative.** This condition describes an endothermic process that involves a decrease in system entropy. In this case, Δ*G* will be positive regardless of the temperature. Such a process is *nonspontaneous at all temperatures.*
4. **Δ*H* is negative and Δ*S* is positive.** This condition describes an exothermic process that involves an increase in system entropy. In this case, Δ*G* will be negative regardless of the temperature. Such a process is *spontaneous at all temperatures.*

These four scenarios are summarized in Figure 16.12.

Summary of the Four Scenarios for Enthalpy and Entropy Changes

	$\Delta H > 0$ (endothermic)	$\Delta H < 0$ (exothermic)
$\Delta S > 0$ (increase in entropy)	$\Delta G < 0$ at high temperature $\Delta G > 0$ at low temperature Process is spontaneous at high temperature	$\Delta G < 0$ at any temperature Process is spontaneous at any temperature
$\Delta S < 0$ (decrease in entropy)	$\Delta G > 0$ at any temperature Process is nonspontaneous at any temperature	$\Delta G < 0$ at low temperature $\Delta G > 0$ at high temperature Process is spontaneous at low temperature

Figure 16.12 There are four possibilities regarding the signs of enthalpy and entropy changes.

12.3.0.1: Example 16.10

12.3.0.0.1: Predicting the Temperature Dependence of Spontaneity

The incomplete combustion of carbon is described by the following equation:

$$2\mathrm{C}(s) + \mathrm{O_2}(g) \longrightarrow 2\mathrm{CO}(g)$$

How does the spontaneity of this process depend upon temperature?

12.3.0.0.2: Solution

Combustion processes are exothermic ($\Delta H < 0$). This particular reaction involves an increase in entropy due to the accompanying increase in the amount of gaseous species (net gain of one mole of gas, $\Delta S > 0$). The reaction is therefore spontaneous ($\Delta G < 0$) at all temperatures.

12.3.0.0.3: Check Your Learning

Popular chemical hand warmers generate heat by the air-oxidation of iron:

$$4\mathrm{Fe}(s) + 3\mathrm{O_2}(g) \longrightarrow 2\mathrm{Fe_2O_3}(s)$$

How does the spontaneity of this process depend upon temperature?

12.3.0.1: Answer:

ΔH and ΔS are negative; the reaction is spontaneous at low temperatures.

When considering the conclusions drawn regarding the temperature dependence of spontaneity, it is important to keep in mind what the terms “high” and “low” mean. Since these terms are adjectives, the temperatures in question are deemed high or low relative to

some reference temperature. A process that is nonspontaneous at one temperature but spontaneous at another will necessarily undergo a change in "spontaneity" (as reflected by its ΔG) as temperature varies. This is clearly illustrated by a graphical presentation of the free energy change equation, in which ΔG is plotted on the y axis versus T on the x axis:

$$\Delta G = \Delta H - T\Delta S$$
$$y = b + mx$$

Such a plot is shown in Figure 16.13. A process whose enthalpy and entropy changes are of the same arithmetic sign will exhibit a temperature-dependent spontaneity as depicted by the two yellow lines in the plot. Each line crosses from one spontaneity domain (positive or negative ΔG) to the other at a temperature that is characteristic of the process in question. This temperature is represented by the x-intercept of the line, that is, the value of T for which ΔG is zero

$$\Delta G = 0 = \Delta H - T\Delta S$$
$$T = \frac{\Delta H}{\Delta S}$$

So, saying a process is spontaneous at "high" or "low" temperatures means the temperature is above or below, respectively, that temperature at which ΔG for the process is zero. As noted earlier, the condition of $\Delta G = 0$ describes a system at equilibrium.

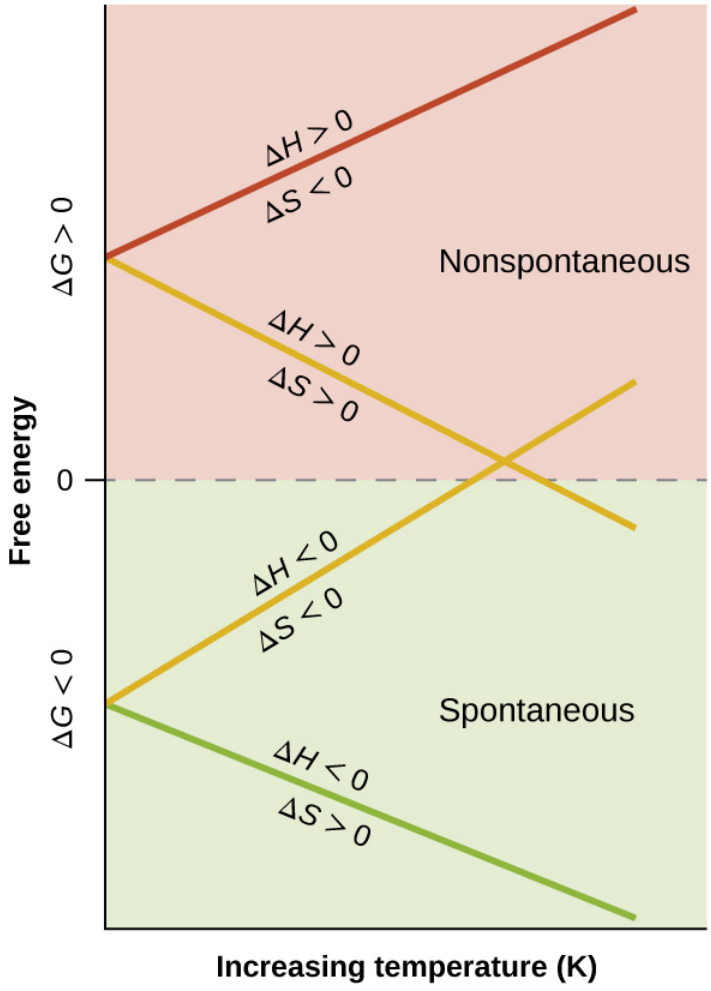


Figure 16.13 These plots show the variation in ΔG with temperature for the four possible combinations of arithmetic sign for ΔH and ΔS.

12.3.0.1: Example 16.11

12.3.0.0.4: Equilibrium Temperature for a Phase Transition

As defined in the chapter on liquids and solids, the boiling point of a liquid is the temperature at which its liquid and gaseous phases are in equilibrium (that is, when vaporization and condensation occur at equal rates). Use the information in Appendix G to estimate the boiling point of water.

12.3.0.0.5: Solution

The process of interest is the following phase change:

$$\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(g)$$

When this process is at equilibrium, $\Delta G = 0$, so the following is true:

$$0 = \Delta H^\circ - T\Delta S^\circ \qquad \text{or} \qquad T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

Using the standard thermodynamic data from Appendix G,

$$\begin{aligned}\Delta H^\circ &= 1\ \text{mol} \times \Delta H_\text{f}^\circ\left(\mathrm{H_2O}(g)\right) - 1\ \text{mol} \times \Delta H_\text{f}^\circ\left(\mathrm{H_2O}(l)\right)\\ &= (1\ \text{mol}) - 241.82\ \text{kJ/mol} - (1\ \text{mol})\,(-286.83\ \text{kJ/mol}) = 44.01\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= 1\ \text{mol} \times \Delta S^\circ\left(\mathrm{H_2O}(g)\right) - 1\ \text{mol} \times \Delta S^\circ\left(\mathrm{H_2O}(l)\right)\\ &= (1\ \text{mol})\ 188.8\ \text{J/K·mol} - (1\ \text{mol})\ 70.0\ \text{J/K·mol} = 118.8\ \text{J/}\end{aligned}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{44.01 \times 10^3\ \text{J}}{118.8\ \text{J/K}} = 370.5\ \text{K} = 97.3\ ^\circ\text{C}$$

The accepted value for water's normal boiling point is 373.2 K (100.0 °C), and so this calculation is in reasonable agreement. Note that the values for enthalpy and entropy changes data used were derived from standard data at 298 K (Appendix G). If desired, you could obtain more accurate results by using enthalpy and entropy changes determined at (or at least closer to) the actual boiling point.

12.3.0.0.6: Check Your Learning

Use the information in Appendix G to estimate the boiling point of CS_2.

12.3.0.1: Answer:

313 K (accepted value 319 K)

This form of the equation provides a useful link between these two essential thermodynamic properties, and it can be used to derive equilibrium constants from standard free energy changes and vice versa. The relations between standard free energy changes and equilibrium constants are summarized in Table 16.4.

Relations between Standard Free Energy Changes and Equilibrium Constants

K	$\Delta G°$	Composition of an Equilibrium Mixture
> 1	< 0	Products are more abundant
< 1	> 0	Reactants are more abundant
= 1	= 0	Reactants and products are comparably abundant

Table 16.4

12.3.0.1: Example 16.13

12.3.0.0.7: Calculating an Equilibrium Constant using Standard Free Energy Change

Given that the standard free energies of formation of $Ag^+(aq)$, $Cl^-(aq)$, and AgCl(s) are 77.1 kJ/mol, −131.2 kJ/mol, and −109.8 kJ/mol, respectively, calculate the solubility product, K_{sp}, for AgCl.

12.3.0.0.8: Solution

The reaction of interest is the following:

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag}^+(aq) + \mathrm{Cl}^-(aq) \qquad\qquad K_{\mathrm{sp}} = [\mathrm{Ag}^+][\mathrm{Cl}^-]$$

The standard free energy change for this reaction is first computed using standard free energies of formation for its reactants and products:

$$\begin{aligned}\Delta G^\circ &= \left[\Delta {G_\mathrm{f}}^\circ\left(\mathrm{Ag}^+(aq)\right) + \Delta {G_\mathrm{f}}^\circ\left(\mathrm{Cl}^-(aq)\right)\right] - \left[\Delta {G_\mathrm{f}}^\circ\left(\mathrm{AgCl}(s)\right)\right] \\ &= [77.1\ \mathrm{kJ/mol} - 131.2\ \mathrm{kJ/mol}] - [-109.8\ \mathrm{kJ/mol}] = 55.7\ \mathrm{kJ/}\end{aligned}$$

The equilibrium constant for the reaction may then be derived from its standard free energy change:

$$K_{\mathrm{sp}} = e^{-\frac{\Delta G^\circ}{RT}} = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(-\frac{55.7 \times 10^3\ \mathrm{J/mol}}{8.314\ \mathrm{J/mol{\cdot}K} \times 298.15\ \mathrm{K}}\right) = \exp\left(-22.470\right) = e^{-22.470} = 1.74 \times 10^-$$

This result is in reasonable agreement with the value provided in Appendix J.

12.3.0.0.9: Check Your Learning

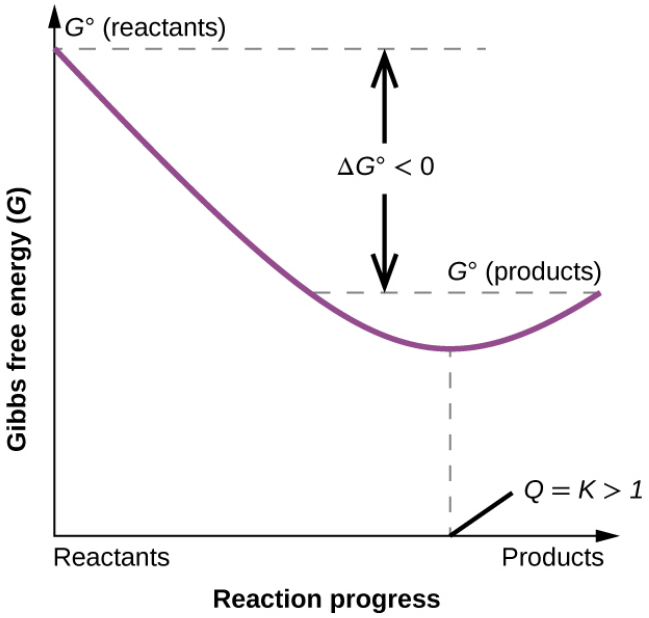
Use the thermodynamic data provided in Appendix G to calculate the equilibrium constant for the dissociation of dinitrogen tetroxide at 25 °C.

$$2\mathrm{NO}_2(g) \rightleftharpoons \mathrm{N}_2\mathrm{O}_4(g)$$

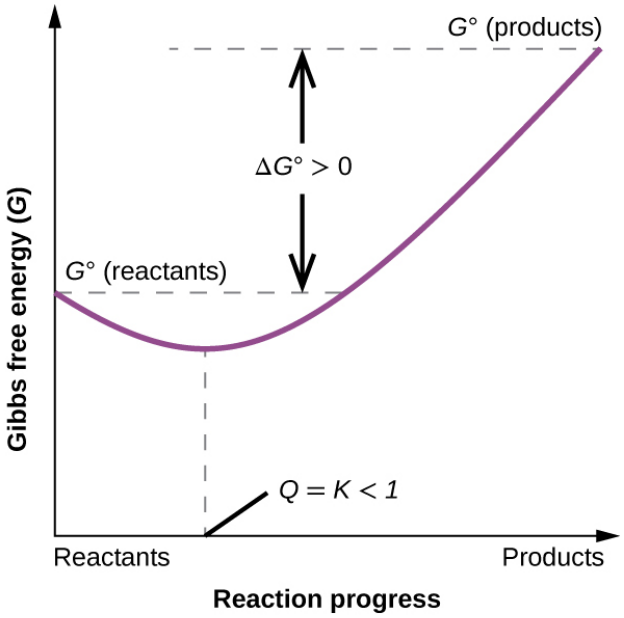
12.3.0.1: Answer:

K = 6.9

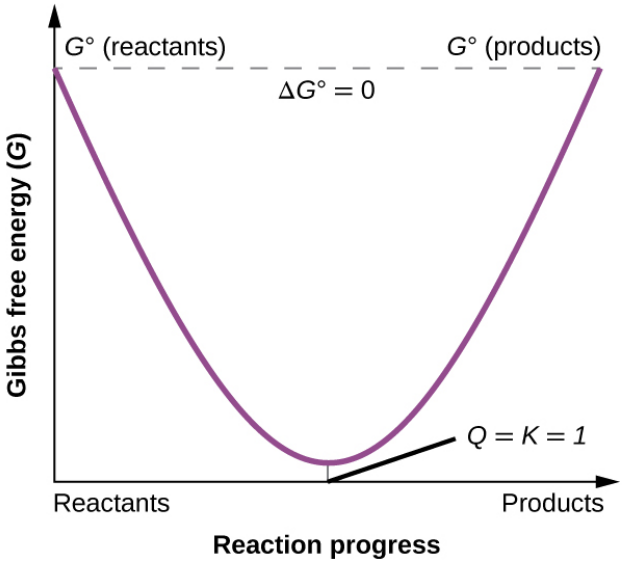
To further illustrate the relation between these two essential thermodynamic concepts, consider the observation that reactions spontaneously proceed in a direction that ultimately establishes equilibrium. As may be shown by plotting the free energy versus the extent of the reaction (for example, as reflected in the value of *Q*), equilibrium is established when the system's free energy is minimized (Figure 16.14). If a system consists of reactants and products in nonequilibrium amounts ($Q \neq K$), the reaction will proceed spontaneously in the direction necessary to establish equilibrium.


G° (reactants)
ΔG° < 0
G° (products)
Gibbs free energy (G)
Q = K > 1
Reactants
Products
Reaction progress

(a)


G° (products)
ΔG° > 0
G° (reactants)
Gibbs free energy (G)
Q = K < 1
Reactants
Products
Reaction progress

(b)


G° (reactants)
G° (products)
ΔG° = 0
Gibbs free energy (G)
Q = K = 1
Reactants
Products
Reaction progress

(c)

Figure 16.14 These plots show the free energy versus reaction progress for systems whose standard free energy changes are (a) negative, (b) positive, and (c) zero. Nonequilibrium systems will proceed spontaneously in whatever direction is necessary to minimize free energy and establish equilibrium.

This page titled 12.3: Free 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.

12.E: Thermodynamics - Homework

12.E.1: Spontaneity

1. Indicate whether the following processes are spontaneous or nonspontaneous.
   a. Liquid water freezing at a temperature below its freezing point
   b. Liquid water freezing at a temperature above its freezing point
   c. The combustion of gasoline
   d. A ball thrown into the air
   e. A raindrop falling to the ground
   f. Iron rusting in a moist atmosphere

   Answer

   a. spontaneous
   b. nonspontaneous
   c. spontaneous
   d. nonspontaneous
   e. spontaneous
   f. spontaneous

2. Many plastic materials are organic polymers that contain carbon and hydrogen. The oxidation of these plastics in air to form carbon dioxide and water is a spontaneous process; however, plastic materials tend to persist in the environment. Explain.

   Answer

   Although the oxidation of plastics is spontaneous, the rate of oxidation is very slow. Plastics are therefore kinetically stable and do not decompose appreciably even over relatively long periods of time.

12.E.2: Entropy

1. Determine the entropy change for the combustion of gaseous propane, C_3H_8, under the standard conditions to give gaseous carbon dioxide and water.

   Answer

   100.6 J/K

2. By calculating ΔS_{univ} at each temperature, determine if the melting of 1 mole of NaCl(s) is spontaneous at 500 °C and at 700 °C.
   $S^{(s)}_{\text{NaCl}} = 72.11 \frac{\text{J}}{\text{mol·K}}$ $S^{\circ}_{\text{NaCl}(l)} = 95.06 \frac{\text{J}}{\text{mol·K}}$ $\Delta H^{\circ}_{\text{fusion}} = 27.95 \text{ kJ/}$

   Answer

   As $\Delta S_{\text{univ}} < 0$ at each of these temperatures, melting is not spontaneous at either of them. The given values for entropy and enthalpy are for NaCl at 298 K.

3. What assumptions are made about the thermodynamic information (entropy and enthalpy values) used to solve this problem?

   Answer

   It is assumed that these do not change significantly at the higher temperatures used in the problem.

12.E.3: Free Energy

1. A reaction has ΔH° = 100 kJ/mol and $\Delta S^{\circ} = 250 \text{ J/mol·K}$. Is the reaction spontaneous at room temperature? If not, under what temperature conditions will it become spontaneous?

   Answer

The reaction is nonspontaneous at room temperature.
Above 400 K, ΔG will become negative, and the reaction will become spontaneous.

2. Consider a system similar to the one in Figure 16.8, except that it contains six particles instead of four. What is the probability of having all the particles in only one of the two boxes in the case? Compare this with the similar probability for the system of four particles that we have derived to be equal to $\frac{1}{8}$. What does this comparison tell us about even larger systems?

Answer

The probability for all the particles to be on one side is 1/32. This probability is noticeably lower than the 1/8 result for the four-particle system. The conclusion we can make is that the probability for all the particles to stay in only one part of the system will decrease rapidly as the number of particles increases, and, for instance, the probability for all molecules of gas to gather in only one side of a room at room temperature and pressure is negligible since the number of gas molecules in the room is very large.

3. Consider the system shown in Figure 16.9. What is the change in entropy for the process where the energy is initially associated with particles A and B, and the energy is distributed between two particles in different boxes (one in A-B, the other in C-D)?

Answer

There is only one initial state. For the final state, the energy can be contained in pairs A-C, A-D, B-C, or B-D. Thus, there are four final possible states. Δ S = 1.91 x 10^{-23} J/K

4. At room temperature, the entropy of the halogens increases from I_2 to Br_2 to Cl_2. Explain.

Answer

The masses of these molecules would suggest the opposite trend in their entropies. The observed trend is a result of the more significant variation of entropy with a physical state. At room temperature, I_2 is a solid, Br_2 is a liquid, and Cl_2 is a gas.

5. Indicate which substance in the given pairs has the higher entropy value. Explain your choices.
   a. $C_2H_5OH(l)$ or $C_3H_7OH(l)$
   b. $C_2H_5OH(l)$ or $C_2H_5OH(g)$
   c. $2H(g)$ or $H(g)$

Answer

   a. $C_3H_7OH(l)$ as it is a larger molecule (more complex and more massive), and so more microstates describing its motions are available at any given temperature.
   b. $C_2H_5OH(g)$ as it is in the gaseous state.
   c. $2H(g)$, since entropy is an extensive property, and so two H atoms (or two moles of H atoms) possess twice as much entropy as one atom (or one mole of atoms).

6. Predict the sign of the entropy change for the following processes. Give a reason for your prediction.
   a. $Na^+ (aq) + Cl^- (aq) \rightarrow NaCl (s)$
   b. $2C_6H_{14}(l) + 19O_2(g) \longrightarrow 14H_2O(g) + 12CO_2(g)$

Answer

   a. Negative. The relatively ordered solid precipitating decreases the number of mobile ions in solution.
   b. Positive. There is a net increase of seven moles of gas from reactants to products.

7. Consider the decomposition of red mercury(II) oxide under standard state conditions.
   $2HgO(s, \text{ red}) \longrightarrow 2Hg(l) + O_2(g)$
   a. Is the decomposition spontaneous under standard state conditions?
   b. Above what temperature does the reaction become spontaneous?

Answer

a. The reaction is nonspontaneous;
b. Above 566 °C the process is spontaneous

8. Calculate $\Delta G°$ for each of the following reactions from the equilibrium constant at the temperature given.
   a. $N_2(g) + O_2(g) \longrightarrow 2NO(g)$ $\quad T = 2000\ ^\circ C$ $\quad K_p = 4.1 \times 10^{-}$
   b. $CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$ $\quad T = 980\ ^\circ C$ $\quad K_p = 1.67$

   Answer

   a. The reaction is nonspontaneous;
   b. Above 566 °C the process is spontaneous.

9. Calculate the equilibrium constant at 25 °C for each of the following reactions from the value of $\Delta G°$ given.
   a. $O_2(g) + 2F_2(g) \longrightarrow 2OF_2(g)$ $\quad \Delta G^\circ = -9.2$
   b. $I_2(s) + Br_2(l) \longrightarrow 2IBr(g)$ $\quad \Delta G^\circ = 7.3$

   Answer

   a. K = 41;
   b. K = 0.053

10. The evaporation of one mole of water at 298 K has a standard free energy change of 8.58 kJ.
    $H_2O(l) \rightleftharpoons H_2O(g)$ $\quad \Delta G^\circ = 8.58$
    a. Is the evaporation of water under standard thermodynamic conditions spontaneous?
    b. Determine the equilibrium constant, K_P, for this physical process.
    c. By calculating ΔG, determine if the evaporation of water at 298 K is spontaneous when the partial pressure of water, P_{H_2O}, is 0.011 atm.
    d. If the evaporation of water were always nonspontaneous at room temperature, wet laundry would never dry when placed outside. In order for laundry to dry, what must be the value of P_{H_2O} in the air?

    Answer

    a. (a) Under standard thermodynamic conditions, the evaporation is nonspontaneous; (b)
    b. K_p = 0.031
    c. The evaporation of water is spontaneous
    d. P_{H2O} must always be less than K_p or less than 0.031 atm. 0.031 atm represents air saturated with water vapor at 25 °C, or 100% humidity.

11. One of the important reactions in the biochemical pathway glycolysis is the reaction of glucose-6-phosphate (G6P) to form fructose-6-phosphate (F6P):
    $G6P \rightleftharpoons F6P$ $\quad \Delta G^\circ = 1.7$
    a. Is the reaction spontaneous or nonspontaneous under standard thermodynamic conditions?
    b. Standard thermodynamic conditions imply the concentrations of G6P and F6P to be 1 *M*, however, in a typical cell, they are not even close to these values. Calculate ΔG when the concentrations of G6P and F6P are 120 μ*M* and 28 μ*M* respectively, and discuss the spontaneity of the forward reaction under these conditions. Assume the temperature is 37 °C.

    Answer

    a. Nonspontaneous as $\Delta G < 0$
    b. $\Delta G = \Delta G^o + RT \ln Q$. ΔG=-2.1 kJ. The forward reaction to produce F6P is spontaneous under these conditions.

12. When ammonium chloride is added to water and stirred, it dissolves spontaneously and the resulting solution feels cold. Without doing any calculations, deduce the signs of ΔG, ΔH, and ΔS for this process, and justify your choices.

    Answer

ΔG is negative as the process is spontaneous. ΔH is positive as with the solution becoming cold, the dissolving must be endothermic. ΔS must be positive as this drives the process, and it is expected for the dissolution of any soluble ionic compound.

13. What happens to ΔG (becomes more negative or more positive) for the following chemical reactions when the partial pressure of oxygen is increased?
    a. $\mathrm{S}(s) + \mathrm{O}_2(g) \longrightarrow \mathrm{SO}_2(g)$
    b. $2\mathrm{SO}_2(g) + \mathrm{O}_2(g) \longrightarrow 2\mathrm{SO}_3(g)$
    c. $\mathrm{HgO}(s) \longrightarrow \mathrm{Hg}(l) + \mathrm{O}_2(g)$

Answer

a. Increasing the oxygen partial pressure will yield a decrease in Q and ΔG thus becomes more negative.
b. Increasing the oxygen partial pressure will yield a decrease in Q and ΔG thus becomes more negative.
c. Increasing the oxygen partial pressure will yield an increase in Q and ΔG thus becomes more positive

This page titled 12.E: Thermodynamics - Homework 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

13: Appendices

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

General Chemistry

13.1: Dr Martin's Math Minutes
13.2: Composition of Commercial Acids and Bases
13.3: Essential Mathematics
13.4: Fundamental Physical Constants
13.5: Standard Thermodynamic Properties for Selected Substances
13.6: The Periodic Table
13.7: Units and Conversion Factors
13.8: Water Properties

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 13: Appendices is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

13.1: Dr Martin's Math Minutes

Introduction

https://bit.ly/3zW6vuz

This series of videos introduces many common skills students need to solve problems and use their calculators for general chemistry class. The videos were all created by Dr. Andrea Martin at Widener University.



Units of Measurement

https://bit.ly/3zRtrv6

A key chemistry skill is to use units along with numbers in calculations. This video introduces common measurements in chemistry and the metric units for those measurements. It shows why metric units are actually much easier to work with than our common English units.



Fractions, Decimals & Percentages

https://bit.ly/3pgbamn

Fractions, decimals and percentages are all related, and they appear frequently in chemistry problems. This video refreshes your understanding of these quantities and shows you how to interconvert between them.



Metric System – small units

https://bit.ly/3C3yuvk

The metric system is used extensively in chemistry, and because atoms are so small, we units for very small measurements. This video introduces the most important metric prefixes for quantities smaller than a base unit.



Metric System – large units

https://bit.ly/3PhJqZ3

We frequently need to describe very large quantities in chemistry, particularly when we are dealing with numbers of atoms or energy units. This video introduces the important metric prefixes for quantities larger than a base unit.



Significant Figures Part 1

https://bit.ly/3pjii1n

This video explains the difference between exact and measured numbers. The uncertainty in measured numbers is the basis for the concept of significant figures. The video shows you how to count significant figures in a measured number.



Significant Figures Part 2 – calculations

https://bit.ly/3Qo9jaZ

This video explains the rules for recording the correct number of significant figures after doing calculations with measured numbers.



Scientific Notation Part 1

https://bit.ly/3Ajgn36

Chemistry uses very small and very large numbers. Fluency in scientific notation is a must! This video explains scientific notation and gives you practice in interconverting between regular (decimal) and scientific notation.



Scientific Notation in Your Calculator

https://bit.ly/3PlIhj6

This video shows you how to input scientific notation into your calculator and shows you how to avoid a very common calculator error that almost every student makes!



Conversion Problems Part 1

https://bit.ly/3PAbnf3

In this video, we use the “factor-label” method or “dimensional analysis” to interconvert between units. Unit conversions appear in almost every chemistry problem and it’s important to have a process to follow that will reliably lead you to the correct answer.



Complicated Conversion Problems

https://bit.ly/3AjgCLy

In this video, we apply the factor-label method to solve problems involving multiple conversions or complex units. As you progress through chemistry, these complex problems will become more common.



Word Problems

https://bit.ly/3pgRZZO

Many students struggle with word problems. This video shows you a process that will help you find the important information in a question and apply it to solving the problem.



This page titled 13.1: Dr Martin's Math Minutes is shared under a not declared license and was authored, remixed, and/or curated by Scott Van Bramer.

13.2: Composition of Commercial Acids and Bases

Composition of Commercial Acids and Bases

Composition of Commercial Acids and Bases			
Acid or Base[1]	Density (g/mL)[2]	Percentage by Mass	Molarity
acetic acid, glacial	1.05	99.5%	17.4
aqueous ammonia[3]	0.90	28%	14.8
hydrochloric acid	1.18	36%	11.6
nitric acid	1.42	71%	16.0
perchloric acid	1.67	70%	11.65
phosphoric acid	1.70	85%	14.7
sodium hydroxide	1.53	50%	19.1
sulfuric acid	1.84	96%	18.0

Footnotes

1. 1 Acids and bases are commercially available as aqueous solutions. This table lists properties (densities and concentrations) of common acid and base solutions. Nominal values are provided in cases where the manufacturer cites a range of concentrations and densities.
2. 2 This column contains specific gravity data. In the case of this table, specific gravity is the ratio of density of a substance to the density of pure water at the same conditions. Specific gravity is often cited on commercial labels.
3. 3 This solution is sometimes called “ammonium hydroxide,” although this term is not chemically accurate.

This page titled 13.2: Composition of Commercial Acids and Bases is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

- **22.1: Composition of Commercial Acids and Bases** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

13.3: Essential Mathematics

13.3.1: Exponential Arithmetic

Exponential notation is used to express very large and very small numbers as a product of two numbers. The first number of the product, the *digit term*, is usually a number not less than 1 and not greater than 10. The second number of the product, the *exponential term*, is written as 10 with an exponent. Some examples of exponential notation are:

$$\begin{aligned} 1000 &= 1 \times 10^3 \\ 100 &= 1 \times 10^2 \\ 10 &= 1 \times 10^1 \\ 1 &= 1 \times 10^0 \\ 0.1 &= 1 \times 10^{-1} \\ 0.001 &= 1 \times 10^{-3} \\ 2386 &= 2.386 \times 1000 = 2.386 \times 10^3 \\ 0.123 &= 1.23 \times 0.1 = 1.23 \times 10^{-1} \end{aligned}$$

The power (exponent) of 10 is equal to the number of places the decimal is shifted to give the digit number. The exponential method is particularly useful notation for every large and very small numbers. For example, 1,230,000,000 = 1.23×10^9, and 0.00000000036 = 3.6×10^{-10}.

13.3.1.1: Addition of Exponentials

Convert all numbers to the same power of 10, add the digit terms of the numbers, and if appropriate, convert the digit term back to a number between 1 and 10 by adjusting the exponential term.

Exercise 13.3.1: Adding Exponentials

Add 5.00×10^{-5} and 3.00×10^{-3}.

Solution

$$\begin{aligned} 3.00 \times 10^{-3} &= 300 \times 10^{-5} \\ (5.00 \times 10^{-5}) + (300 \times 10^{-5}) &= 305 \times 10^{-5} = 3.05 \times 10^{-3} \end{aligned}$$

13.3.1.2: Subtraction of Exponentials

Convert all numbers to the same power of 10, take the difference of the digit terms, and if appropriate, convert the digit term back to a number between 1 and 10 by adjusting the exponential term.

Exercise 13.3.2: Subtracting Exponentials

Subtract 4.0×10^{-7} from 5.0×10^{-6}.

Solution

$$\begin{aligned} 4.0 \times 10^{-7} &= 0.40 \times 10^{-6} \\ (5.0 \times 10^{-6}) - (0.40 \times 10^{-6}) &= 4.6 \times 10^{-6} \end{aligned}$$

13.3.1.3: Multiplication of Exponentials

Multiply the digit terms in the usual way and add the exponents of the exponential terms.

Exercise 13.3.3: Multiplying Exponentials

Multiply 4.2×10^{-8} by 2.0×10^3.

Solution

$$(4.2 \times 10^{-8}) \times (2.0 \times 10^3) = (4.2 \times 2.0) \times 10^{(-8)+(+3)} = 8.4 \times 10^{-5}$$

13.3.1.4: Division of Exponentials

Divide the digit term of the numerator by the digit term of the denominator and subtract the exponents of the exponential terms.

Exercise 13.3.4: Dividing Exponentials

Divide 3.6×10^{5} by 6.0×10^{-4}.

Solution

$$\frac{3.6 \times 10^{-5}}{6.0 \times 10^{-4}} = \left(\frac{3.6}{6.0}\right) \times 10^{(-5)-(-4)} = 0.60 \times 10^{-1} = 6.0 \times 10^{-2}$$

13.3.1.5: Squaring of Exponentials

Square the digit term in the usual way and multiply the exponent of the exponential term by 2.

Exercise 13.3.5: Squaring Exponentials

Square the number 4.0×10^{-6}.

Solution

$$(4.0 \times 10^{-6})^2 = 4 \times 4 \times 10^{2 \times (-6)} = 16 \times 10^{-12} = 1.6 \times 10^{-11}$$

13.3.1.6: Cubing of Exponentials

Cube the digit term in the usual way and multiply the exponent of the exponential term by 3.

Exercise 13.3.6: Cubing Exponentials

Cube the number 2×10^{4}.

Solution

$$(2 \times 10^{4})^3 = 2 \times 2 \times 2 \times 10^{3 \times 4} = 8 \times 10^{12}$$

13.3.1.7: Taking Square Roots of Exponentials

If necessary, decrease or increase the exponential term so that the power of 10 is evenly divisible by 2. Extract the square root of the digit term and divide the exponential term by 2.

Exercise 13.3.7: Finding the Square Root of Exponentials

Find the square root of 1.6×10^{-7}.

Solution

$$1.6 \times 10^{-7} = 16 \times 10^{-8}$$

$$\sqrt{16 \times 10^{-8}} = \sqrt{16} \times \sqrt{10^{-8}} = \sqrt{16} \times 10^{-\frac{8}{2}} = 4.0 \times 10^{-4}$$

13.3.2: Significant Figures

A beekeeper reports that he has 525,341 bees. The last three figures of the number are obviously inaccurate, for during the time the keeper was counting the bees, some of them died and others hatched; this makes it quite difficult to determine the exact number of bees. It would have been more accurate if the beekeeper had reported the number 525,000. In other words, the last three figures are not significant, except to set the position of the decimal point. Their exact values have no meaning useful in this situation. In reporting any information as numbers, use only as many significant figures as the accuracy of the measurement warrants.

The importance of significant figures lies in their application to fundamental computation. In addition and subtraction, the sum or difference should contain as many digits to the right of the decimal as that in the least certain of the numbers used in the

computation (indicated by underscoring in the following example).

Exercise 13.3.8: Addition and Subtraction with Significant Figures

Add 4.383 g and 0.0023 g.

Solution

$$\begin{array}{r} 4.38\underline{3}\ \text{g} \\ +\ 0.00\underline{23}\ \text{g} \\ \hline 4.38\underline{5}\ \text{g} \end{array}$$

In multiplication and division, the product or quotient should contain no more digits than that in the factor containing the least number of significant figures.

Exercise 13.3.9: Multiplication and Division with Significant Figures

Multiply 0.6238 by 6.6.

Solution

$$0.623\underline{8} \times 6.\underline{6} = 4.\underline{1}$$

When rounding numbers, increase the retained digit by 1 if it is followed by a number larger than 5 (“round up”). Do not change the retained digit if the digits that follow are less than 5 (“round down”). If the retained digit is followed by 5, round up if the retained digit is odd, or round down if it is even (after rounding, the retained digit will thus always be even).

13.3.3: The Use of Logarithms and Exponential Numbers

The common logarithm of a number (log) is the power to which 10 must be raised to equal that number. For example, the common logarithm of 100 is 2, because 10 must be raised to the second power to equal 100. Additional examples follow.

Logarithms and Exponential Numbers

Number	Number Expressed Exponentially	Common Logarithm
1000	10^3	3
10	10^1	1
1	10^0	0
0.1	10^{-1}	−1
0.001	10^{-3}	−3

What is the common logarithm of 60? Because 60 lies between 10 and 100, which have logarithms of 1 and 2, respectively, the logarithm of 60 is 1.7782; that is,

$$60 = 10^{1.7782}$$

The common logarithm of a number less than 1 has a negative value. The logarithm of 0.03918 is −1.4069, or

$$0.03918 = 10^{-1.4069} = \frac{1}{10^{1.4069}}$$

To obtain the common logarithm of a number, use the *log* button on your calculator. To calculate a number from its logarithm, take the inverse log of the logarithm, or calculate 10^x (where x is the logarithm of the number).

The natural logarithm of a number (ln) is the power to which e must be raised to equal the number; e is the constant 2.7182818. For example, the natural logarithm of 10 is 2.303; that is,

$$10 = e^{2.303} = 2.7182818^{2.303}$$

To obtain the natural logarithm of a number, use the *ln* button on your calculator. To calculate a number from its natural logarithm, enter the natural logarithm and take the inverse ln of the natural logarithm, or calculate e^x (where x is the natural logarithm of the number).

Logarithms are exponents; thus, operations involving logarithms follow the same rules as operations involving exponents.

1. The logarithm of a product of two numbers is the sum of the logarithms of the two numbers. \[\log xy= \log x + \log y, \textrm{ and }\ln xy=\ln x + \ln y \nonumber \]
2. The logarithm of the number resulting from the division of two numbers is the difference between the logarithms of the two numbers. \[\log\dfrac{x}{y}=\log x-\log y,\textrm{ and } \ln\dfrac{x}{y}=\ln x-\ln y \nonumber \]
3. The logarithm of a number raised to an exponent is the product of the exponent and the logarithm of the number.

$$\log x^n = n \log x \text{ and } \ln x^n = n \ln x$$

13.3.4: The Solution of Quadratic Equations

Mathematical functions of this form are known as second-order polynomials or, more commonly, quadratic functions.

$$ax^2 + bx + c = 0$$

The solution or roots for any quadratic equation can be calculated using the following formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Solving Quadratic Equations Solve the quadratic equation $3x^2 + 13x - 10 = 0$.

Solution Substituting the values $a = 3$, $b = 13$, $c = -10$ in the formula, we obtain

$$x = \frac{-13 \pm \sqrt{(13)^2 - 4 \times 3 \times (-10)}}{2 \times 3}$$

$$x = \frac{-13 \pm \sqrt{169 + 120}}{6} = \frac{-13 \pm \sqrt{289}}{6} = \frac{-13 \pm 17}{6}$$

The two roots are therefore

$$x = \frac{-13 + 17}{6} = \frac{2}{3} \text{ and } x = \frac{-13 - 17}{6} = -5$$

Quadratic equations constructed on physical data always have real roots, and of these real roots, often only those having positive values are of any significance.

13.3.5: Two-Dimensional (*x*-*y*) Graphing

The relationship between any two properties of a system can be represented graphically by a two-dimensional data plot. Such a graph has two axes: a horizontal one corresponding to the independent variable, or the variable whose value is being controlled (x), and a vertical axis corresponding to the dependent variable, or the variable whose value is being observed or measured (y).

When the value of y is changing as a function of x (that is, different values of x correspond to different values of y), a graph of this change can be plotted or sketched. The graph can be produced by using specific values for (x,y) data pairs.

Exercise 13.3.10

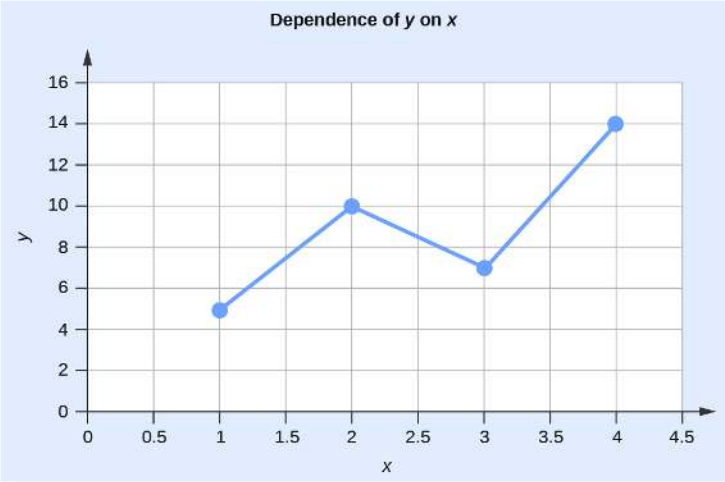
Graphing the Dependence of y on x

Table for Exercise 10

x	y
1	5
2	10
3	7

x	y
4	14

This table contains the following points: (1,5), (2,10), (3,7), and (4,14). Each of these points can be plotted on a graph and connected to produce a graphical representation of the dependence of y on x.



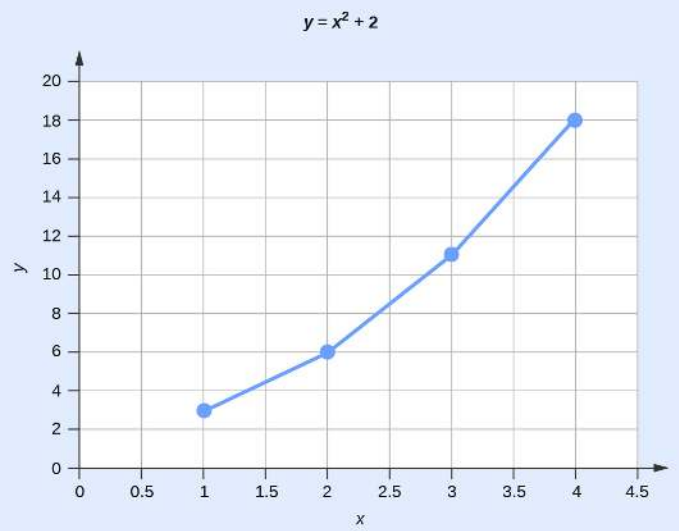
If the function that describes the dependence of y on x is known, it may be used to compute x,y data pairs that may subsequently be plotted.

Exercise 13.3.11

Plotting Data Pairs If we know that $y = x^2 + 2$, we can produce a table of a few (x,y) values and then plot the line based on the data shown here.

Table for Exercise 11

x	$y = x^2 + 2$
1	3
2	6
3	11
4	18



This page titled 13.3: Essential Mathematics is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

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

13.4: Fundamental Physical Constants

Fundamental Physical Constants

Fundamental Physical Constants	
Name and Symbol	Value
atomic mass unit (amu)	$1.6605402 \times 10^{-27}$ kg
Avogadro's number	6.0221367×10^{23} mol^{-1}
Boltzmann's constant (k)	1.380658×10^{-23} J K^{-1}
charge-to-mass ratio for electron (e/m_e)	$1.75881962 \times 10^{11}$ C kg^{-1}
electron charge (e)	$1.60217733 \times 10^{-19}$ C
electron rest mass (m_e)	$9.1093897 \times 10^{-31}$ kg
Faraday's constant (F)	9.6485309×10^{4} C mol^{-1}
gas constant (R)	8.205784×10^{-2} L atm mol^{-1} K^{-1} = 8.314510 J mol^{-1} K^{-1}
molar volume of an ideal gas, 1 atm, 0 °C	22.41409 L mol^{-1}
molar volume of an ideal gas, 1 bar, 0 °C	22.71108 L mol^{-1}
neutron rest mass (m_n)	$1.6749274 \times 10^{-27}$ kg
Planck's constant (h)	$6.6260755 \times 10^{-34}$ J s
proton rest mass (m_p)	$1.6726231 \times 10^{-27}$ kg
Rydberg constant (R)	$1.0973731534 \times 10^{7}$ m^{-1} = $2.1798736 \times 10^{-18}$ J
speed of light (in vacuum) (c)	2.99792458×10^{8} m s^{-1}

This page titled 13.4: Fundamental Physical Constants is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

- **22.4: Fundamental Physical Constants** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

13.5: Standard Thermodynamic Properties for Selected Substances

Standard Thermodynamic Properties for Selected Substances

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol⁻)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
aluminum			
Al(s)	0	0	28.3
Al(g)	324.4	285.7	164.54
$Al^{3+}(aq)$	-531	-485	-321.7
$Al_2O_3(s)$	–1676	–1582	50.92
$AlF_3(s)$	–1510.4	–1425	66.5
$AlCl_3(s)$	–704.2	–628.8	110.67
$AlCl_3 \cdot 6H_2O(s)$	–2691.57	–2269.40	376.56
$Al_2S_3(s)$	–724.0	–492.4	116.9
$Al_2(SO_4)_3(s)$	–3445.06	–3506.61	239.32
antimony			
Sb(s)	0	0	45.69
Sb(g)	262.34	222.17	180.16
$Sb_4O_6(s)$	–1440.55	–1268.17	220.92
$SbCl_3(g)$	–313.8	–301.2	337.80
$SbCl_5(g)$	–394.34	–334.29	401.94
$Sb_2S_3(s)$	–174.89	–173.64	182.00
$SbCl_3(s)$	–382.17	–323.72	184.10
SbOCl(s)	–374.0	—	—
arsenic			
As(s)	0	0	35.1
As(g)	302.5	261.0	174.21
$As_4(g)$	143.9	92.4	314
$As_4O_6(s)$	–1313.94	–1152.52	214.22
$As_2O_5(s)$	–924.87	–782.41	105.44
$AsCl_3(g)$	–261.50	–248.95	327.06
$As_2S_3(s)$	–169.03	–168.62	163.59
$AsH_3(g)$	66.44	68.93	222.78
$H_3AsO_4(s)$	–906.3	—	—
barium			
Ba(s)	0	0	62.5
Ba(g)	180	146	170.24

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
$Ba^{2+}(aq)$	-537.6	-560.8	9.6
BaO(*s*)	–548.0	–520.3	72.1
$BaCl_2(s)$	–855.0	–806.7	123.7
$BaSO_4(s)$	–1473.2	–1362.3	132.2
beryllium			
Be(*s*)	0	0	9.50
Be(*g*)	324.3	286.6	136.27
BeO(*s*)	–609.4	–580.1	13.8
bismuth			
Bi(*s*)	0	0	56.74
Bi(*g*)	207.1	168.2	187.00
$Bi_2O_3(s)$	–573.88	–493.7	151.5
$BiCl_3(s)$	–379.07	–315.06	176.98
$Bi_2S_3(s)$	–143.1	–140.6	200.4
boron			
B(*s*)	0	0	5.86
B(*g*)	565.0	521.0	153.4
$B_2O_3(s)$	–1273.5	–1194.3	53.97
$B_2H_6(g)$	36.4	87.6	232.1
$H_3BO_3(s)$	–1094.33	–968.92	88.83
$BF_3(g)$	–1136.0	–1119.4	254.4
$BCl_3(g)$	–403.8	–388.7	290.1
$B_3N_3H_6(l)$	–540.99	–392.79	199.58
$HBO_2(s)$	–794.25	–723.41	37.66
bromine			
$Br_2(l)$	0	0	152.23
$Br_2(g)$	30.91	3.142	245.5
Br(*g*)	111.88	82.429	175.0
$Br^-(aq)$	-120.9	-102.82	80.71
$BrF_3(g)$	–255.60	–229.45	292.42
HBr(*g*)	–36.3	–53.43	198.7
cadmium			
Cd(*s*)	0	0	51.76
Cd(*g*)	112.01	77.41	167.75

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
$Cd^{2+}(aq)$	-75.90	-77.61	-73.2
CdO(*s*)	–258.2	–228.4	54.8
$CdCl_2(s)$	–391.5	–343.9	115.3
$CdSO_4(s)$	–933.3	–822.7	123.0
CdS(*s*)	–161.9	–156.5	64.9
calcium			
Ca(*s*)	0	0	41.6
Ca(*g*)	178.2	144.3	154.88
$Ca^{2+}(aq)$	-542.96	-553.04	-55.2
CaO(*s*)	–634.9	–603.3	38.1
$Ca(OH)_2(s)$	–985.2	–897.5	83.4
$CaSO_4$(s)	–1434.5	–1322.0	106.5
$CaSO_4 \cdot 2H_2O(s)$	–2022.63	–1797.45	194.14
$CaCO_3$(s) (calcite)	–1220.0	–1081.4	110.0
$CaSO_3 \cdot H_2O(s)$	–1752.68	–1555.19	184.10
carbon			
C(*s*) (graphite)	0	0	5.740
C(*s*) (diamond)	1.89	2.90	2.38
C(*g*)	716.681	671.2	158.1
CO(*g*)	–110.52	–137.15	197.7
$CO_2(g)$	–393.51	–394.36	213.8
$CO_3^{2-}(aq)$	-677.1	-527.8	-56.9
$CH_4(g)$	–74.6	–50.5	186.3
$CH_3OH(l)$	–239.2	–166.6	126.8
$CH_3OH(g)$	–201.0	–162.3	239.9
$CCl_4(l)$	–128.2	–62.5	214.4
$CCl_4(g)$	–95.7	–58.2	309.7
$CHCl_3(l)$	–134.1	–73.7	201.7
$CHCl_3(g)$	–103.14	–70.34	295.71
$CS_2(l)$	89.70	65.27	151.34
$CS_2(g)$	116.9	66.8	238.0
$C_2H_2(g)$	227.4	209.2	200.9
$C_2H_4(g)$	52.4	68.4	219.3
$C_2H_6(g)$	–84.0	–32.0	229.2

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
$CH_3CO_2H(l)$	–484.3	–389.9	159.8
$CH_3CO_2H(g)$	–434.84	–376.69	282.50
$C_2H_5OH(l)$	–277.6	–174.8	160.7
$C_2H_5OH(g)$	–234.8	–167.9	281.6
$HCO_3^-\,(aq)$	-691.11	-587.06	95
$C_3H_8(g)$	–103.8	–23.4	270.3
$C_6H_6(g)$	82.927	129.66	269.2
$C_6H_6(l)$	49.1	124.50	173.4
$CH_2Cl_2(l)$	–124.2	–63.2	177.8
$CH_2Cl_2(g)$	–95.4	–65.90	270.2
$CH_3Cl(g)$	–81.9	–60.2	234.6
$C_2H_5Cl(l)$	–136.52	–59.31	190.79
$C_2H_5Cl(g)$	–112.17	–60.39	276.00
$C_2N_2(g)$	308.98	297.36	241.90
$HCN(l)$	108.9	125.0	112.8
$HCN(g)$	135.5	124.7	201.8
cesium			
$Cs^+\,(aq)$	-248	-282.0	133
chlorine			
$Cl_2(g)$	0	0	223.1
$Cl(g)$	121.3	105.70	165.2
$Cl^-\,(aq)$	-167.2	-131.2	56.5
$ClF(g)$	–54.48	–55.94	217.78
$ClF_3(g)$	–158.99	–118.83	281.50
$Cl_2O(g)$	80.3	97.9	266.2
$Cl_2O_7(l)$	238.1	—	—
$Cl_2O_7(g)$	272.0	—	—
$HCl(g)$	–92.307	–95.299	186.9
$HClO_4(l)$	–40.58	—	—
chromium			
$Cr(s)$	0	0	23.77
$Cr(g)$	396.6	351.8	174.50
$CrO_4^{2-}\,(aq)$	-881.2	-727.8	50.21
$Cr_2O_7^{2-}\,(aq)$	-1490.3	-1301.1	261.9

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
$Cr_2O_3(s)$	–1139.7	–1058.1	81.2
$CrO_3(s)$	–589.5	—	—
$(NH_4)_2Cr_2O_7(s)$	–1806.7	—	—
cobalt			
$Co(s)$	0	0	30.0
$Co^{2+}(aq)$	-67.4	-51.5	-155
$Co^{3+}(aq)$	92	134	-305.0
$CoO(s)$	–237.9	–214.2	52.97
$Co_3O_4(s)$	–910.02	–794.98	114.22
$Co(NO_3)_2(s)$	–420.5	—	—
copper			
$Cu(s)$	0	0	33.15
$Cu(g)$	338.32	298.58	166.38
$Cu^{+}(aq)$	51.9	50.2	-26
$Cu^{2+}(aq)$	64.77	65.49	-99.6
$CuO(s)$	–157.3	–129.7	42.63
$Cu_2O(s)$	–168.6	–146.0	93.14
$CuS(s)$	–53.1	–53.6	66.5
$Cu_2S(s)$	–79.5	–86.2	120.9
$CuSO_4(s)$	–771.36	–662.2	109.2
$Cu(NO_3)_2(s)$	–302.9	—	—
fluorine			
$F_2(g)$	0	0	202.8
$F(g)$	79.4	62.3	158.8
$F^{-}(aq)$	-332.6	-278.8	-13.8
$F_2O(g)$	24.7	41.9	247.43
$HF(g)$	–273.3	–275.4	173.8
hydrogen			
$H_2(g)$	0	0	130.7
$H(g)$	217.97	203.26	114.7
$H^{+}(aq)$	0	0	0
$OH^{-}(aq)$	-230.0	-157.2	-10.75
$H_3O^{+}(aq)$	-285.8		69.91
$H_2O(l)$	–285.83	–237.1	70.0

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
$H_2O(g)$	–241.82	–228.59	188.8
$H_2O_2(l)$	–187.78	–120.35	109.6
$H_2O_2(g)$	–136.3	–105.6	232.7
$HF(g)$	–273.3	–275.4	173.8
$HCl(g)$	–92.307	–95.299	186.9
$HBr(g)$	–36.3	–53.43	198.7
$HI(g)$	26.48	1.70	206.59
$H_2S(g)$	–20.6	–33.4	205.8
$H_2Se(g)$	29.7	15.9	219.0
iodine			
$I_2(s)$	0	0	116.14
$I_2(g)$	62.438	19.3	260.7
$I(g)$	106.84	70.2	180.8
$I^-(aq)$	-55.19	-51.57	11.13
$IF(g)$	95.65	–118.49	236.06
$ICl(g)$	17.78	–5.44	247.44
$IBr(g)$	40.84	3.72	258.66
$IF_7(g)$	–943.91	–818.39	346.44
$HI(g)$	26.48	1.70	206.59
iron			
$Fe(s)$	0	0	27.3
$Fe(g)$	416.3	370.7	180.5
$Fe^{2+}(aq)$	-89.1	-78.90	-137.7
$Fe^{3+}(aq)$	-48.5	-4.7	-315.9
$Fe_2O_3(s)$	–824.2	–742.2	87.40
$Fe_3O_4(s)$	–1118.4	–1015.4	146.4
$Fe(CO)_5(l)$	–774.04	–705.42	338.07
$Fe(CO)_5(g)$	–733.87	–697.26	445.18
$FeCl_2(s)$	–341.79	–302.30	117.95
$FeCl_3(s)$	–399.49	–334.00	142.3
$FeO(s)$	–272.0	–255.2	60.75
$Fe(OH)_2(s)$	–569.0	–486.5	88.
$Fe(OH)_3(s)$	–823.0	–696.5	106.7
$FeS(s)$	–100.0	–100.4	60.29

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
$Fe_3C(s)$	25.10	20.08	104.60
lead			
$Pb(s)$	0	0	64.81
$Pb(g)$	195.2	162.	175.4
$Pb^{2+}(aq)$	-1.7	-24.43	10.5
PbO(s) (yellow)	–217.32	–187.89	68.70
PbO(s) (red)	–218.99	–188.93	66.5
$Pb(OH)_2(s)$	–515.9	—	—
$PbS(s)$	–100.4	–98.7	91.2
$Pb(NO_3)_2(s)$	–451.9	—	—
$PbO_2(s)$	–277.4	–217.3	68.6
$PbCl_2(s)$	–359.4	–314.1	136.0
lithium			
$Li(s)$	0	0	29.1
$Li(g)$	159.3	126.6	138.8
$Li^+(aq)$	-278.5	-293.3	13.4
$LiH(s)$	–90.5	–68.3	20.0
$Li(OH)(s)$	–487.5	–441.5	42.8
$LiF(s)$	–616.0	–587.5	35.7
$Li_2CO_3(s)$	–1216.04	–1132.19	90.17
magnesium			
$Mg^{2+}(aq)$	-466.9	-454.8	-138.1
manganese			
$Mn(s)$	0	0	32.0
$Mn(g)$	280.7	238.5	173.7
$Mn^{2+}(aq)$	-220.8	-228.1	-73.6
$MnO(s)$	–385.2	–362.9	59.71
$MnO_2(s)$	–520.03	–465.1	53.05
$Mn_2O_3(s)$	–958.97	–881.15	110.46
$Mn_3O_4(s)$	–1378.83	–1283.23	155.64
$MnO_4^-(aq)$	-541.4	-447.2	191.2
$MnO_4^{2-}(aq)$	-653.0	-500.7	59
mercury			
$Hg(l)$	0	0	75.9

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
Hg(g)	61.4	31.8	175.0
$Hg^{2+}(aq)$		164.8	
$Hg_2^{2+}(aq)$	172.4	153.9	84.5
HgO(s) (red)	–90.83	–58.5	70.29
HgO(s) (yellow)	–90.46	–58.43	71.13
$HgCl_2(s)$	–224.3	–178.6	146.0
$Hg_2Cl_2(s)$	–265.4	–210.7	191.6
HgS(s) (red)	–58.16	–50.6	82.4
HgS(s) (black)	–53.56	–47.70	88.28
$HgSO_4(s)$	–707.51	–594.13	0.00
nitrogen			
$N_2(g)$	0	0	191.6
N(g)	472.704	455.5	153.3
NO(g)	90.25	87.6	210.8
$NO_2(g)$	33.2	51.30	240.1
$N_2O(g)$	81.6	103.7	220.0
$N_2O_3(g)$	83.72	139.41	312.17
$NO_3^-(aq)$	-205.0	-108.7	146.4
$N_2O_4(g)$	11.1	99.8	304.4
$N_2O_5(g)$	11.3	115.1	355.7
$NH_3(g)$	–45.9	–16.5	192.8
$NH_4^+(aq)$	-132.5	-79.31	113.4
$N_2H_4(l)$	50.63	149.43	121.21
$N_2H_4(g)$	95.4	159.4	238.5
$NH_4NO_3(s)$	–365.56	–183.87	151.08
$NH_4Cl(s)$	–314.43	–202.87	94.6
$NH_4Br(s)$	–270.8	–175.2	113.0
$NH_4I(s)$	–201.4	–112.5	117.0
$NH_4NO_2(s)$	–256.5	—	—
$HNO_3(l)$	–174.1	–80.7	155.6
$HNO_3(g)$	–133.9	–73.5	266.9
oxygen			
$O_2(g)$	0	0	205.2
O(g)	249.17	231.7	161.1

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
$O_3(g)$	142.7	163.2	238.9
phosphorus			
$P_4(s)$	0	0	164.4
$P_4(g)$	58.91	24.4	280.0
$P(g)$	314.64	278.25	163.19
$PH_3(g)$	5.4	13.5	210.2
$PCl_3(g)$	–287.0	–267.8	311.78
$PCl_5(g)$	–374.9	–305.0	364.4
$P_4O_6(s)$	–1640.1	—	—
$P_4O_{10}(s)$	–2984.0	–2697.0	228.86
$PO_4^{3-}(aq)$	-1277	-1019	-222
$HPO_3(s)$	–948.5	—	—
$HPO_4^{2-}(aq)$	-1292.1	-1089.3	-33
$H_2PO_4^-(aq)$	-1296.3	-1130.4	90.4
$H_3PO_2(s)$	–604.6	—	—
$H_3PO_3(s)$	–964.4	—	—
$H_3PO_4(s)$	–1279.0	–1119.1	110.50
$H_3PO_4(l)$	–1266.9	–1124.3	110.5
$H_4P_2O_7(s)$	–2241.0	—	—
$POCl_3(l)$	–597.1	–520.8	222.5
$POCl_3(g)$	–558.5	–512.9	325.5
potassium			
$K(s)$	0	0	64.7
$K(g)$	89.0	60.5	160.3
$K^+(aq)$	-252.4	-283.3	102.5
$KF(s)$	–576.27	–537.75	66.57
$KCl(s)$	–436.5	–408.5	82.6
rubidium			
$Rb^+(aq)$	-246	-282.2	124
silicon			
$Si(s)$	0	0	18.8
$Si(g)$	450.0	405.5	168.0
$SiO_2(s)$	–910.7	–856.3	41.5
$SiH_4(g)$	34.3	56.9	204.6

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
$H_2SiO_3(s)$	–1188.67	–1092.44	133.89
$H_4SiO_4(s)$	–1481.14	–1333.02	192.46
$SiF_4(g)$	–1615.0	–1572.8	282.8
$SiCl_4(l)$	–687.0	–619.8	239.7
$SiCl_4(g)$	–662.75	–622.58	330.62
SiC(*s, beta cubic*)	–73.22	–70.71	16.61
SiC(*s, alpha hexagonal*)	–71.55	–69.04	16.48
silver			
Ag(*s*)	0	0	42.55
Ag(*g*)	284.9	246.0	172.89
$Ag^+(aq)$	105.6	77.11	72.68
$Ag_2O(s)$	–31.05	–11.20	121.3
AgCl(*s*)	–127.0	–109.8	96.3
$Ag_2S(s)$	–32.6	–40.7	144.0
sodium			
Na(*s*)	0	0	51.3
Na(*g*)	107.5	77.0	153.7
$Na^+(aq)$	-240.1	-261.9	59
$Na_2O(s)$	–414.2	–375.5	75.1
NaCl(*s*)	–411.2	–384.1	72.1
strontium			
$Sr^{2+}(aq)$	-545.8	-557.3	-32.6
sulfur			
$S_8(s)$ (rhombic)	0	0	256.8
S(*g*)	278.81	238.25	167.82
$S^{2-}(aq)$	41.8	83.7	22
$SO_2(g)$	–296.83	–300.1	248.2
$SO_3(g)$	–395.72	–371.06	256.76
$SO_4^{2-}(aq)$	-909.3	-744.5	20.1
$S_2O_3^{2-}(aq)$	-648.5	-522.5	67
$H_2S(g)$	–20.6	–33.4	205.8
$HS^-(aq)$	-17.7	12.6	61.1
$H_2SO_4(l)$	–813.989	690.00	156.90
$HSO_4^-(aq)$	-885.75	-752.87	126.9

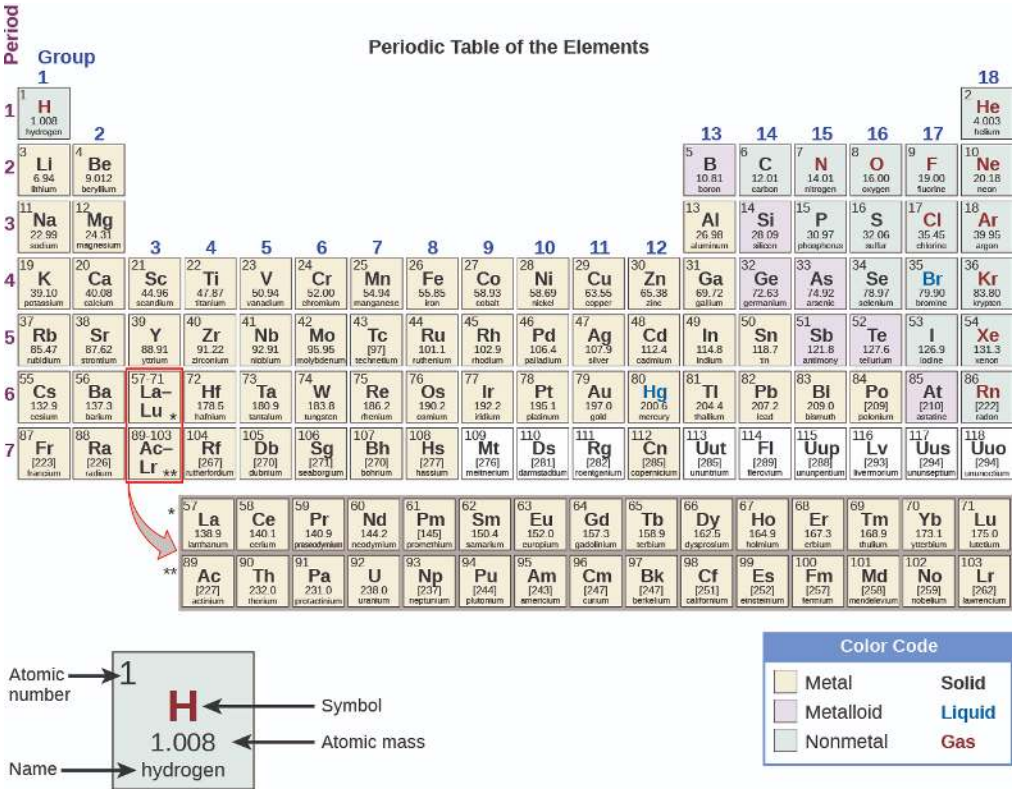
Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
$H_2S_2O_7(s)$	–1273.6	—	—
$SF_4(g)$	–728.43	–684.84	291.12
$SF_6(g)$	–1220.5	–1116.5	291.5
$SCl_2(l)$	–50	—	—
$SCl_2(g)$	–19.7	—	—
$S_2Cl_2(l)$	–59.4	—	—
$S_2Cl_2(g)$	–19.50	–29.25	319.45
$SOCl_2(g)$	–212.55	–198.32	309.66
$SOCl_2(l)$	–245.6	—	—
$SO_2Cl_2(l)$	–394.1	—	—
SO_2Cl_2(g)	–354.80	–310.45	311.83
tin			
Sn(s)	0	0	51.2
Sn(g)	301.2	266.2	168.5
SnO(s)	–285.8	–256.9	56.5
$SnO_2(s)$	–577.6	–515.8	49.0
$SnCl_4(l)$	–511.3	–440.1	258.6
$SnCl_4(g)$	–471.5	–432.2	365.8
titanium			
Ti(s)	0	0	30.7
Ti(g)	473.0	428.4	180.3
$TiO_2(s)$	–944.0	–888.8	50.6
$TiCl_4(l)$	–804.2	–737.2	252.4
$TiCl_4(g)$	–763.2	–726.3	353.2
tungsten			
W(s)	0	0	32.6
W(g)	849.4	807.1	174.0
$WO_3(s)$	–842.9	–764.0	75.9
zinc			
Zn(s)	0	0	41.6
Zn(g)	130.73	95.14	160.98
$Zn^{2+}(aq)$	-153.9	-147.1	-112.1
ZnO(s)	–350.5	–320.5	43.7
$ZnCl_2(s)$	–415.1	–369.43	111.5

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
$ZnS(s)$	–206.0	–201.3	57.7
$ZnSO_4(s)$	–982.8	–871.5	110.5
$ZnCO_3(s)$	–812.78	–731.57	82.42
complexes			
$[Co(NH_3)_4(NO_2)_2]NO_3$, *cis*	–898.7	—	—
$[Co(NH_3)_4(NO_2)_2]NO_3$, *trans*	–896.2	—	—
$NH_4[Co(NH_3)_2(NO_2)_4]$	–837.6	—	—
$[Co(NH_3)_6][Co(NH_3)_2(NO_2)_4]_3$	–2733.0	—	—
$[Co(NH_3)_4Cl_2]Cl$, *cis*	–874.9	—	—
$[Co(NH_3)_4Cl_2]Cl$, *trans*	–877.4	—	—
$[Co(en)_2(NO_2)_2]NO_3$, *cis*	–689.5	—	—
$[Co(en)_2Cl_2]Cl$, *cis*	–681.2	—	—
$[Co(en)_2Cl_2]Cl$, *trans*	–677.4	—	—
$[Co(en)_3](ClO_4)_3$	–762.7	—	—
$[Co(en)_3]Br_2$	–595.8	—	—
$[Co(en)_3]I_2$	–475.3	—	—
$[Co(en)_3]I_3$	–519.2	—	—
$[Co(NH_3)_6](ClO_4)_3$	–1034.7	–221.1	615
$[Co(NH_3)_5NO_2](NO_3)_2$	–1088.7	–412.9	331
$[Co(NH_3)_6](NO_3)_3$	–1282.0	–524.5	448
$[Co(NH_3)_5Cl]Cl_2$	–1017.1	–582.5	366.1
$[Pt(NH_3)_4]Cl_2$	–725.5	—	—
$[Ni(NH_3)_6]Cl_2$	–994.1	—	—
$[Ni(NH_3)_6]Br_2$	–923.8	—	—
$[Ni(NH_3)_6]I_2$	–808.3	—	—

This page titled 13.5: Standard Thermodynamic Properties for Selected Substances is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

- **22.9: Standard Thermodynamic Properties for Selected Substances** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

13.6: The Periodic Table



This page titled 13.6: The Periodic Table is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

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

13.7: Units and Conversion Factors

For an exhaustive listing of conversion factors see NIST SP 811 Appendix B.8.

Units of Length			
meter (m)	= 39.37 inches (in.) = 1.094 yards (yd)	angstrom (Å)	= 10^{-8} cm (exact, definition) = 10^{-10} m (exact, definition)
centimeter (cm)	= 0.01 m (exact, definition)	yard (yd)	= 0.9144 m
millimeter (mm)	= 0.001 m (exact, definition)	inch (in.)	= 2.54 cm (exact, definition)
kilometer (km)	= 1000 m (exact, definition)	mile (US)	= 1.60934 km

Units of Volume			
liter (L)	= 0.001 m^3 (exact, definition) = 1000 cm^3 (exact, definition) = 1.057 (US) quarts	liquid quart (US)	= 32 (US) liquid ounces (exact, definition) = 0.25 (US) gallon (exact, definition) = 0.9463 L
milliliter (mL)	= 0.001 L (exact, definition) = 1 cm^3 (exact, definition)	dry quart	= 1.1012 L
microliter (μL)	= 10^{-6} L (exact, definition) = 10^{-3} cm^3 (exact, definition)	cubic foot (US)	= 28.316 L

Units of Mass			
gram (g)	= 0.001 kg (exact, definition)	ounce (oz) (avoirdupois)	= 28.35 g
milligram (mg)	= 0.001 g (exact, definition)	pound (lb) (avoirdupois)	= 0.4535924 kg
kilogram (kg)	= 1000 g (exact, definition) = 2.205 lb	ton (short)	=2000 lb (exact, definition) = 907.185 kg
ton (metric)	=1000 kg (exact, definition) = 2204.62 lb	ton (long)	= 2240 lb (exact, definition) = 1.016 metric ton

Units of Energy	
4.184 joule (J)	= 1 thermochemical calorie (cal)
1 thermochemical calorie (cal)	= 4.184 × 10^7 erg
erg	= 10^{-7} J (exact, definition)
electron-volt (eV)	= 1.60218 × 10^{-19} J = 23.061 kcal mol^{-1}
liter·atmosphere	= 24.217 cal = 101.325 J (exact, definition)
nutritional calorie (Cal)	= 1000 cal (exact, definition) = 4184 J
British thermal unit (BTU)	= 1054.804 J[1]

Units of Pressure	
torr	= 1 mm Hg (exact, definition)
pascal (Pa)	= N m^{-2} (exact, definition) = kg m^{-1} s^{-2} (exact, definition)

Units of Pressure	
atmosphere (atm)	= 760 mm Hg (exact, definition) = 760 torr (exact, definition) = 101,325 N m^{-2} (exact, definition) = 101,325 Pa (exact, definition)
bar	= 10^5 Pa (exact, definition) = 10^5 kg m^{-1} s^{-2} (exact, definition)

Footnotes

1. 1 BTU is the amount of energy needed to heat one pound of water by one degree Fahrenheit. Therefore, the exact relationship of BTU to joules and other energy units depends on the temperature at which BTU is measured. 59 °F (15 °C) is the most widely used reference temperature for BTU definition in the United States. At this temperature, the conversion factor is the one provided in this table.

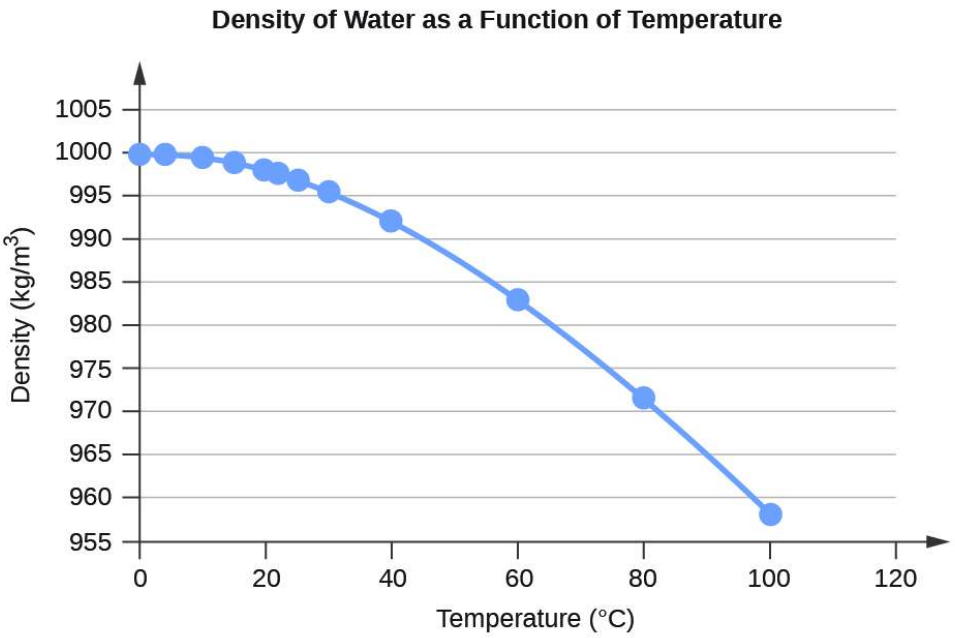
This page titled 13.7: Units and Conversion Factors is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

- **22.11: Units and Conversion Factors** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

13.8: Water Properties

Water Density (kg/m3) at Different Temperatures (°C)

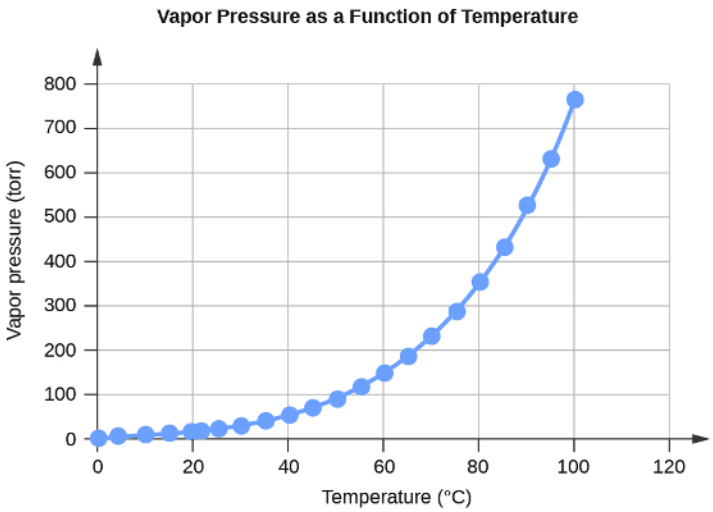
Temperature[1]	Density
0	999.8395
4	999.9720 (density maximum)
10	999.7026
15	999.1026
20	998.2071
22	997.7735
25	997.0479
30	995.6502
40	992.2
60	983.2
80	971.8
100	958.4



Water Vapor Pressure at Different Temperatures (°C)

Temperature	Vapor Pressure (torr)	Vapor Pressure (Pa)
0	4.6	613.2812
4	6.1	813.2642
10	9.2	1226.562

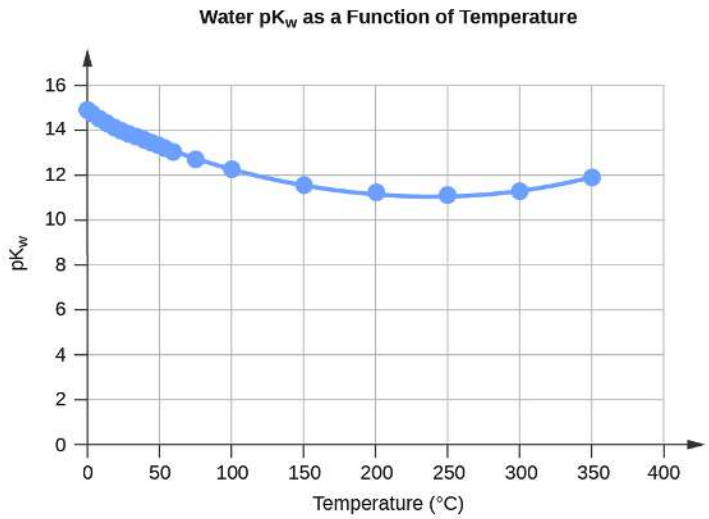
Temperature	Vapor Pressure (torr)	Vapor Pressure (Pa)
15	12.8	1706.522
20	17.5	2333.135
22	19.8	2639.776
25	23.8	3173.064
30	31.8	4239.64
35	42.2	5626.188
40	55.3	7372.707
45	71.9	9585.852
50	92.5	12332.29
55	118.0	15732
60	149.4	19918.31
65	187.5	24997.88
70	233.7	31157.35
75	289.1	38543.39
80	355.1	47342.64
85	433.6	57808.42
90	525.8	70100.71
95	633.9	84512.82
100	760.0	101324.7



Water Kw and pKw at Different Temperatures (°C)

Temperature	K_w 10^{-14}	pK_w[2]
0	0.112	14.95

Temperature	$K_w\ 10^{-14}$	pK_w[2]
5	0.182	14.74
10	0.288	14.54
15	0.465	14.33
20	0.671	14.17
25	0.991	14.00
30	1.432	13.84
35	2.042	13.69
40	2.851	13.55
45	3.917	13.41
50	5.297	13.28
55	7.080	13.15
60	9.311	13.03
75	19.95	12.70
100	56.23	12.25



Specific Heat Capacity for Water

Specific Heat Capacity for Water
$C°(H_2O(l)) = 4184\ J·K^{-1}·kg^{-1} = 4.184\ J·g^{-1}·°C^{-1}$
$C°(H_2O(s)) = 1864\ J·K^{-1}·kg^{-1}$
$C°(H_2O(g)) = 2093\ J·K^{-1}·kg^{-1}$

Standard Water Melting and Boiling Temperatures and Enthalpies of the Transitions

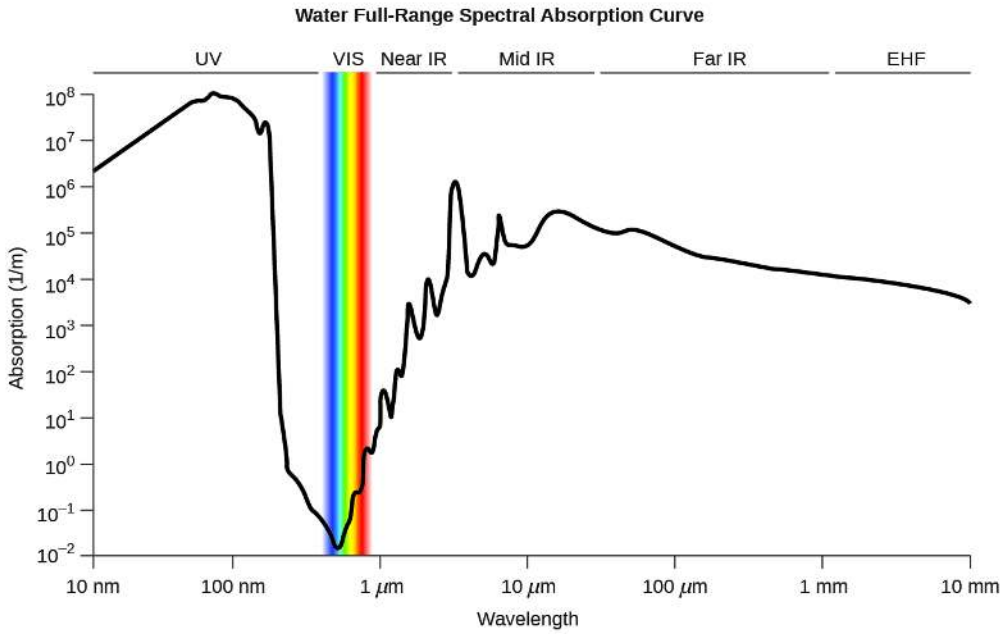
Standard Water Melting and Boiling Temperatures and Enthalpies of the Transitions	
Temperature (K)	ΔH (kJ/mol)

Standard Water Melting and Boiling Temperatures and Enthalpies of the Transitions		
	Temperature (K)	ΔH (kJ/mol)
melting	273.15	6.088
boiling	373.15	40.656 (44.016 at 298 K)

Water Cryoscopic (Freezing Point Depression) and Ebullioscopic (Boiling Point Elevation) Constants

Water Cryoscopic (Freezing Point Depression) and Ebullioscopic (Boiling Point Elevation) Constants
$K_f = 1.86°C \cdot kg \cdot mol^{-1}$ (cryoscopic constant)
$K_b = 0.51°C \cdot kg \cdot mol^{-1}$ (ebullioscopic constant)

<figure class="ui-has-child-figcaption" >



Water full-range spectral absorption curve. This curve shows the full-range spectral absorption for water. The y-axis signifies the absorption in 1/cm. If we divide 1 by this value, we will obtain the length of the path (in cm) after which the intensity of a light beam passing through water decays by a factor of the base of the natural logarithm e (e = 2.718281828).

Footnotes

1. 1 Data for t < 0 °C are for supercooled water
2. 2 $pK_w = -\log_{10}(K_w)$

This page titled 13.8: Water Properties is shared under a CC BY license and was authored, remixed, and/or curated by Scott Van Bramer.

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

Index

A

acidic
10.2: pH, pOH, and Relative Strengths of Acids and Bases
activated complex
8.2: Collision Theory and Reaction Mechanisms
activation energy
8.2: Collision Theory and Reaction Mechanisms
amplitude
5.1: Light and Atomic Structure
angular momentum quantum number
5.2: Development of Quantum Theory
anion
2.2: Atomic Structure, Isotopes, and Atomic Mass
aqueous solution
3.4: Molarity
Arrhenius equation
8.2: Collision Theory and Reaction Mechanisms
atomic mass
2.2: Atomic Structure, Isotopes, and Atomic Mass
atomic mass unit
2.2: Atomic Structure, Isotopes, and Atomic Mass
atomic number
2.2: Atomic Structure, Isotopes, and Atomic Mass
atomic orbital
5.2: Development of Quantum Theory
Aufbau principle
5.3: Electronic Structure of Atoms (Electron Configurations)
Avogadro's number
3.1: Formula Mass and the Mole Concept
axial position
6.4: Molecular Structure and Polarity

B

balanced equation
4.1: Writing and Balancing Chemical Equations
basic
10.2: pH, pOH, and Relative Strengths of Acids and Bases
blackbody
5.1: Light and Atomic Structure
bomb calorimeter
11.2: Calorimetry
bond angle
6.4: Molecular Structure and Polarity
bond dipole moment
6.4: Molecular Structure and Polarity
bond distance
6.4: Molecular Structure and Polarity
buffer
10.4: Buffers
buffer capacity
10.4: Buffers

C

calorie
11.1: Energy Basics
calorimeter
11.2: Calorimetry
calorimetry
11.2: Calorimetry
cation
2.2: Atomic Structure, Isotopes, and Atomic Mass
Celsius
1.2: Measurements
chemical equation
4.1: Writing and Balancing Chemical Equations
chemical symbol
2.2: Atomic Structure, Isotopes, and Atomic Mass
chemical thermodynamics
11.3: Enthalpy- Introduction
11.4: Enthalpy- Heat of Combustion
11.5: Enthalpy- Heat of Formation
coefficient
4.1: Writing and Balancing Chemical Equations
collision theory
8.2: Collision Theory and Reaction Mechanisms
combustion reaction
4.3: Classifying Chemical Reactions - Precipitation Reactions
4.4: Classifying Chemical Reactions - Acid Base Reactions
4.5: Classifying Chemical Reactions - Combustion Reactions
complete ionic equation
4.1: Writing and Balancing Chemical Equations
concentrated
3.4: Molarity
concentration
3.4: Molarity
continuous spectrum
5.1: Light and Atomic Structure
conversion factors
1.3: Mathematical Treatment of Measurement Results
core electron
5.3: Electronic Structure of Atoms (Electron Configurations)
covalent radius
5.4: Periodic Variations in Element Properties
cubic centimeter
1.2: Measurements
cubic meter
1.2: Measurements

D

d orbital
5.2: Development of Quantum Theory
Dalton unit
2.2: Atomic Structure, Isotopes, and Atomic Mass
density
1.2: Measurements
dilution
3.4: Molarity
dimensional analysis
1.3: Mathematical Treatment of Measurement Results
dipole moment
6.4: Molecular Structure and Polarity
dispersion
6.5: Intermolecular Forces
dissolved
3.4: Molarity
double bond
6.2: Lewis Symbols and Structures

E

effective nuclear charge
5.4: Periodic Variations in Element Properties
electromagnetic radiation
5.1: Light and Atomic Structure
electromagnetic spectrum
5.1: Light and Atomic Structure
electron affinity
5.4: Periodic Variations in Element Properties
electron configuration
5.3: Electronic Structure of Atoms (Electron Configurations)
electron density
5.2: Development of Quantum Theory
empirical formula
2.3: Chemical Formulas
empirical formula mass
3.2: Determining Empirical and Molecular Formulas
endothermic process
11.1: Energy Basics
energy
11.1: Energy Basics
enthalpy
11.3: Enthalpy- Introduction
11.4: Enthalpy- Heat of Combustion
11.5: Enthalpy- Heat of Formation
enthalpy change
11.3: Enthalpy- Introduction
11.4: Enthalpy- Heat of Combustion
11.5: Enthalpy- Heat of Formation
equatorial position
6.4: Molecular Structure and Polarity
equilibrium
9.1: Chemical Equilibria
equilibrium constant
9.2: Equilibrium Constants
exothermic process
11.1: Energy Basics
expansion work
11.3: Enthalpy- Introduction
11.4: Enthalpy- Heat of Combustion
11.5: Enthalpy- Heat of Formation

F

f orbital
5.2: Development of Quantum Theory
Fahrenheit
1.3: Mathematical Treatment of Measurement Results
first law of thermodynamics
11.3: Enthalpy- Introduction
11.4: Enthalpy- Heat of Combustion
11.5: Enthalpy- Heat of Formation
formal charge
6.3: Formal Charge and Resonance
Formula Mass
3.1: Formula Mass and the Mole Concept
free radical
6.2: Lewis Symbols and Structures
frequency
5.1: Light and Atomic Structure
frequency factor
8.2: Collision Theory and Reaction Mechanisms
fundamental unit of charge
2.2: Atomic Structure, Isotopes, and Atomic Mass

G

Gibbs free energy
- 12.3: Free Energy

goiter
- 2.2: Atomic Structure, Isotopes, and Atomic Mass

H

heat
- 11.1: Energy Basics

heat capacity
- 11.1: Energy Basics

Heisenberg uncertainty principle
- 5.2: Development of Quantum Theory

hertz
- 5.1: Light and Atomic Structure

Hess's law
- 11.3: Enthalpy- Introduction
- 11.4: Enthalpy- Heat of Combustion
- 11.5: Enthalpy- Heat of Formation

heterogeneous catalyst
- 8.3: Catalysis

heterogeneous equilibria
- 9.2: Equilibrium Constants

homogeneous catalyst
- 8.3: Catalysis

homogeneous equilibria
- 9.2: Equilibrium Constants

Hund's rule
- 5.3: Electronic Structure of Atoms (Electron Configurations)

hydrocarbon
- 11.3: Enthalpy- Introduction
- 11.4: Enthalpy- Heat of Combustion
- 11.5: Enthalpy- Heat of Formation

hydrogen bonding
- 6.5: Intermolecular Forces

hypervalent molecule
- 6.2: Lewis Symbols and Structures

I

induced dipole
- 6.5: Intermolecular Forces

instantaneous dipole
- 6.5: Intermolecular Forces

intensity
- 5.1: Light and Atomic Structure

interference pattern
- 5.1: Light and Atomic Structure

intermolecular force
- 6.5: Intermolecular Forces

internal energy
- 11.3: Enthalpy- Introduction
- 11.4: Enthalpy- Heat of Combustion
- 11.5: Enthalpy- Heat of Formation

International System of Units
- 1.2: Measurements

ion
- 2.2: Atomic Structure, Isotopes, and Atomic Mass

ionization energy
- 5.4: Periodic Variations in Element Properties

isoelectronic
- 5.4: Periodic Variations in Element Properties

isomers
- 2.3: Chemical Formulas

J

joule
- 11.1: Energy Basics

K

Kc
- 9.2: Equilibrium Constants

Kelvin
- 1.2: Measurements

kilogram
- 1.2: Measurements

kinetic energy
- 11.1: Energy Basics

Kp
- 9.2: Equilibrium Constants

L

Law of Mass Action
- 9.2: Equilibrium Constants

length
- 1.2: Measurements

Lewis structure
- 6.2: Lewis Symbols and Structures

Lewis symbol
- 6.2: Lewis Symbols and Structures

line spectrum
- 5.1: Light and Atomic Structure

linear
- 6.4: Molecular Structure and Polarity

liter
- 1.2: Measurements

lone pair
- 6.2: Lewis Symbols and Structures

M

magnetic quantum number
- 5.2: Development of Quantum Theory

mass number
- 2.2: Atomic Structure, Isotopes, and Atomic Mass

meter
- 1.2: Measurements

milliliter
- 1.2: Measurements

molar mass
- 3.1: Formula Mass and the Mole Concept

molarity
- 3.4: Molarity

mole
- 3.1: Formula Mass and the Mole Concept

molecular equation
- 4.1: Writing and Balancing Chemical Equations

molecular formula
- 2.3: Chemical Formulas

molecular orbital theory
- 7.3: Molecular Orbital Theory

molecular structure
- 6.3: Formal Charge and Resonance
- 6.4: Molecular Structure and Polarity

N

net ionic equation
- 4.1: Writing and Balancing Chemical Equations

neutral
- 10.2: pH, pOH, and Relative Strengths of Acids and Bases

node
- 5.1: Light and Atomic Structure
- 7.1: Valence Bond Theory and Hybrid Orbitals

nutritional calorie
- 11.2: Calorimetry

O

octahedral
- 6.4: Molecular Structure and Polarity

octet rule
- 6.2: Lewis Symbols and Structures

orbital diagram
- 5.3: Electronic Structure of Atoms (Electron Configurations)

overlap
- 7.1: Valence Bond Theory and Hybrid Orbitals

Oxidation
- 4.3: Classifying Chemical Reactions - Precipitation Reactions
- 4.4: Classifying Chemical Reactions - Acid Base Reactions
- 4.5: Classifying Chemical Reactions - Combustion Reactions

oxidizing agent
- 4.3: Classifying Chemical Reactions - Precipitation Reactions
- 4.4: Classifying Chemical Reactions - Acid Base Reactions
- 4.5: Classifying Chemical Reactions - Combustion Reactions

P

p orbital
- 5.2: Development of Quantum Theory

Pauli exclusion principle
- 5.2: Development of Quantum Theory

percent composition
- 3.2: Determining Empirical and Molecular Formulas

pH
- 10.2: pH, pOH, and Relative Strengths of Acids and Bases

photon
- 5.1: Light and Atomic Structure

pi bond
- 7.1: Valence Bond Theory and Hybrid Orbitals

pOH
- 10.2: pH, pOH, and Relative Strengths of Acids and Bases

polar molecule
- 6.4: Molecular Structure and Polarity

polarizability
- 6.5: Intermolecular Forces

potential energy
- 11.1: Energy Basics

precipitate
- 4.3: Classifying Chemical Reactions - Precipitation Reactions
- 4.4: Classifying Chemical Reactions - Acid Base Reactions
- 4.5: Classifying Chemical Reactions - Combustion Reactions

precipitation reaction
- 4.3: Classifying Chemical Reactions - Precipitation Reactions
- 4.4: Classifying Chemical Reactions - Acid Base Reactions
- 4.5: Classifying Chemical Reactions - Combustion Reactions

principal quantum number
- 5.2: Development of Quantum Theory

product
4.1: Writing and Balancing Chemical Equations

Q

quantization
5.1: Light and Atomic Structure
quantum mechanics
5.2: Development of Quantum Theory

R

reactant
4.1: Writing and Balancing Chemical Equations
reaction quotient
9.2: Equilibrium Constants
Reduction
4.3: Classifying Chemical Reactions - Precipitation Reactions
4.4: Classifying Chemical Reactions - Acid Base Reactions
4.5: Classifying Chemical Reactions - Combustion Reactions
resonance
6.3: Formal Charge and Resonance
7.2: Multiple Bonds
resonance forms
6.3: Formal Charge and Resonance
resonance hybrid
6.3: Formal Charge and Resonance
reversible reaction
9.1: Chemical Equilibria

S

s orbital
5.2: Development of Quantum Theory
second
1.2: Measurements
Second Law of Thermodynamics
12.2: The Second and Third Laws of Thermodynamics
shell
5.2: Development of Quantum Theory
SI units
1.2: Measurements
sigma bond
7.1: Valence Bond Theory and Hybrid Orbitals
single bond
6.2: Lewis Symbols and Structures
solute
3.4: Molarity
solvent
3.4: Molarity
spatial isomers
2.3: Chemical Formulas
specific heat capacity
11.1: Energy Basics
spectator ion
4.1: Writing and Balancing Chemical Equations
spin quantum number
5.2: Development of Quantum Theory
standard enthalpy of combustion
11.3: Enthalpy- Introduction
11.4: Enthalpy- Heat of Combustion
11.5: Enthalpy- Heat of Formation
standard enthalpy of formation
11.3: Enthalpy- Introduction
11.4: Enthalpy- Heat of Combustion
11.5: Enthalpy- Heat of Formation
standard entropy
12.2: The Second and Third Laws of Thermodynamics
standard entropy change
12.2: The Second and Third Laws of Thermodynamics
standard free energy change
12.3: Free Energy
standard free energy of formation
12.3: Free Energy
standard state
11.3: Enthalpy- Introduction
11.4: Enthalpy- Heat of Combustion
11.5: Enthalpy- Heat of Formation
standing wave
5.1: Light and Atomic Structure
state function
11.3: Enthalpy- Introduction
11.4: Enthalpy- Heat of Combustion
11.5: Enthalpy- Heat of Formation
stoichiometric factor
4.2: Reaction Stoichiometry
stoichiometry
4.2: Reaction Stoichiometry
structural formula
2.3: Chemical Formulas
structural isomers
2.3: Chemical Formulas
subshell
5.2: Development of Quantum Theory
surroundings
11.2: Calorimetry
system
11.2: Calorimetry

T

temperature
11.1: Energy Basics
Tetrahedral
6.4: Molecular Structure and Polarity
thermal energy
11.1: Energy Basics
thermochemistry
11.1: Energy Basics
Third Law of Thermodynamics
12.2: The Second and Third Laws of Thermodynamics
trigonal bipyramidal
6.4: Molecular Structure and Polarity
Trigonal Planar
6.4: Molecular Structure and Polarity
triple bond
6.2: Lewis Symbols and Structures

U

unified atomic mass unit
2.2: Atomic Structure, Isotopes, and Atomic Mass
unit
1.2: Measurements

V

valence bond theory
7.1: Valence Bond Theory and Hybrid Orbitals
valence electrons
5.3: Electronic Structure of Atoms (Electron Configurations)
Valence Shell
5.3: Electronic Structure of Atoms (Electron Configurations)
valence shell electron pair repulsion theory
6.4: Molecular Structure and Polarity
van der Waals force
6.5: Intermolecular Forces
volume
1.2: Measurements
VSEPR
6.4: Molecular Structure and Polarity

W

water gas shift reaction
9.2: Equilibrium Constants
wave
5.1: Light and Atomic Structure
wavefunction
5.2: Development of Quantum Theory
wavelength
5.1: Light and Atomic Structure
work
11.1: Energy Basics

Glossary

Sample Word 1 | Sample Definition 1

Detailed Licensing

Overview

Title: CHEM 175 - General Chemistry I (Van Bramer)

Webpages: 90

All licenses found:

- CC BY 4.0: 85.6% (77 pages)
- Undeclared: 14.4% (13 pages)

By Page

- CHEM 175 - General Chemistry I (Van Bramer) - *CC BY 4.0*
  - Front Matter - *Undeclared*
    - TitlePage - *Undeclared*
    - InfoPage - *Undeclared*
    - Table of Contents - *Undeclared*
    - Licensing - *Undeclared*
  - 1: Essential Ideas of Chemistry - *CC BY 4.0*
    - 1.1: Introduction to Chemistry - *CC BY 4.0*
    - 1.2: Measurements - *CC BY 4.0*
    - 1.3: Mathematical Treatment of Measurement Results - *CC BY 4.0*
    - 1.E: Essential Ideas of Chemistry- Homework - *CC BY 4.0*
  - 2: Atoms, Molecules, and Ions - *CC BY 4.0*
    - 2.1: Atomic Theory - *CC BY 4.0*
    - 2.2: Atomic Structure, Isotopes, and Atomic Mass - *CC BY 4.0*
    - 2.3: Chemical Formulas - *CC BY 4.0*
    - 2.E: Atoms, Molecules, and Ions- Homework - *CC BY 4.0*
  - 3: Composition of Substances and Solutions - *CC BY 4.0*
    - 3.1: Formula Mass and the Mole Concept - *CC BY 4.0*
    - 3.2: Determining Empirical and Molecular Formulas - *CC BY 4.0*
    - 3.3: Percent Composition and Molecular Formula - *CC BY 4.0*
    - 3.4: Molarity - *CC BY 4.0*
    - 3.E: Composition of Substances and Solutions- Homework - *CC BY 4.0*
  - 4: Stoichiometry of Chemical Reactions - *CC BY 4.0*
    - 4.1: Writing and Balancing Chemical Equations - *CC BY 4.0*
    - 4.2: Reaction Stoichiometry - *CC BY 4.0*
    - 4.3: Classifying Chemical Reactions - Precipitation Reactions - *CC BY 4.0*
    - 4.4: Classifying Chemical Reactions - Acid Base Reactions - *CC BY 4.0*
    - 4.5: Classifying Chemical Reactions - Combustion Reactions - *CC BY 4.0*
    - 4.E: Stoichiometry of Chemical Reactions- Homework - *CC BY 4.0*
  - 5: Electronic Structure and Periodic Properties - *CC BY 4.0*
    - 5.1: Light and Atomic Structure - *CC BY 4.0*
    - 5.2: Development of Quantum Theory - *CC BY 4.0*
    - 5.3: Electronic Structure of Atoms (Electron Configurations) - *CC BY 4.0*
    - 5.4: Periodic Variations in Element Properties - *CC BY 4.0*
    - 5.E: Electronic Structure and Periodic Properties- Homework - *CC BY 4.0*
  - 6: Chemical Bonding and Molecular Geometry - *CC BY 4.0*
    - 6.1: Ionic and Covalent Bonding - *CC BY 4.0*
    - 6.2: Lewis Symbols and Structures - *CC BY 4.0*
    - 6.3: Formal Charge and Resonance - *CC BY 4.0*
    - 6.4: Molecular Structure and Polarity - *CC BY 4.0*
    - 6.5: Intermolecular Forces - *CC BY 4.0*
    - 6.E: Chemical Bonding and Molecular Geometry- Homework - *CC BY 4.0*
  - 7: Advanced Theories of Covalent Bonding - *CC BY 4.0*
    - 7.1: Valence Bond Theory and Hybrid Orbitals - *CC BY 4.0*
    - 7.2: Multiple Bonds - *CC BY 4.0*
    - 7.3: Molecular Orbital Theory - *CC BY 4.0*
    - 7.E: Advanced Theories of Covalent Bonding- Homework - *CC BY 4.0*
  - 8: Kinetics - *CC BY 4.0*
    - 8.1: Introduction to Chemical Reaction Rates - *CC BY 4.0*
    - 8.2: Collision Theory and Reaction Mechanisms - *CC BY 4.0*
    - 8.3: Catalysis - *CC BY 4.0*
    - 8.E: Kinetics - Homework - *CC BY 4.0*
  - 9: Fundamental Equilibrium Concepts - *CC BY 4.0*

- 9.1: Chemical Equilibria - *CC BY 4.0*
- 9.2: Equilibrium Constants - *CC BY 4.0*
- 9.E: Fundamental Equlibrium Concepts - Homework - *CC BY 4.0*

10: Acid-Base Equilibria - *CC BY 4.0*

- 10.1: Introduction to Brønsted-Lowry Acids and Bases - *CC BY 4.0*
- 10.2: pH, pOH, and Relative Strengths of Acids and Bases - *CC BY 4.0*
- 10.3: Hydrolysis of Salt Solutions - *CC BY 4.0*
- 10.4: Buffers - *CC BY 4.0*
- 10.E: Acid-Base Equilibria - Homework - *CC BY 4.0*

11: Thermochemistry - *CC BY 4.0*

- 11.1: Energy Basics - *CC BY 4.0*
- 11.2: Calorimetry - *CC BY 4.0*
- 11.3: Enthalpy- Introduction - *CC BY 4.0*
- 11.4: Enthalpy- Heat of Combustion - *CC BY 4.0*
- 11.5: Enthalpy- Heat of Formation - *CC BY 4.0*
- 11.6: Bond Energy - *Undeclared*
- 11.E: Thermochemistry- Homework - *CC BY 4.0*

12: Thermodynamics - *CC BY 4.0*

- 12.1: Introduction to Spontaneity and Entropy - *CC BY 4.0*
- 12.2: The Second and Third Laws of Thermodynamics - *CC BY 4.0*
- 12.3: Free Energy - *CC BY 4.0*
- 12.E: Thermodynamics - Homework - *CC BY 4.0*

13: Appendices - *CC BY 4.0*

- 13.1: Dr Martin's Math Minutes - *Undeclared*
- 13.2: Composition of Commercial Acids and Bases - *CC BY 4.0*
- 13.3: Essential Mathematics - *CC BY 4.0*
- 13.4: Fundamental Physical Constants - *CC BY 4.0*
- 13.5: Standard Thermodynamic Properties for Selected Substances - *CC BY 4.0*
- 13.6: The Periodic Table - *CC BY 4.0*
- 13.7: Units and Conversion Factors - *CC BY 4.0*
- 13.8: Water Properties - *CC BY 4.0*

Back Matter - *Undeclared*

- Index - *Undeclared*
- Glossary - *Undeclared*
- Detailed Licensing - *Undeclared*
- Detailed Licensing - *Undeclared*
- Detailed Licensing - *Undeclared*

Detailed Licensing

Overview

Title: CHEM 175 - General Chemistry I (Van Bramer)

Webpages: 90

All licenses found:

- CC BY 4.0: 85.6% (77 pages)
- Undeclared: 14.4% (13 pages)

By Page

- CHEM 175 - General Chemistry I (Van Bramer) - *CC BY 4.0*
  - Front Matter - *Undeclared*
    - TitlePage - *Undeclared*
    - InfoPage - *Undeclared*
    - Table of Contents - *Undeclared*
    - Licensing - *Undeclared*
  - 1: Essential Ideas of Chemistry - *CC BY 4.0*
    - 1.1: Introduction to Chemistry - *CC BY 4.0*
    - 1.2: Measurements - *CC BY 4.0*
    - 1.3: Mathematical Treatment of Measurement Results - *CC BY 4.0*
    - 1.E: Essential Ideas of Chemistry- Homework - *CC BY 4.0*
  - 2: Atoms, Molecules, and Ions - *CC BY 4.0*
    - 2.1: Atomic Theory - *CC BY 4.0*
    - 2.2: Atomic Structure, Isotopes, and Atomic Mass - *CC BY 4.0*
    - 2.3: Chemical Formulas - *CC BY 4.0*
    - 2.E: Atoms, Molecules, and Ions- Homework - *CC BY 4.0*
  - 3: Composition of Substances and Solutions - *CC BY 4.0*
    - 3.1: Formula Mass and the Mole Concept - *CC BY 4.0*
    - 3.2: Determining Empirical and Molecular Formulas - *CC BY 4.0*
    - 3.3: Percent Composition and Molecular Formula - *CC BY 4.0*
    - 3.4: Molarity - *CC BY 4.0*
    - 3.E: Composition of Substances and Solutions- Homework - *CC BY 4.0*
  - 4: Stoichiometry of Chemical Reactions - *CC BY 4.0*
    - 4.1: Writing and Balancing Chemical Equations - *CC BY 4.0*
    - 4.2: Reaction Stoichiometry - *CC BY 4.0*
    - 4.3: Classifying Chemical Reactions - Precipitation Reactions - *CC BY 4.0*
    - 4.4: Classifying Chemical Reactions - Acid Base Reactions - *CC BY 4.0*
    - 4.5: Classifying Chemical Reactions - Combustion Reactions - *CC BY 4.0*
    - 4.E: Stoichiometry of Chemical Reactions- Homework - *CC BY 4.0*
  - 5: Electronic Structure and Periodic Properties - *CC BY 4.0*
    - 5.1: Light and Atomic Structure - *CC BY 4.0*
    - 5.2: Development of Quantum Theory - *CC BY 4.0*
    - 5.3: Electronic Structure of Atoms (Electron Configurations) - *CC BY 4.0*
    - 5.4: Periodic Variations in Element Properties - *CC BY 4.0*
    - 5.E: Electronic Structure and Periodic Properties- Homework - *CC BY 4.0*
  - 6: Chemical Bonding and Molecular Geometry - *CC BY 4.0*
    - 6.1: Ionic and Covalent Bonding - *CC BY 4.0*
    - 6.2: Lewis Symbols and Structures - *CC BY 4.0*
    - 6.3: Formal Charge and Resonance - *CC BY 4.0*
    - 6.4: Molecular Structure and Polarity - *CC BY 4.0*
    - 6.5: Intermolecular Forces - *CC BY 4.0*
    - 6.E: Chemical Bonding and Molecular Geometry- Homework - *CC BY 4.0*
  - 7: Advanced Theories of Covalent Bonding - *CC BY 4.0*
    - 7.1: Valence Bond Theory and Hybrid Orbitals - *CC BY 4.0*
    - 7.2: Multiple Bonds - *CC BY 4.0*
    - 7.3: Molecular Orbital Theory - *CC BY 4.0*
    - 7.E: Advanced Theories of Covalent Bonding- Homework - *CC BY 4.0*
  - 8: Kinetics - *CC BY 4.0*
    - 8.1: Introduction to Chemical Reaction Rates - *CC BY 4.0*
    - 8.2: Collision Theory and Reaction Mechanisms - *CC BY 4.0*
    - 8.3: Catalysis - *CC BY 4.0*
    - 8.E: Kinetics - Homework - *CC BY 4.0*
  - 9: Fundamental Equilibrium Concepts - *CC BY 4.0*

- 9.1: Chemical Equilibria - *CC BY 4.0*
- 9.2: Equilibrium Constants - *CC BY 4.0*
- 9.E: Fundamental Equlibrium Concepts - Homework - *CC BY 4.0*

10: Acid-Base Equilibria - *CC BY 4.0*

- 10.1: Introduction to Brønsted-Lowry Acids and Bases - *CC BY 4.0*
- 10.2: pH, pOH, and Relative Strengths of Acids and Bases - *CC BY 4.0*
- 10.3: Hydrolysis of Salt Solutions - *CC BY 4.0*
- 10.4: Buffers - *CC BY 4.0*
- 10.E: Acid-Base Equilibria - Homework - *CC BY 4.0*

11: Thermochemistry - *CC BY 4.0*

- 11.1: Energy Basics - *CC BY 4.0*
- 11.2: Calorimetry - *CC BY 4.0*
- 11.3: Enthalpy- Introduction - *CC BY 4.0*
- 11.4: Enthalpy- Heat of Combustion - *CC BY 4.0*
- 11.5: Enthalpy- Heat of Formation - *CC BY 4.0*
- 11.6: Bond Energy - *Undeclared*
- 11.E: Thermochemistry- Homework - *CC BY 4.0*

12: Thermodynamics - *CC BY 4.0*

- 12.1: Introduction to Spontaneity and Entropy - *CC BY 4.0*
- 12.2: The Second and Third Laws of Thermodynamics - *CC BY 4.0*
- 12.3: Free Energy - *CC BY 4.0*
- 12.E: Thermodynamics - Homework - *CC BY 4.0*

13: Appendices - *CC BY 4.0*

- 13.1: Dr Martin's Math Minutes - *Undeclared*
- 13.2: Composition of Commercial Acids and Bases - *CC BY 4.0*
- 13.3: Essential Mathematics - *CC BY 4.0*
- 13.4: Fundamental Physical Constants - *CC BY 4.0*
- 13.5: Standard Thermodynamic Properties for Selected Substances - *CC BY 4.0*
- 13.6: The Periodic Table - *CC BY 4.0*
- 13.7: Units and Conversion Factors - *CC BY 4.0*
- 13.8: Water Properties - *CC BY 4.0*

Back Matter - *Undeclared*

- Index - *Undeclared*
- Glossary - *Undeclared*
- Detailed Licensing - *Undeclared*
- Detailed Licensing - *Undeclared*
- Detailed Licensing - *Undeclared*

Detailed Licensing

Overview

Title: CHEM 175 - General Chemistry I (Van Bramer)

Webpages: 90

All licenses found:

- CC BY 4.0: 85.6% (77 pages)
- Undeclared: 14.4% (13 pages)

By Page

- CHEM 175 - General Chemistry I (Van Bramer) - *CC BY 4.0*
  - Front Matter - *Undeclared*
    - TitlePage - *Undeclared*
    - InfoPage - *Undeclared*
    - Table of Contents - *Undeclared*
    - Licensing - *Undeclared*
  - 1: Essential Ideas of Chemistry - *CC BY 4.0*
    - 1.1: Introduction to Chemistry - *CC BY 4.0*
    - 1.2: Measurements - *CC BY 4.0*
    - 1.3: Mathematical Treatment of Measurement Results - *CC BY 4.0*
    - 1.E: Essential Ideas of Chemistry- Homework - *CC BY 4.0*
  - 2: Atoms, Molecules, and Ions - *CC BY 4.0*
    - 2.1: Atomic Theory - *CC BY 4.0*
    - 2.2: Atomic Structure, Isotopes, and Atomic Mass - *CC BY 4.0*
    - 2.3: Chemical Formulas - *CC BY 4.0*
    - 2.E: Atoms, Molecules, and Ions- Homework - *CC BY 4.0*
  - 3: Composition of Substances and Solutions - *CC BY 4.0*
    - 3.1: Formula Mass and the Mole Concept - *CC BY 4.0*
    - 3.2: Determining Empirical and Molecular Formulas - *CC BY 4.0*
    - 3.3: Percent Composition and Molecular Formula - *CC BY 4.0*
    - 3.4: Molarity - *CC BY 4.0*
    - 3.E: Composition of Substances and Solutions- Homework - *CC BY 4.0*
  - 4: Stoichiometry of Chemical Reactions - *CC BY 4.0*
    - 4.1: Writing and Balancing Chemical Equations - *CC BY 4.0*
    - 4.2: Reaction Stoichiometry - *CC BY 4.0*
    - 4.3: Classifying Chemical Reactions - Precipitation Reactions - *CC BY 4.0*
    - 4.4: Classifying Chemical Reactions - Acid Base Reactions - *CC BY 4.0*
    - 4.5: Classifying Chemical Reactions - Combustion Reactions - *CC BY 4.0*
    - 4.E: Stoichiometry of Chemical Reactions- Homework - *CC BY 4.0*
  - 5: Electronic Structure and Periodic Properties - *CC BY 4.0*
    - 5.1: Light and Atomic Structure - *CC BY 4.0*
    - 5.2: Development of Quantum Theory - *CC BY 4.0*
    - 5.3: Electronic Structure of Atoms (Electron Configurations) - *CC BY 4.0*
    - 5.4: Periodic Variations in Element Properties - *CC BY 4.0*
    - 5.E: Electronic Structure and Periodic Properties- Homework - *CC BY 4.0*
  - 6: Chemical Bonding and Molecular Geometry - *CC BY 4.0*
    - 6.1: Ionic and Covalent Bonding - *CC BY 4.0*
    - 6.2: Lewis Symbols and Structures - *CC BY 4.0*
    - 6.3: Formal Charge and Resonance - *CC BY 4.0*
    - 6.4: Molecular Structure and Polarity - *CC BY 4.0*
    - 6.5: Intermolecular Forces - *CC BY 4.0*
    - 6.E: Chemical Bonding and Molecular Geometry- Homework - *CC BY 4.0*
  - 7: Advanced Theories of Covalent Bonding - *CC BY 4.0*
    - 7.1: Valence Bond Theory and Hybrid Orbitals - *CC BY 4.0*
    - 7.2: Multiple Bonds - *CC BY 4.0*
    - 7.3: Molecular Orbital Theory - *CC BY 4.0*
    - 7.E: Advanced Theories of Covalent Bonding- Homework - *CC BY 4.0*
  - 8: Kinetics - *CC BY 4.0*
    - 8.1: Introduction to Chemical Reaction Rates - *CC BY 4.0*
    - 8.2: Collision Theory and Reaction Mechanisms - *CC BY 4.0*
    - 8.3: Catalysis - *CC BY 4.0*
    - 8.E: Kinetics - Homework - *CC BY 4.0*
  - 9: Fundamental Equilibrium Concepts - *CC BY 4.0*

- 9.1: Chemical Equilibria - *CC BY 4.0*
- 9.2: Equilibrium Constants - *CC BY 4.0*
- 9.E: Fundamental Equlibrium Concepts - Homework - *CC BY 4.0*

10: Acid-Base Equilibria - *CC BY 4.0*

- 10.1: Introduction to Brønsted-Lowry Acids and Bases - *CC BY 4.0*
- 10.2: pH, pOH, and Relative Strengths of Acids and Bases - *CC BY 4.0*
- 10.3: Hydrolysis of Salt Solutions - *CC BY 4.0*
- 10.4: Buffers - *CC BY 4.0*
- 10.E: Acid-Base Equilibria - Homework - *CC BY 4.0*

11: Thermochemistry - *CC BY 4.0*

- 11.1: Energy Basics - *CC BY 4.0*
- 11.2: Calorimetry - *CC BY 4.0*
- 11.3: Enthalpy- Introduction - *CC BY 4.0*
- 11.4: Enthalpy- Heat of Combustion - *CC BY 4.0*
- 11.5: Enthalpy- Heat of Formation - *CC BY 4.0*
- 11.6: Bond Energy - *Undeclared*
- 11.E: Thermochemistry- Homework - *CC BY 4.0*

12: Thermodynamics - *CC BY 4.0*

- 12.1: Introduction to Spontaneity and Entropy - *CC BY 4.0*
- 12.2: The Second and Third Laws of Thermodynamics - *CC BY 4.0*
- 12.3: Free Energy - *CC BY 4.0*
- 12.E: Thermodynamics - Homework - *CC BY 4.0*

13: Appendices - *CC BY 4.0*

- 13.1: Dr Martin's Math Minutes - *Undeclared*
- 13.2: Composition of Commercial Acids and Bases - *CC BY 4.0*
- 13.3: Essential Mathematics - *CC BY 4.0*
- 13.4: Fundamental Physical Constants - *CC BY 4.0*
- 13.5: Standard Thermodynamic Properties for Selected Substances - *CC BY 4.0*
- 13.6: The Periodic Table - *CC BY 4.0*
- 13.7: Units and Conversion Factors - *CC BY 4.0*
- 13.8: Water Properties - *CC BY 4.0*

Back Matter - *Undeclared*

- Index - *Undeclared*
- Glossary - *Undeclared*
- Detailed Licensing - *Undeclared*
- Detailed Licensing - *Undeclared*
- Detailed Licensing - *Undeclared*