OLD TEXTBOOK FOR CHEMISTRY 143 - 2019 TO 2021



OpenStax

LibreTexts™

OpenStax CNX

Textbook for Chemistry 143

Paul Flowers, Klaus Theopold & Richard Langley et al.

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 an 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 01/12/2026

TABLE OF CONTENTS

Licensing

1: Essential Ideas of Chemistry

- 1.1: Chemistry in Context
- 1.2: Measurements
- 1.3: Measurement Uncertainty, Accuracy, and Precision
- 1.4: Mathematical Treatment of Measurement Results
- 1.5: Phases and Classification of Matter
- 1.6: Physical and Chemical Properties
- 1.E: Essential Ideas of Chemistry (Exercises)

2: Atoms, Molecules, and Ions

- 2.1: Early Ideas in Atomic Theory
- 2.2: Evolution of Atomic Theory
- 2.3: Atomic Structure and Symbolism
- 2.4: Chemical Formulas
- 2.5: Formula Mass and the Mole Concept
- 2.6: Determining Empirical and Molecular Formulas
- 2.7: Chemical Nomenclature

3: Electronic Structure and Periodic Properties

- 3.1: Electromagnetic Energy
- 3.2: The Bohr Model
- 3.3: Electronic Structure of Atoms (Electron Configurations)
- 3.4: The Periodic Table
- 3.5: Periodic Variations in Element Properties
- 3.6: Molecular and Ionic Compounds
- 3.E: Electronic Structure and Periodic Properties (Exercises)

4: Chemical Bonding and Molecular Geometry

- 4.1: Ionic Bonding
- 4.2: Covalent Bonding
- 4.3: Lewis Symbols and Structures
- 4.4: Molecular Structure and Polarity

5: Chemical Reactions

- 5.1: Evidence of a Chemical Reaction
- 5.2: Chemical Equations
- 5.3: How to Write Balanced Chemical Equations
- 5.4: Aqueous Solutions and Solubility - Compounds Dissolved in Water
- 5.5: Precipitation Reactions
- 5.6: Writing Chemical Equations for Reactions in Solution- Molecular, Complete Ionic, and Net Ionic Equations
- 5.7: Acid–Base and Gas Evolution Reactions
- 5.8: Oxidation–Reduction Reactions

- 5.9: Classifying Chemical Reactions

6: Stoichiometry of Chemical Reactions

- 6.1: Reaction Stoichiometry
- 6.2: Reaction Yields
- 6.3: Quantitative Chemical Analysis
- 6.E: Stoichiometry of Chemical Reactions (Exercises)

7: Gases

- 7.1: Gas Pressure
- 7.2: Relating Pressure, Volume, Amount, and Temperature- The Ideal Gas Law
- 7.3: Stoichiometry of Gaseous Substances, Mixtures, and Reactions
- 7.4: The Kinetic-Molecular Theory
- 7.E: Gases (Exercises)

8: Thermochemistry

- 8.1: Energy Basics
- 8.2: Enthalpy

9: Liquids and Solids

- 9.1: Intermolecular Forces
- 9.2: Properties of Liquids
- 9.3: Phase Transitions

10: Solutions and Colloids

- 10.1: The Dissolution Process
- 10.2: Molarity
- 10.3: Other Units for Solution Concentrations
- 10.4: Solubility
- 10.5: Colligative Properties
- 10.6: Colloids

11: Fundamental Equilibrium Concepts

- 11.1: Chemical Equilibria
- 11.2: Equilibrium Constants
- 11.3: Shifting Equilibria- Le Châtelier's Principle
- 11.4: Equilibrium Calculations

12: Acid-Base Equilibria

- 12.1: Brønsted-Lowry Acids and Bases
- 12.2: pH and pOH
- 12.3: Relative Strengths of Acids and Bases
- 12.4: Polyprotic Acids
- 12.5: Buffers
- 12.6: Acid-Base Titrations

13: Nuclear Chemistry and Other Topics

- 13.1: Nuclear Chemistry Introduction
- 13.2: The Effects of Radiation on Life
- 13.3: Radioactivity in Medicine and Other Applications

14: Appendices

- 14.1: The Periodic Table
- 14.2: Essential Mathematics
- 14.3: Fundamental Physical Constants
- 14.4: Ionization Constants of Weak Acids
- 14.5: Ionization Constants of Weak Bases
- 14.6: Units and Conversion Factors
- 14.7: Water Properties

Index

Glossary

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 Textmap organized around the textbook
General Chemistry -Atoms First
By OpenStax

I II III IV V VI VII VIII IX X XI XII XIII XIV XV XVI XVII XVIII XIX XX XXI ● **Homework**

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: Chemistry in Context
1.2: Measurements
1.3: Measurement Uncertainty, Accuracy, and Precision
1.4: Mathematical Treatment of Measurement Results
1.5: Phases and Classification of Matter
1.6: Physical and Chemical Properties
1.E: Essential Ideas of Chemistry (Exercises)

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 OpenStax.

1.1: Chemistry in Context

Learning Objectives

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

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

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

Attempts to understand the behavior of matter extend back for more than 2500 years. As early as the sixth century BC, Greek philosophers discussed a system in which water was the basis of all things. You may have heard of the Greek postulate that matter consists of four elements: earth, air, fire, and water. Subsequently, an amalgamation of chemical technologies and philosophical speculations were spread from Egypt, China, and the eastern Mediterranean by alchemists, who endeavored to transform “base metals” such as lead into “noble metals” like gold, and to create elixirs to cure disease and extend life (Figure **1.1.1**).



Figure **1.1.1**: This portrayal shows an alchemist’s workshop circa 1580. Although alchemy made some useful contributions to how to manipulate matter, it was not scientific by modern standards. (credit: Chemical Heritage Foundation).

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

Chemistry: The Central Science

Chemistry is sometimes referred to as “the central science” due to its interconnectedness with a vast array of other STEM disciplines (STEM stands for areas of study in the science, technology, engineering, and math fields). Chemistry and the language of chemists play vital roles in biology, medicine, materials science, forensics, environmental science, and many other fields (Figure **1.1.2**). The basic principles of physics are essential for understanding many aspects of chemistry, and there is extensive overlap between many subdisciplines within the two fields, such as chemical physics and nuclear chemistry. Mathematics, computer science, and information theory provide important tools that help us calculate, interpret, describe, and generally make sense of the chemical world. Biology and chemistry converge in biochemistry, which is crucial to understanding the many complex factors and processes that keep living organisms (such as us) alive. Chemical engineering, materials science, and nanotechnology combine chemical principles and empirical findings to produce useful substances, ranging from gasoline to fabrics to electronics. Agriculture, food science, veterinary science, and brewing and wine making help provide sustenance in the form of food and drink to the world’s population. Medicine, pharmacology, biotechnology, and botany identify and produce substances that help keep us healthy. Environmental science, geology, oceanography, and atmospheric science incorporate many chemical ideas to help us better understand and protect our physical world. Chemical ideas are used to help understand the universe in astronomy and cosmology.

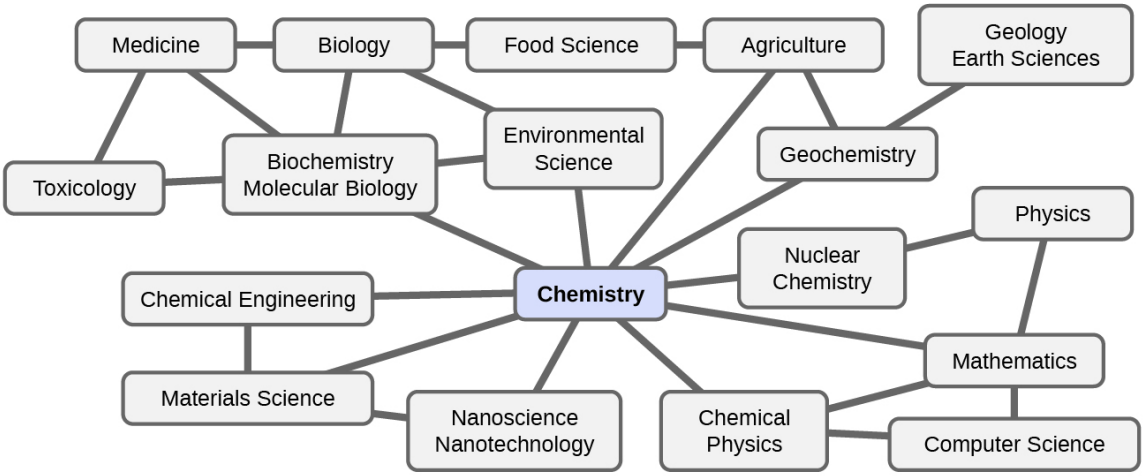


Figure **1.1.2**: Knowledge of chemistry is central to understanding a wide range of scientific disciplines. This diagram shows just some of the interrelationships between chemistry and other fields.

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

The Scientific Method

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

Some hypotheses are attempts to explain the behavior that is summarized in laws. The laws of science summarize a vast number of experimental observations, and describe or predict some facet of the natural world. If such a hypothesis turns out to be capable of explaining a large body of experimental data, it can reach the status of a theory. Scientific theories are well-substantiated, comprehensive, testable explanations of particular aspects of nature. Theories are accepted because they provide satisfactory

explanations, but they can be modified if new data become available. The path of discovery that leads from question and observation to law or hypothesis to theory, combined with experimental verification of the hypothesis and any necessary modification of the theory, is called the scientific method (Figure **1.1.3**).

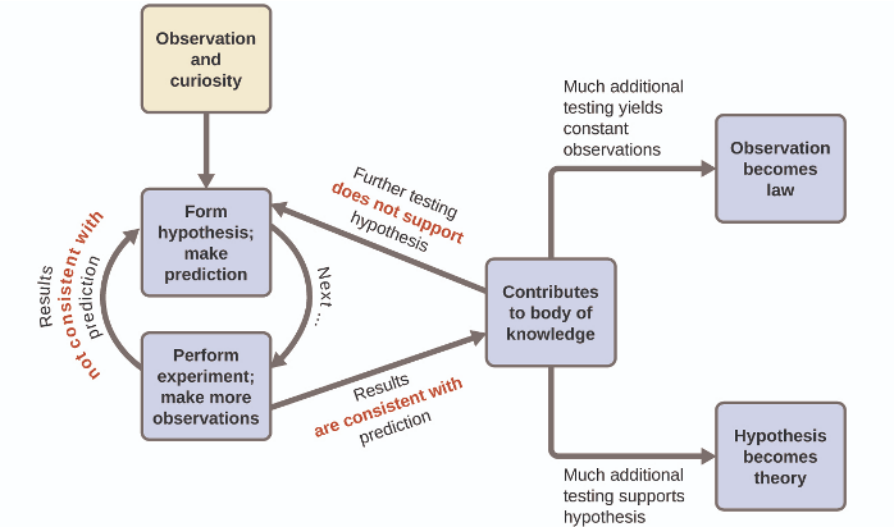


Figure **1.1.3**: The scientific method follows a process similar to the one shown in this diagram. All the key components are shown, in roughly the right order. Scientific progress is seldom neat and clean: It requires open inquiry and the reworking of questions and ideas in response to findings.

The Domains of Chemistry

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

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

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

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

The symbolic domain contains the specialized language used to represent components of the macroscopic and microscopic domains. Chemical symbols (such as those used in the periodic table), chemical formulas, and chemical equations are part of the symbolic domain, as are graphs and drawings. We can also consider calculations as part of the symbolic domain. These symbols play an important role in chemistry because they help interpret the behavior of the macroscopic domain in terms of the components of the microscopic domain. One of the challenges for students learning chemistry is recognizing that the same symbols can represent different things in the macroscopic and microscopic domains, and one of the features that makes chemistry fascinating is the use of a domain that must be imagined to explain behavior in a domain that can be observed.

A helpful way to understand the three domains is via the essential and ubiquitous substance of water. That water is a liquid at moderate temperatures, will freeze to form a solid at lower temperatures, and boil to form a gas at higher temperatures (Figure 1.1.4) are macroscopic observations. But some properties of water fall into the microscopic domain—what we cannot observe with

the naked eye. The description of water as comprised of two hydrogen atoms and one oxygen atom, and the explanation of freezing and boiling in terms of attractions between these molecules, is within the microscopic arena. The formula H_2O, which can describe water at either the macroscopic or microscopic levels, is an example of the symbolic domain. The abbreviations (*g*) for gas, (*s*) for solid, and (*l*) for liquid are also symbolic.

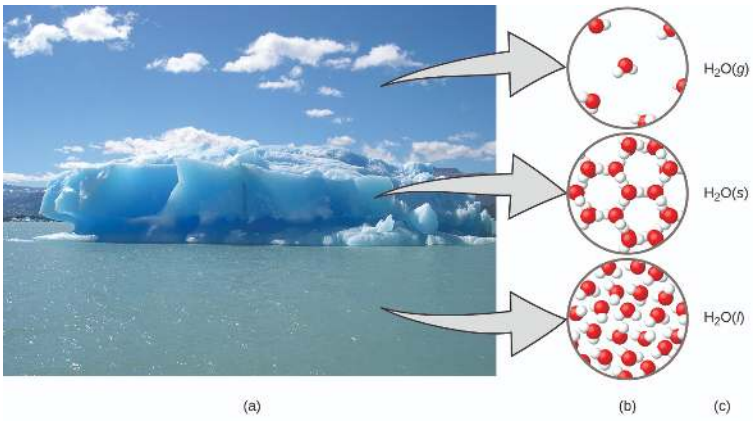


Figure **1.1.4**: (a) Moisture in the air, icebergs, and the ocean represent water in the macroscopic domain. (b) At the molecular level (microscopic domain), gas molecules are far apart and disorganized, solid water molecules are close together and organized, and liquid molecules are close together and disorganized. (c) The formula H_2O symbolizes water, and (g), (s), and (l) symbolize its phases. Note that clouds are actually comprised of either very small liquid water droplets or solid water crystals; gaseous water in our atmosphere is not visible to the naked eye, although it may be sensed as humidity. (credit a: modification of work by "Gorkaazk"/Wikimedia Commons).

Key Concepts and Summary

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

Glossary

chemistry
study of the composition, properties, and interactions of matter

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

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

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

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

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

symbolic domain

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

theory

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

Contributors and Attributions

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

This page titled 1.1: Chemistry in Context is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

- **1.1: Chemistry in Context** 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. While the number and unit are explicitly represented when a quantity is written, the uncertainty is an aspect of the measurement result that is more implicitly represented and will be discussed later.

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

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

We usually report the results of scientific measurements in SI units, an updated version of the metric system, using the units listed in Table **1.2.1**. 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
electric current	ampere	A
amount of substance	mole	mol
luminous intensity	candela	cd

Sometimes we use units that are fractions or multiples of a base unit. Ice cream is sold in quarts (a familiar, non-SI base unit), pints (0.5 quart), or gallons (4 quarts). We also use fractions or multiples of units in the SI system, but these fractions or multiples are always powers of 10. Fractional or multiple SI units are named using a prefix and the name of the base unit. For example, a length of 1000 meters is also called a kilometer because the prefix *kilo* means "one thousand," which in scientific notation is 10^3 (1 kilometer = 1000 m = 10^3 m). The prefixes used and the powers to which 10 are raised are listed in Table **1.2.2**.

NG, equals 4 times ten to the negative 9, or 0.000000004 g. The prefix micro has the greek letter mu as its symbol and a factor of 10 to the negative sixth power. Therefore, 1 microliter, or mu L, is equal to one times ten to the negative 6 or 0.000001 L. The prefix milli has a lowercase M as its symbol and a factor of 10 to the negative third power. Therefore, 2 millimoles, or M mol, are equal to two times ten to the negative 3 or 0.002 mol. The prefix centi has a lowercase C as its symbol and a factor of 10 to the negative second power. Therefore, 7 centimeters, or C M, are equal to seven times ten to the negative 2 meters or 0.07 M O L. The prefix deci has a lowercase D as its symbol and a factor of 10 to the negative first power. Therefore, 1 deciliter, or lowercase D uppercase L, are equal to one times ten to the negative 1 meters or 0.1 L. The prefix kilo has a lowercase K as its symbol and a factor of 10 to the third power. Therefore, 1 kilometer, or K M, is equal to one times ten to the third meters or 1000 M. The prefix mega has an uppercase M as its symbol and a factor of 10 to the sixth power. Therefore, 3 megahertz, or M H Z, are equal to three times 10 to the sixth hertz, or 3000000 H Z. The prefix giga has an uppercase G as its symbol and a factor of 10 to the ninth power. Therefore, 8 gigayears, or G Y R, are equal to eight times 10 to the ninth years, or 800000000 G Y R. The prefix tera has an uppercase T as its symbol and a factor of 10 to the twelfth power. Therefore, 5 terawatts, or T W, are equal to five times 10 to the twelfth watts, or 5000000000000 W." data-quail-id="64" data-mt-width="1076">

Table **1.2.2**: Common Unit Prefixes

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

SI Base Units

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

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).

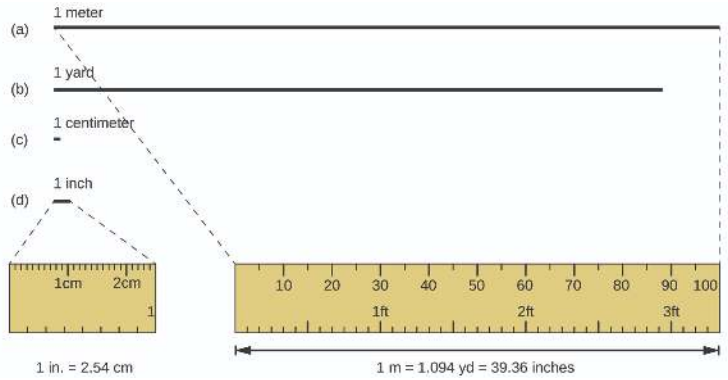


Figure **1.2.1**: The relative lengths of 1 m, 1 yd, 1 cm, and 1 in. are shown (not actual size), as well as comparisons of 2.54 cm and 1 in., and of 1 m and 1.094 yd.

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

Mass

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



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

Temperature

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

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.

Derived SI Units

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

Volume

Volume is the measure of the amount of space occupied by an object. The standard SI unit of volume is defined by the base unit of length (Figure **1.2.3**). The standard volume is a cubic meter (m^3), a cube with an edge length of exactly one meter. To dispense a cubic meter of water, we could build a cubic box with edge lengths of exactly one meter. This box would hold a cubic meter of water or any other substance.

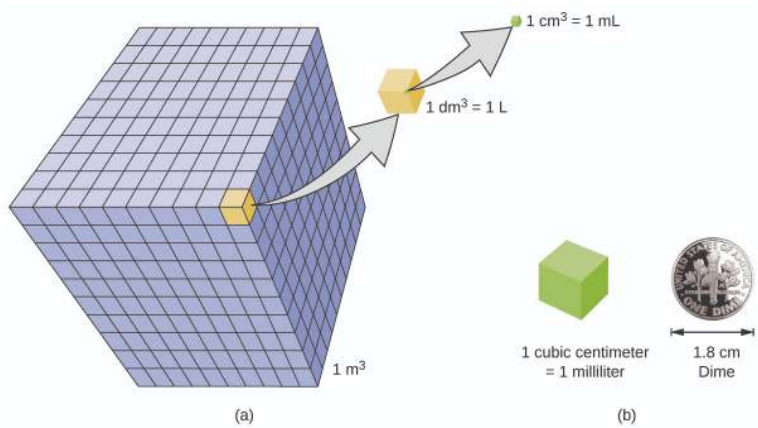


Figure **1.2.3**: (a) The relative volumes are shown for cubes of 1 m^3, 1 dm^3 (1 L), and 1 cm^3 (1 mL) (not to scale). (b) The diameter of a dime is compared relative to the edge length of a 1-cm^3 (1-mL) cube.

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

Density

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

The density of a substance is the ratio of the mass of a sample of the substance to its volume. The SI unit for density is the kilogram per cubic meter (kg/m^3). For many situations, however, this as an inconvenient unit, and we often use grams per cubic centimeter (g/cm^3) for the densities of solids and liquids, and grams per liter (g/L) for gases. Although there are exceptions, most liquids and solids have densities that range from about 0.7 g/cm^3 (the density of gasoline) to 19 g/cm^3 (the density of gold). The density of air is about 1.2 g/L. Table **1.2.3** shows the densities of some common substances.

Table **1.2.3**: Densities of Common Substances

https://chem.libretexts.org/@go/page/216723

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

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

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

Example 1.2.1

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 1.2.1

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

Answer

2.00 kg/L

Summary

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

Key Equations

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

Glossary

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

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

cubic meter (m^3)
SI unit of volume

density
ratio of mass to volume for a substance or object

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

kilogram (kg)

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

length
measure of one dimension of an object

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

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

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

second (s)
SI unit of time

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

unit
standard of comparison for measurements

volume
amount of space occupied by an object

This page titled 1.2: Measurements is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

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

https://chem.libretexts.org/@go/page/216723



https://chem.libretexts.org/@go/page/216723

1.3: Measurement Uncertainty, Accuracy, and Precision

Learning Objectives

- Define accuracy and precision
- Distinguish exact and uncertain numbers
- Correctly represent uncertainty in quantities using significant figures
- Apply proper rounding rules to computed quantities

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.

Significant Figures in Measurement

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

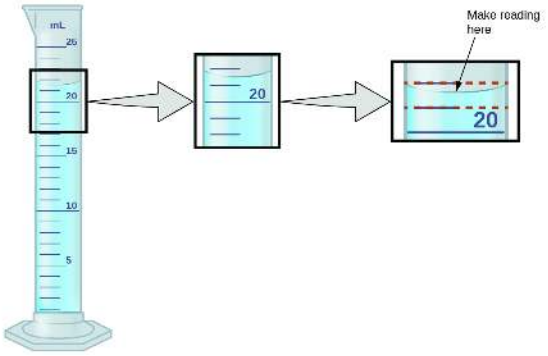
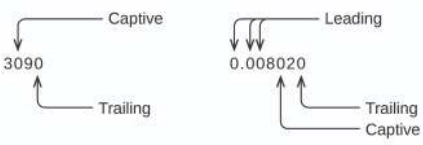


Figure **1.3.1**: To measure the volume of liquid in this graduated cylinder, you must mentally subdivide the distance between the 21 and 22 mL marks into tenths of a milliliter, and then make a reading (estimate) at the bottom of the meniscus.

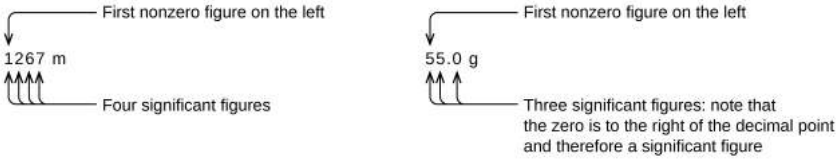
Refer to the illustration in Figure **1.3.1**. The bottom of the meniscus in this case clearly lies between the 21 and 22 markings, meaning the liquid volume is *certainly* greater than 21 mL but less than 22 mL. The meniscus appears to be a bit closer to the 22-mL mark than to the 21-mL mark, and so 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 must be measured to the nearest 0.1 mL.

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

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



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

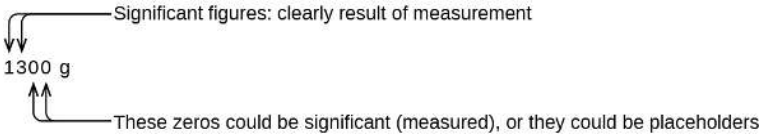


Captive zeros result from measurement and are therefore always significant. Leading zeros, however, are never significant—they merely tell us where the decimal point is located.



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

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



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

Significant Figures in Calculations

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

1. When we add or subtract numbers, we should round the result to the same number of decimal places as the number with the least number of decimal places (the least precise value in terms of addition and subtraction).
2. When we multiply or divide numbers, we should round the result to the same number of digits as the number with the least number of significant figures (the least precise value in terms of multiplication and division).
3. If the digit to be dropped (the one immediately to the right of the digit to be retained) is less than 5, we "round down" and leave the retained digit unchanged; if it is more than or equal to 5, we "round up" and increase the retained digit by 1.

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

- 0.028675 rounds "up" to 0.0287 (the dropped digit, 7, is greater than or equal to 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)
- 92.85 rounds "up" to 92.9 (the dropped digit is 5)

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

Example 1.3.1: Rounding Numbers

Round the following to the indicated number of significant figures:

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

Solution

a. 31.57 rounds "up" to 32 (the dropped digit is 5)
b. 8.1649 rounds "down" to 8.16 (the dropped digit, 4, is less than 5)
c. 0.051065 rounds "up" to 0.05107 (the dropped digit is 5)
d. 0.90275 rounds "up" to 0.9028 (the dropped digit is 5)

Exercise 1.3.1

Round the following to the indicated number of significant figures:

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

Answer a

0.42

Answer b

0.00387

Answer c

421.3

Answer d

28,684

Example 1.3.2: Addition and Subtraction with Significant Figures Rule:

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

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

Solution

(a)

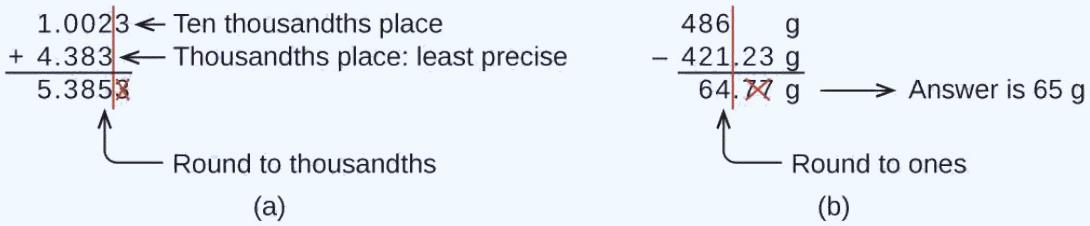
$$\begin{array}{r} 1.0023\ \text{g} \\ +\ 4.383\ \text{g} \\ \hline 5.3853\ \text{g} \end{array}$$

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

(b)

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

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



Exercise 1.3.2

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

Answer a

2.64 mL

Answer b

0.658 m

Example 1.3.3: Multiplication and Division with Significant Figures

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

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

Solution

(a)

$$0.6238\ \text{cm} \times 6.6\ \text{cm} = 4.11708\ \text{cm}^2 \rightarrow \text{result is } 4.1\ \text{cm}^2 \quad (1.3.1)$$
$$\text{(round to two significant figures)}$$

$$\text{four significant figures} \times \text{two significant figures} \rightarrow \text{two significant figures answer} \tag{1.3.2}$$

(b)

$$\frac{421.23\ \text{g}}{486\ \text{mL}} = 0.86728...\ \text{g/mL} \rightarrow \text{result is } 0.867\ \text{g/mL} \quad \text{(round to three significant figures)} \tag{1.3.3}$$

$$\frac{\text{five significant figures}}{\text{three significant figures}} \rightarrow \text{three significant figures answer} \tag{1.3.4}$$

Exercise 1.3.3

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

Answer a

0.747 cm^2

Answer b

0.9884 m/s

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

Example 1.3.4: Calculation with Significant Figures

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

Solution

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

Exercise 1.3.4: Determination of Density Using Water Displacement

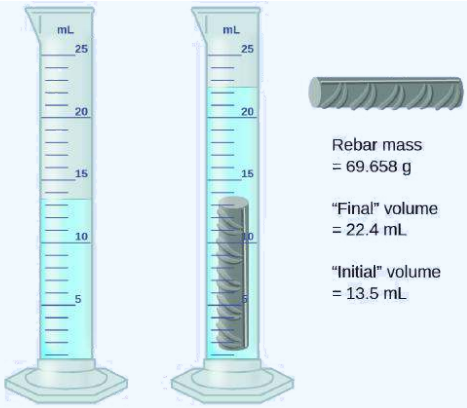
What is the density of a liquid with a mass of 31.1415 g and a volume of 30.13 cm^3?

Answer

1.034 g/mL

Example 1.3.4

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 figures, per the rule for multiplication and division)

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

Exercise 1.3.4

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.

Accuracy and Precision

Scientists typically make repeated measurements of a quantity to ensure the quality of their findings and to know both the precision and the accuracy of their results. Measurements are said to be precise if they yield very similar results when repeated in the same manner. A measurement is considered accurate if it yields a result that is very close to the true or accepted value. Precise values agree with each other; accurate values agree with a true value. These characterizations can be extended to other contexts, such as the results of an archery competition (Figure **1.3.2**).

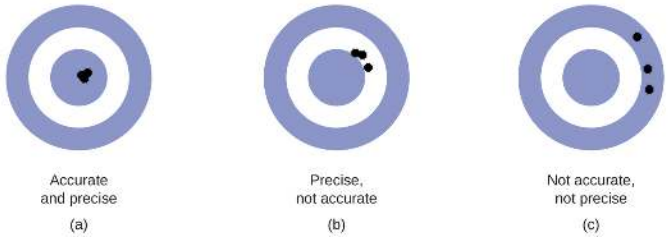


Figure **1.3.2**: (a) These arrows are close to both the bull's eye and one another, so they are both accurate and precise. (b) These arrows are close to one another but not on target, so they are precise but not accurate. (c) These arrows are neither on target nor close to one another, so they are neither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

Summary

Quantities can be exact or measured. Measured quantities have an associated uncertainty that is represented by the number of significant figures in the measurement. The uncertainty of a calculated value depends on the uncertainties in the values used in the calculation and is reflected in how the value is rounded. Calculations involving multiplication and division are rounded to the least number of significant figures of the original, measured values. Calculations involving subtraction or addition are rounded based on the least decimal places. Mixed calculation types should be solved using order of operation rules, with proper rounding after each steps. Measured values can be accurate (close to the true value) and/or precise (showing little variation when measured repeatedly).

Glossary

uncertainty
estimate of amount by which measurement differs from true value

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

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

precision
how closely a measurement matches the same measurement when repeated

exact number
number derived by counting or by definition

accuracy
how closely a measurement aligns with a correct value

meniscus
the lowest part of the curved surface of a liquid

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 1.3: Measurement Uncertainty, Accuracy, and Precision is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

1.4: Mathematical Treatment of Measurement Results

Learning Objectives

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

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

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

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

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

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

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

The time can then be computed as:

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

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

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

Conversion Factors and Dimensional Analysis

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

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

Several other commonly used conversion factors are given in Table **1.4.1**.

Table **1.4.1**: Common Conversion Factors

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

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

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

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

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

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

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

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

Example 1.4.1: 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 **1.4.1**).

Solution

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

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

We write the unit conversion factor in its two forms:

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

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

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

? Exercise 1.4.1

Convert a volume of 9.345 qt to liters.

Answer

8.844 L

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

✓ Example 1.4.2: Computing Quantities from Measurement Results

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

Solution

Since $\text{density} = \frac{\text{mass}}{\text{volume}}$, we need to divide the mass in grams by the volume in milliliters. In general: the number of units of B = the number of units of A × 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 1.4.2

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

Answer

2.956×10^{-2} L

✓ Example 1.4.3: Computing Quantities from Measurement Results

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

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

Solution

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

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

and then convert volume from liters to gallons:

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

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 1.4.3

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

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

Answer a

51 mpg

Answer b

$62

Conversion of Temperature Units

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

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

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

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

where

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

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

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

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

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

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

The equation relating the temperature scales is then:

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

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

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

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

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

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

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

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

$$T_{°C} = T_K - 273.15$$

The 273.15 in these equations has been determined experimentally, so it is not exact. Figure 1.4.1 shows the relationship among the three temperature scales. Recall that we do not use the degree sign with temperatures on the kelvin scale.

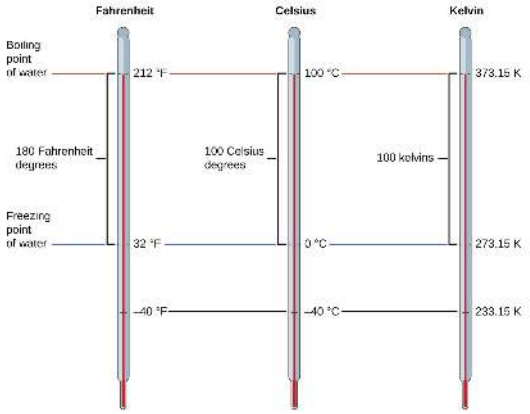


Figure 1.4.1: The Fahrenheit, Celsius, and kelvin temperature scales are compared.

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

Example 1.4.4: Conversion from Celsius

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

Solution

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

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

Exercise 1.4.4

Convert 80.92 °C to K and °F.

Answer

354.07 K, 177.7 °F

Example 1.4.5: Conversion from Fahrenheit

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

Solution

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

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

Exercise 1.4.5

Convert 50 °F to °C and K.

Answer

10 °C, 280 K

Summary

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

Key Equations

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

Glossary

dimensional analysis

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

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

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

---

This page titled 1.4: Mathematical Treatment of Measurement Results is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

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

https://chem.libretexts.org/@go/page/216725

1.5: Phases and Classification of Matter

Learning Objectives

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

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

Solids, liquids, and gases are the three states of matter commonly found on earth (Figure **1.5.1**). A solid is rigid and possesses a definite shape. A liquid flows and takes the shape of a container, except that it forms a flat or slightly curved upper surface when acted upon by gravity. (In zero gravity, liquids assume a spherical shape.) Both liquid and solid samples have volumes that are very nearly independent of pressure. A gas takes both the shape and volume of its container.

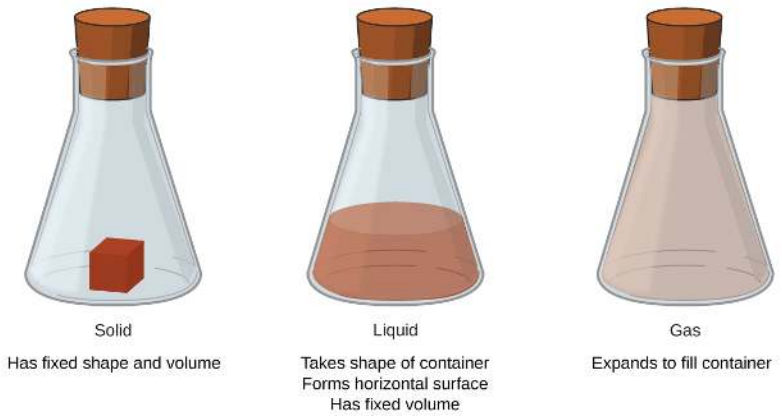


Figure **1.5.1**: The three most common states or phases of matter are solid, liquid, and gas.

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

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

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

The law of conservation of matter summarizes many scientific observations about matter: It states that *there is no detectable change in the total quantity of matter present when matter converts from one type to another (a chemical change) or changes among solid, liquid, or gaseous states (a physical change)*. Brewing beer and the operation of batteries provide examples of the conservation of matter (Figure **1.5.4**). During the brewing of beer, the ingredients (water, yeast, grains, malt, hops, and sugar) are converted into beer (water, alcohol, carbonation, and flavoring substances) with no actual loss of substance. This is most clearly

seen during the bottling process, when glucose turns into ethanol and carbon dioxide, and the total mass of the substances does not change. This can also be seen in a lead-acid car battery: The original substances (lead, lead oxide, and sulfuric acid), which are capable of producing electricity, are changed into other substances (lead sulfate and water) that do not produce electricity, with no change in the actual amount of matter.

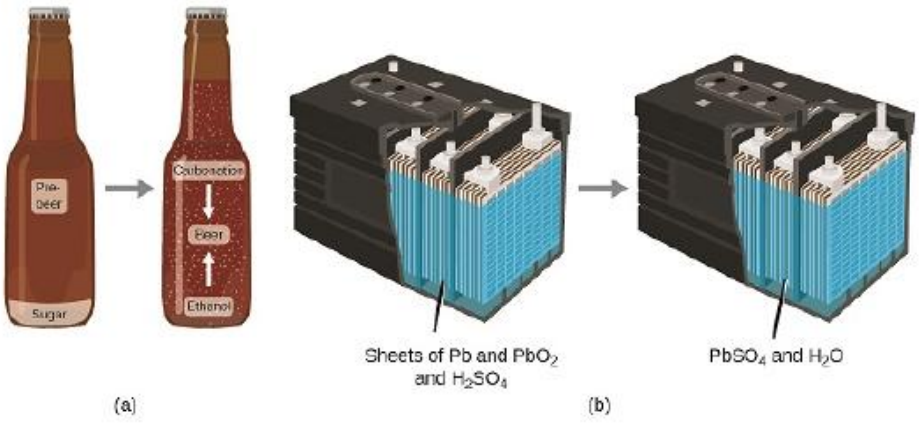


Figure 1.5.3: (a) The mass of beer precursor materials is the same as the mass of beer produced: Sugar has become alcohol and carbonation. (b) The mass of the lead, lead oxide plates, and sulfuric acid that goes into the production of electricity is exactly equal to the mass of lead sulfate and water that is formed.

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

Atoms and Molecules

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

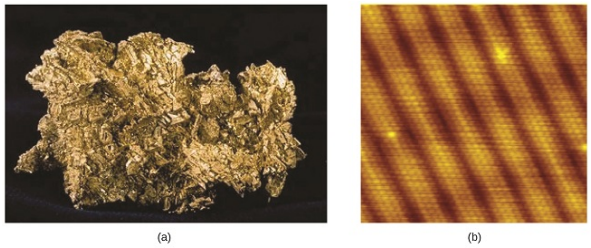


Figure 1.5.4: (a) This photograph shows a gold nugget. (b) A scanning-tunneling microscope (STM) can generate views of the surfaces of solids, such as this image of a gold crystal. Each sphere represents one gold atom. (credit a: modification of work by United States Geological Survey; credit b: modification of work by “Erwinrossen”/Wikimedia Commons)

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

An atom is so small that its size is difficult to imagine. One of the smallest things we can see with our unaided eye is a single thread of a spider web: These strands are about 1/10,000 of a centimeter (0.0001 cm) in diameter. Although the cross-section of one strand is almost impossible to see without a microscope, it is huge on an atomic scale. A single carbon atom in the web has a diameter of about 0.000000015 centimeter, and it would take about 7000 carbon atoms to span the diameter of the strand. To put this in perspective, if a carbon atom were the size of a dime, the cross-section of one strand would be larger than a football field, which would require about 150 million carbon atom "dimes" to cover it. (Figure **1.5.5**) shows increasingly close microscopic and atomic-level views of ordinary cotton.

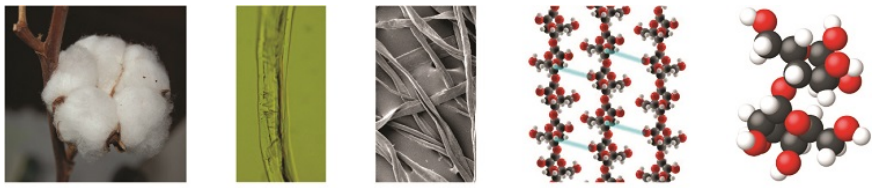


Figure **1.5.5**: These images provide an increasingly closer view: (a) a cotton boll, (b) a single cotton fiber viewed under an optical microscope (magnified 40 times), (c) an image of a cotton fiber obtained with an electron microscope (much higher magnification than with the optical microscope); and (d and e) atomic-level models of the fiber (spheres of different colors represent atoms of different elements). (credit c: modification of work by "Featheredtar"/Wikimedia Commons)

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

It is rare to find collections of individual atoms. Only a few elements, such as the gases helium, neon, and argon, consist of a collection of individual atoms that move about independently of one another. Other elements, such as the gases hydrogen, nitrogen, oxygen, and chlorine, are composed of units that consist of pairs of atoms (Figure **1.5.6**). One form of the element phosphorus consists of units composed of four phosphorus atoms. The element sulfur exists in various forms, one of which consists of units composed of eight sulfur atoms. These units are called molecules. A molecule consists of two or more atoms joined by strong forces called chemical bonds. The atoms in a molecule move around as a unit, much like the cans of soda in a six-pack or a bunch of keys joined together on a single key ring. A molecule may consist of two or more identical atoms, as in the molecules found in the elements hydrogen, oxygen, and sulfur, or it may consist of two or more different atoms, as in the molecules found in water. Each water molecule is a unit that contains two hydrogen atoms and one oxygen atom. Each glucose molecule is a unit that contains 6 carbon atoms, 12 hydrogen atoms, and 6 oxygen atoms. Like atoms, molecules are incredibly small and light. If an ordinary glass of water were enlarged to the size of the earth, the water molecules inside it would be about the size of golf balls.

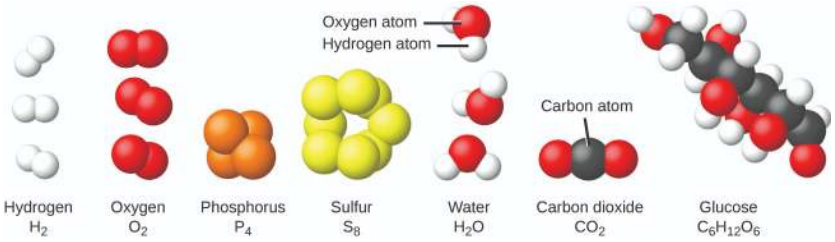


Figure **1.5.6**: The elements hydrogen, oxygen, phosphorus, and sulfur form molecules consisting of two or more atoms of the same element. The compounds water, carbon dioxide, and glucose consist of combinations of atoms of different elements.

Classifying Matter

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

We can divide pure substances into two classes: elements and compounds. Pure substances that cannot be broken down into simpler substances by chemical changes are called elements. Iron, silver, gold, aluminum, sulfur, oxygen, and copper are familiar examples

of the more than 100 known elements, of which about 90 occur naturally on the earth, and two dozen or so have been created in laboratories.

Pure substances that can be broken down by chemical changes are called compounds. This breakdown may produce either elements or other compounds, or both. Mercury(II) oxide, an orange, crystalline solid, can be broken down by heat into the elements mercury and oxygen (Figure **1.5.7**). When heated in the absence of air, the compound sucrose is broken down into the element carbon and the compound water. (The initial stage of this process, when the sugar is turning brown, is known as caramelization—this is what imparts the characteristic sweet and nutty flavor to caramel apples, caramelized onions, and caramel). Silver(I) chloride is a white solid that can be broken down into its elements, silver and chlorine, by absorption of light. This property is the basis for the use of this compound in photographic films and photochromic eyeglasses (those with lenses that darken when exposed to light).

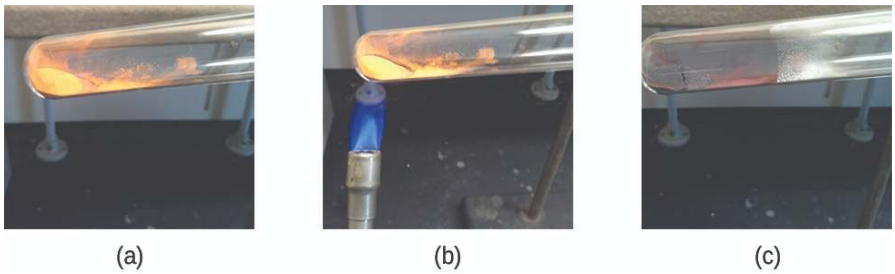


Figure **1.5.7**: (a)The compound mercury(II) oxide, (b)when heated, (c) decomposes into silvery droplets of liquid mercury and invisible oxygen gas. (credit: modification of work by Paul Flowers)

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

A mixture is composed of two or more types of matter that can be present in varying amounts and can be separated by physical changes, such as evaporation (you will learn more about this later). A mixture with a composition that varies from point to point is called a heterogeneous mixture. Italian dressing is an example of a heterogeneous mixture (Figure **1.5.1*a***). Its composition can vary because we can make it from varying amounts of oil, vinegar, and herbs. It is not the same from point to point throughout the mixture—one drop may be mostly vinegar, whereas a different drop may be mostly oil or herbs because the oil and vinegar separate and the herbs settle. Other examples of heterogeneous mixtures are chocolate chip cookies (we can see the separate bits of chocolate, nuts, and cookie dough) and granite (we can see the quartz, mica, feldspar, and more).

A homogeneous mixture, also called a solution, exhibits a uniform composition and appears visually the same throughout. An example of a solution is a sports drink, consisting of water, sugar, coloring, flavoring, and electrolytes mixed together uniformly (Figure **1.5.1*b***). Each drop of a sports drink tastes the same because each drop contains the same amounts of water, sugar, and other components. Note that the composition of a sports drink can vary—it could be made with somewhat more or less sugar, flavoring, or other components, and still be a sports drink. Other examples of homogeneous mixtures include air, maple syrup, gasoline, and a solution of salt in water.



Figure **1.5.7**: (a) Oil and vinegar salad dressing is a heterogeneous mixture because its composition is not uniform throughout. (b) A commercial sports drink is a homogeneous mixture because its composition is uniform throughout. (credit a “left”: modification of work by John Mayer; credit a “right”: modification of work by Umberto Salvagnin; credit b “left: modification of work by Jeff Bedford)

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

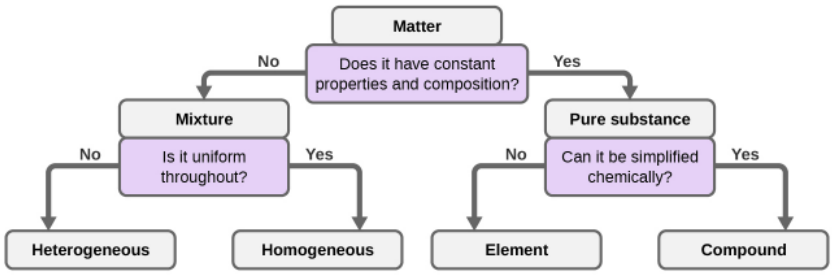


Figure **1.5.8**: Depending on its properties, a given substance can be classified as a homogeneous mixture, a heterogeneous mixture, a compound, or an element.

Eleven elements make up about 99% of the earth's crust and atmosphere (Table **1.5.1**). Oxygen constitutes nearly one-half and silicon about one-quarter of the total quantity of these elements. A majority of elements on earth are found in chemical combinations with other elements; about one-quarter of the elements are also found in the free state.

Table **1.5.1**: Elemental Composition of Earth

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

Decomposition of Water / Production of Hydrogen

Water consists of the elements hydrogen and oxygen combined in a 2 to 1 ratio. Water can be broken down into hydrogen and oxygen gases by the addition of energy. One way to do this is with a battery or power supply, as shown in (Figure **1.5.9**).

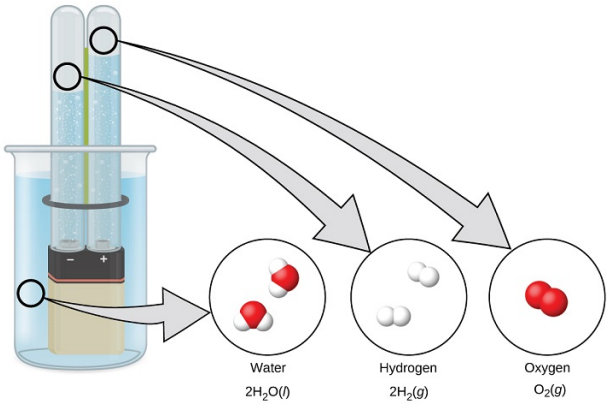


Figure **1.5.9**: The decomposition of water is shown at the macroscopic, microscopic, and symbolic levels. The battery provides an electric current (microscopic) that decomposes water. At the macroscopic level, the liquid separates into the gases hydrogen (on the left) and oxygen (on the right). Symbolically, this change is presented by showing how liquid H_2O separates into H_2 and O_2 gases.

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

The two gases produced have distinctly different properties. Oxygen is not flammable but is required for combustion of a fuel, and hydrogen is highly flammable and a potent energy source. How might this knowledge be applied in our world? One application involves research into more fuel-efficient transportation. Fuel-cell vehicles (FCV) run on hydrogen instead of gasoline (Figure **1.5.10**). They are more efficient than vehicles with internal combustion engines, are nonpolluting, and reduce greenhouse gas emissions, making us less dependent on fossil fuels. FCVs are not yet economically viable, however, and current hydrogen production depends on natural gas. If we can develop a process to economically decompose water, or produce hydrogen in another environmentally sound way, FCVs may be the way of the future.

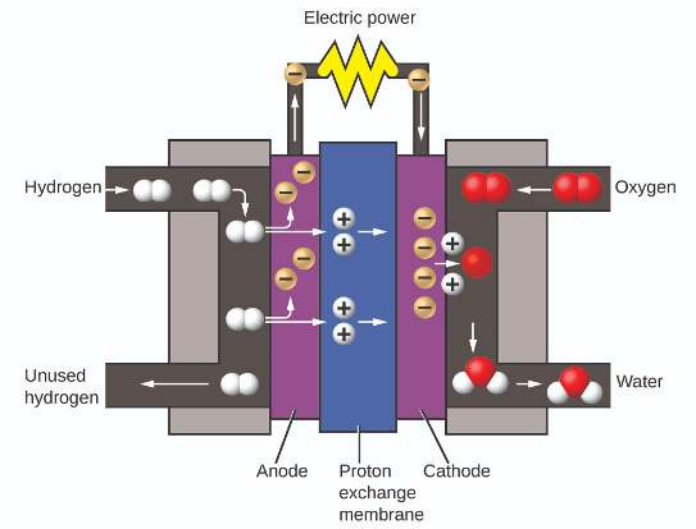


Figure **1.5.10**: A fuel cell generates electrical energy from hydrogen and oxygen via an electrochemical process and produces only water as the waste product.

Chemistry of Cell Phones

Imagine how different your life would be without cell phones (Figure **1.5.11**) and other smart devices. Cell phones are made from numerous chemical substances, which are extracted, refined, purified, and assembled using an extensive and in-depth understanding of chemical principles. About 30% of the elements that are found in nature are found within a typical smart phone. The case/body/frame consists of a combination of sturdy, durable polymers comprised primarily of carbon, hydrogen, oxygen, and nitrogen [acrylonitrile butadiene styrene (ABS) and polycarbonate thermoplastics], and light, strong, structural metals, such as aluminum, magnesium, and iron. The display screen is made from a specially toughened glass (silica glass strengthened by the

addition of aluminum, sodium, and potassium) and coated with a material to make it conductive (such as indium tin oxide). The circuit board uses a semiconductor material (usually silicon); commonly used metals like copper, tin, silver, and gold; and more unfamiliar elements such as yttrium, praseodymium, and gadolinium. The battery relies upon lithium ions and a variety of other materials, including iron, cobalt, copper, polyethylene oxide, and polyacrylonitrile.



Figure **1.5.11**: Almost one-third of naturally occurring elements are used to make a modern cell phone. (credit: modification of work by John Taylor)

Contributors and Attributions

Summary

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

Glossary

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

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

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

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

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

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

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

law of conservation of matter

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

mass

fundamental property indicating amount of matter

matter

anything that occupies space and has mass

mixture

matter that can be separated into its components by physical means

molecule

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

pure substance

homogeneous substance that has a constant composition

solid

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

weight

force that gravity exerts on an object

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 1.5: Phases and Classification of Matter is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

1.6: Physical and Chemical Properties

Learning Objectives

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

The characteristics that enable us to distinguish one substance from another are called properties. A physical property is a characteristic of matter that is not associated with a change in its chemical composition. Familiar examples of physical properties include density, color, hardness, melting and boiling points, and electrical conductivity. We can observe some physical properties, such as density and color, without changing the physical state of the matter observed. Other physical properties, such as the melting temperature of iron or the freezing temperature of water, can only be observed as matter undergoes a physical change. A physical change is a change in the state or properties of matter without any accompanying change in its chemical composition (the identities of the substances contained in the matter). We observe a physical change when wax melts, when sugar dissolves in coffee, and when steam condenses into liquid water (Figure **1.6.1**). Other examples of physical changes include magnetizing and demagnetizing metals (as is done with common antitheft security tags) and grinding solids into powders (which can sometimes yield noticeable changes in color). In each of these examples, there is a change in the physical state, form, or properties of the substance, but no change in its chemical composition.



Figure **1.6.1**: (a) Wax undergoes a physical change when solid wax is heated and forms liquid wax. (b) Steam condensing inside a cooking pot is a physical change, as water vapor is changed into liquid water. (credit a: modification of work by "95jb14"/Wikimedia Commons; credit b: modification of work by "mjneuby"/Flickr).

The change of one type of matter into another type (or the inability to change) is a chemical property. Examples of chemical properties include flammability, toxicity, acidity, reactivity (many types), and heat of combustion. Iron, for example, combines with oxygen in the presence of water to form rust; chromium does not oxidize (Figure **1.6.2**). Nitroglycerin is very dangerous because it explodes easily; neon poses almost no hazard because it is very unreactive.

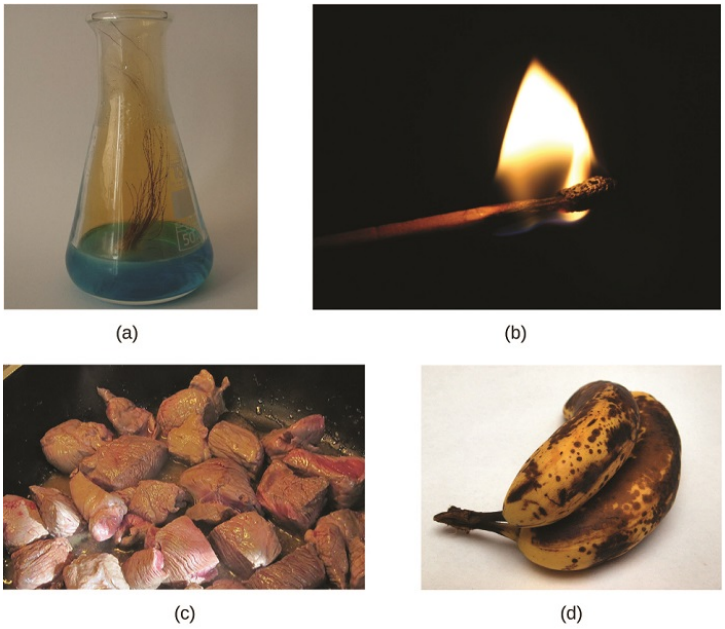


(a) (b)

Figure **1.6.2**: (a) One of the chemical properties of iron is that it rusts; (b) one of the chemical properties of chromium is that it does not. (credit a: modification of work by Tony Hisgett; credit b: modification of work by "Atoma"/Wikimedia Commons)

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

To identify a chemical property, we look for a chemical change. A chemical change always produces one or more types of matter that differ from the matter present before the change. The formation of rust is a chemical change because rust is a different kind of matter than the iron, oxygen, and water present before the rust formed. The explosion of nitroglycerin is a chemical change because the gases produced are very different kinds of matter from the original substance. Other examples of chemical changes include reactions that are performed in a lab (such as copper reacting with nitric acid), all forms of combustion (burning), and food being cooked, digested, or rotting (Figure **1.6.3**).



(a) (b)

(c) (d)

Figure **1.6.3**: (a) Copper and nitric acid undergo a chemical change to form copper nitrate and brown, gaseous nitrogen dioxide. (b) During the combustion of a match, cellulose in the match and oxygen from the air undergo a chemical change to form carbon dioxide and water vapor. (c) Cooking red meat causes a number of chemical changes, including the oxidation of iron in myoglobin that results in the familiar red-to-brown color change. (d) A banana turning brown is a chemical change as new, darker (and less tasty) substances form. (credit b: modification of work by Jeff Turner; credit c: modification of work by Gloria Cabada-Leman; credit d: modification of work by Roberto Verzo)

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

Properties of matter fall into one of two categories. If the property depends on the amount of matter present, it is an extensive property. The mass and volume of a substance are examples of extensive properties; for instance, a gallon of milk has a larger mass and volume than a cup of milk. The value of an extensive property is directly proportional to the amount of matter in question. If the property of a sample of matter does not depend on the amount of matter present, it is an intensive property. Temperature is an example of an intensive property. If the gallon and cup of milk are each at 20 °C (room temperature), when they are combined, the temperature remains at 20 °C. As another example, consider the distinct but related properties of heat and temperature. A drop of

hot cooking oil spattered on your arm causes brief, minor discomfort, whereas a pot of hot oil yields severe burns. Both the drop and the pot of oil are at the same temperature (an intensive property), but the pot clearly contains much more heat (extensive property).

Hazard Diamond

You may have seen the symbol shown in Figure 1.6.4 on containers of chemicals in a laboratory or workplace. Sometimes called a "fire diamond" or "hazard diamond," this chemical hazard diamond provides valuable information that briefly summarizes the various dangers of which to be aware when working with a particular substance.

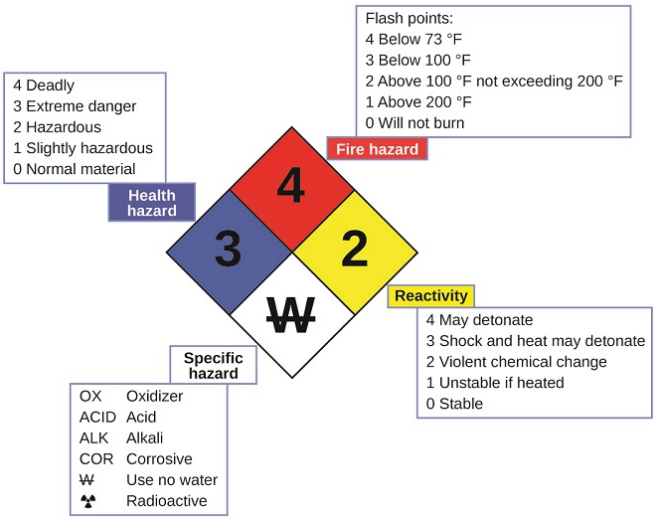


Figure 1.6.4: The National Fire Protection Agency (NFPA) hazard diamond summarizes the major hazards of a chemical substance.

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

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

The periodic table is a table of elements that places elements with similar properties close together (Figure 1.6.5). You will learn more about the periodic table as you continue your study of chemistry.

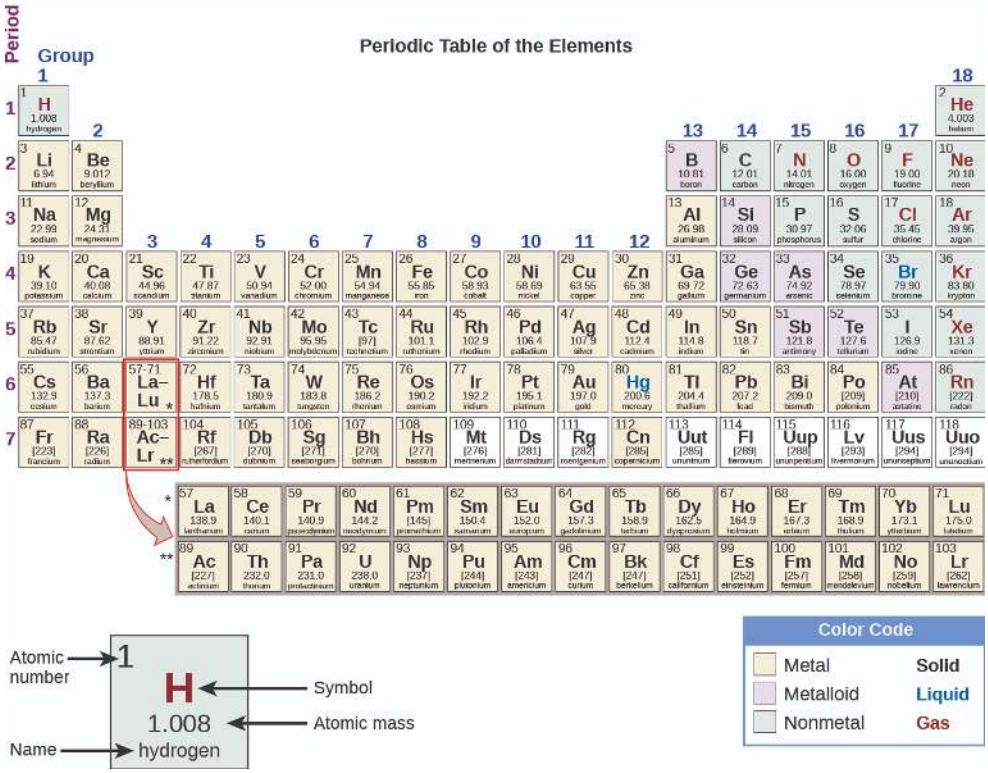


Figure **1.6.5**: The periodic table shows how elements may be grouped according to certain similar properties. Note the background color denotes whether an element is a metal, metalloid, or nonmetal, whereas the element symbol color indicates whether it is a solid, liquid, or gas.

Summary

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

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

Glossary

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

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

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

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

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

physical property

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

---

This page titled 1.6: Physical and Chemical Properties is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

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

1.E: Essential Ideas of Chemistry (Exercises)

1.1: Chemistry in Context

Q1.1.1

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

S1.1.1

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

Q1.1.2

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

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

Q1.1.3

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

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

S1.1.3

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

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

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

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

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

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

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

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

Macroscopic. The heat required is determined from macroscopic properties.

1.2: Phases and Classification of Matter

Questions

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

b. When magnesium burns in air a white flaky ash of magnesium oxide is produced. Is the mass of magnesium oxide less than, greater than, or the same as the original piece of magnesium? Explain.
c. Antoine Lavoisier, the French scientist credited with first stating the law of conservation of matter, heated a mixture of tin and air in a sealed flask to produce tin oxide. Did the mass of the sealed flask and contents decrease, increase, or remain the same after the heating?

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

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

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

Solutions

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

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

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

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

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

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

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

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

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

1.3: Physical and Chemical Properties

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

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

Classify each of the following changes as physical or chemical:

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

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

Classify each of the following changes as physical or chemical:

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

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

physical

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

Explain the difference between extensive properties and intensive properties.

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

Identify the following properties as either extensive or intensive.

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

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

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

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

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

1.4: Measurements

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

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

about a yard

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

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

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

1. (a) the mass of the moon
2. (b) the distance from Dallas to Oklahoma City
3. (c) the speed of sound

4. (d) the density of air
5. (e) the temperature at which alcohol boils
6. (f) the area of the state of Delaware
7. (g) the volume of a flu shot or a measles vaccination

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

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

1. (a) 10^3
2. (b) 10^{-2}
3. (c) 0.1
4. (d) 10^{-3}
5. (e) 1,000,000
6. (f) 0.000001

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

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

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

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

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

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

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

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

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

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

Visit this PhET density simulation and select Mystery Blocks.

1. (a) Pick one of the Mystery Blocks and determine its mass, volume, density, and its likely identity.

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

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

1.5: Measurement Uncertainty, Accuracy, and Precision

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

1. (a) 711.0
2. (b) 0.239
3. (c) 90743
4. (d) 134.2
5. (e) 0.05499
6. (f) 10000.0
7. (g) 0.000000738592

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

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

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

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

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

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

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

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

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

1. (a) 38.7 g
2. (b) 2×10^{18} m
3. (c) 3,486,002 kg

4. (d) 9.74150×10^{-4} J
5. (e) 0.0613 cm^3
6. (f) 17.0 kg
7. (g) 0.01400 g/mL

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

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

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

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

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

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

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

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

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

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

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

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

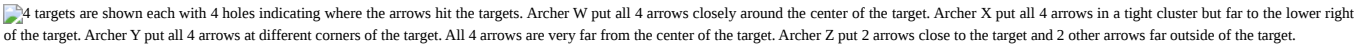
(a) 2.15×10^5; (b) 4.2×10^6; (c) 2.08; (d) 0.19; (e) 27,440; (f) 43.0

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

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

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

1. (a) Which archer is most precise?
2. (b) Which archer is most accurate?
3. (c) Who is both least precise and least accurate?


4 targets are shown each with 4 holes indicating where the arrows hit the targets. Archer W put all 4 arrows closely around the center of the target. Archer X put all 4 arrows in a tight cluster but far to the lower right of the target. Archer Y put all 4 arrows at different corners of the target. All 4 arrows are very far from the center of the target. Archer Z put 2 arrows close to the target and 2 other arrows far outside of the target.

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

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

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

1.6: Mathematical Treatment of Measurement Results

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

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

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

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

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

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

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

Only two significant figures are justified.

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

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

68–71 cm; 400–450 g

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

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

355 mL

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

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

8×10^{-4} cm

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

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

yes; weight = 89.4 kg

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

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

5.0×10^{-3} mL

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

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

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

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

Complete the following conversions between SI units.

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

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

45.4 L

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

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

1.0160×10^3 kg

Make the conversion indicated in each of the following:

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

Make the conversion indicated in each of the following:

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

1. (a) 394 ft
2.
3. (b) 5.9634 km
4.
5. (c) 6.0×10^2
6.
7. (d) 2.64 L
8.
9. (e) 5.1×10^{18} kg
10.
11. (f) 14.5 kg
12.
13. (g) 324 mg

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

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

0.46 m; 1.5 ft/cubit

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

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

Yes, the acid's volume is 123 mL.

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

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

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

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

Solve these problems about lumber dimensions.

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

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

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

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

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

2.70 g/cm^3

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

Calculate these masses.

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

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

(a) 81.6 g; (b) 17.6 g

Calculate these masses.

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

Calculate these volumes.

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

(a) 5.1 mL; (b) 37 L

Calculate these volumes.

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

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

5371 °F, 3239 K

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

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

−23 °C, 250 K

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

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

−33.4 °C, 239.8 K

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

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

113 °F

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 (Exercises) is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

CHAPTER OVERVIEW

2: Atoms, Molecules, and Ions

A general chemistry Libretexts Textmap organized around the textbook
General Chemistry -Atoms First
By OpenStax

I II III IV V VI VII VIII IX X XI XII XIII XIV XV XVI XVII XVIII XIX XX XXI ● **Homework**

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: Early Ideas in Atomic Theory
2.2: Evolution of Atomic Theory
2.3: Atomic Structure and Symbolism
2.4: Chemical Formulas
2.5: Formula Mass and the Mole Concept
2.6: Determining Empirical and Molecular Formulas
2.7: Chemical Nomenclature

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 OpenStax.

2.1: Early Ideas in Atomic Theory

Skills to Develop

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

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

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

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

Atomic Theory through the Nineteenth Century

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

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

Here are the postulates of Dalton's atomic theory.

1. Matter is composed of exceedingly small particles called atoms. An atom is the smallest unit of an element that can participate in a chemical change.
2. An element consists of only one type of atom, which has a mass that is characteristic of the element and is the same for all atoms of that element (Figure **2.1.1**). A macroscopic sample of an element contains an incredibly large number of atoms, all of which have identical chemical properties.

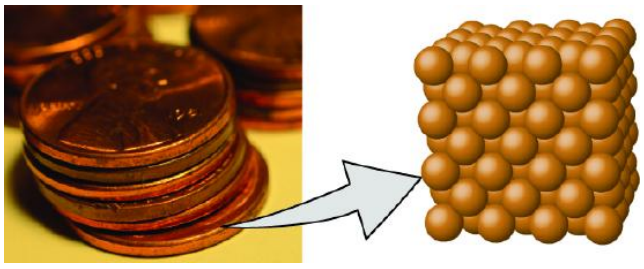


Figure **2.1.1**: A pre-1982 copper penny (left) contains approximately 3×10^{22} copper atoms (several dozen are represented as brown spheres at the right), each of which has the same chemical properties. (credit: modification of work by "slgckgc"/Flickr)

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 **2.1.2**).

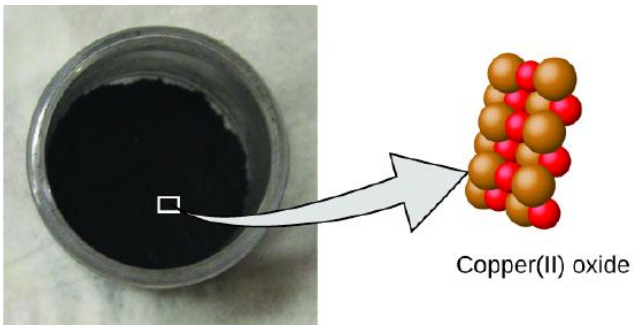


Figure **2.1.2**: Copper(II) oxide, a powdery, black compound, results from the combination of two types of atoms—copper (brown spheres) and oxygen (red spheres)—in a 1:1 ratio. (credit: modification of work by "Chemicalinterest"/Wikimedia Commons)

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* **2.1.3***).*

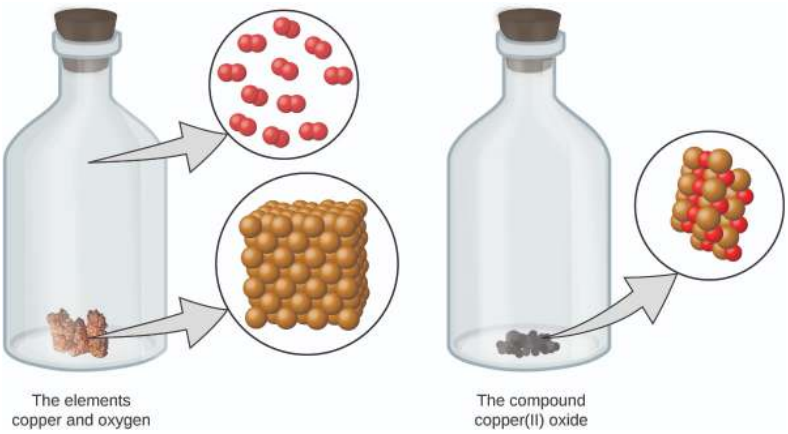
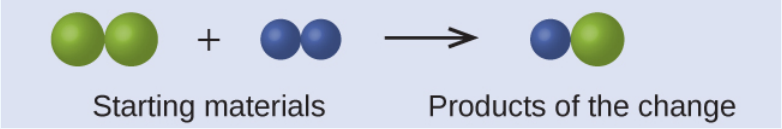


Figure **2.1.3**: When the elements copper (a shiny, red-brown solid, shown here as brown spheres) and oxygen (a clear and colorless gas, shown here as red spheres) react, their atoms rearrange to form a compound containing copper and oxygen (a powdery, black solid). (credit copper: modification of work by 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

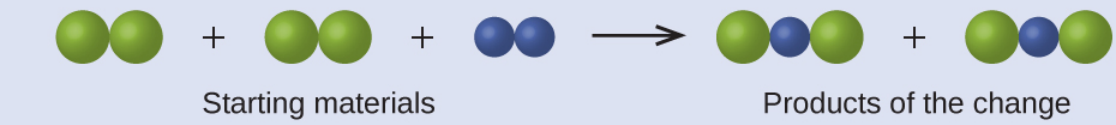
In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres touch, they are part of a single unit of a compound. Does the following chemical change represented by these symbols violate any of the ideas of Dalton's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

Dalton knew of the experiments of French chemist Joseph Proust, who demonstrated that *all samples of a pure compound contain the same elements in the same proportion by mass*. This statement is known as the law of definite proportions or the law of constant composition. The suggestion that the numbers of atoms of the elements in a given compound always exist in the same ratio is consistent with these observations. For example, when different samples of isooctane (a component of gasoline and one of the standards used in the octane rating system) are analyzed, they are found to have a carbon-to-hydrogen mass ratio of 5.33:1, as shown in Table **2.1.1**.

Table **2.1.1**: Constant Composition of Isooctane

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

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

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

$$\frac{\frac{1.116\ \text{g Cl}}{1\ \text{g Cu}}}{\frac{0.558\ \text{g Cl}}{1\ \text{g Cu}}} = \frac{2}{1} \tag{2.1.1}$$

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

This can be explained by atomic theory if the copper-to-chlorine ratio in the brown compound is 1 copper atom to 2 chlorine atoms, and the ratio in the green compound is 1 copper atom to 1 chlorine atom. The ratio of chlorine atoms (and thus the ratio of their masses) is therefore 2 to 1 (Figure **2.1.4**).

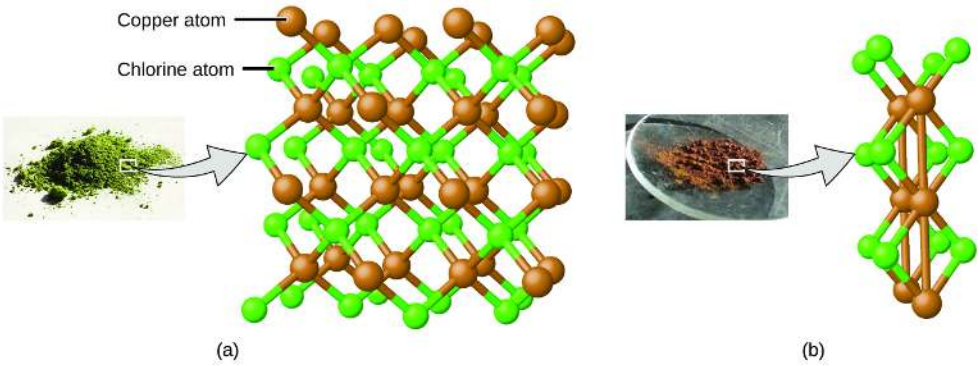


Figure 2.1.4: Compared to the copper chlorine compound in (a), where copper is represented by brown spheres and chlorine by green spheres, the copper chlorine compound in (b) has twice as many chlorine atoms per copper atom. (credit a: modification of work by “Benjah-bmm27”/Wikimedia Commons; credit b: modification of work by “Walkerma”/Wikimedia Commons)

Summary

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

Glossary

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

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

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

law of 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

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: Early Ideas in Atomic Theory is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

2.2: Evolution of Atomic Theory

Learning Objectives

- Outline milestones in the development of modern atomic theory
- Summarize and interpret the results of the experiments of Thomson, Millikan, and Rutherford
- Describe the three subatomic particles that compose atoms
- Define isotopes and give examples for several elements

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.

Atomic Theory after the Nineteenth Century

If matter were composed of atoms, what were atoms composed of? Were they the smallest particles, or was there something smaller? In the late 1800s, a number of scientists interested in questions like these investigated the electrical discharges that could be produced in low-pressure gases, with the most significant discovery made by English physicist J. J. Thomson using a cathode ray tube. This apparatus consisted of a sealed glass tube from which almost all the air had been removed; the tube contained two metal electrodes. When high voltage was applied across the electrodes, a visible beam called a cathode ray appeared between them. This beam was deflected toward the positive charge and away from the negative charge, and was produced in the same way with identical properties when different metals were used for the electrodes. In similar experiments, the ray was simultaneously deflected by an applied magnetic field, and measurements of the extent of deflection and the magnetic field strength allowed Thomson to calculate the charge-to-mass ratio of the cathode ray particles. The results of these measurements indicated that these particles were much lighter than atoms (Figure **2.2.1**).

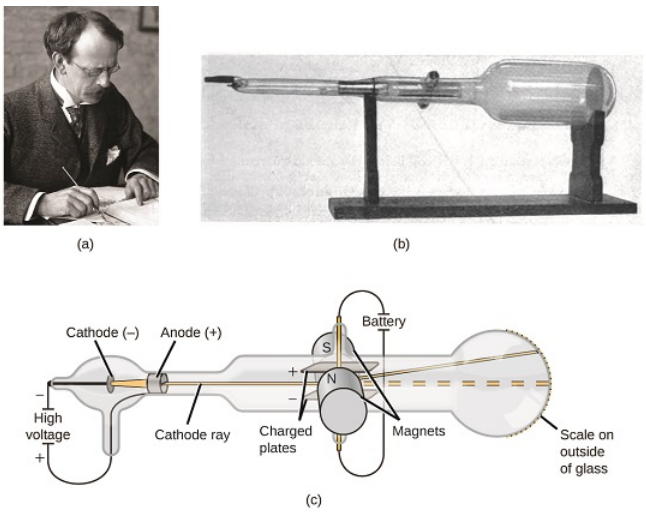
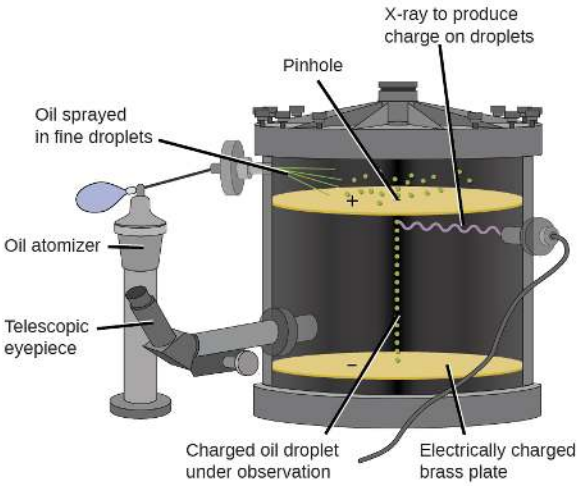


Figure **2.2.1**: (a) J. J. Thomson produced a visible beam in a cathode ray tube. (b) This is an early cathode ray tube, invented in 1897 by Ferdinand Braun. (c) In the cathode ray, the beam (shown in yellow) comes from the cathode and is accelerated past the anode toward a fluorescent scale at the end of the tube. Simultaneous deflections by applied electric and magnetic fields permitted Thomson to calculate the mass-to-charge ratio of the particles composing the cathode ray. (credit a: modification of work by Nobel Foundation; credit b: modification of work by Eugen Nesper; credit c: modification of work by "Kurzon"/Wikimedia Commons).

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

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

In 1909, more information about the electron was uncovered by American physicist Robert A. Millikan via his “oil drop” experiments. Millikan created microscopic oil droplets, which could be electrically charged by friction as they formed or by using X-rays. These droplets initially fell due to gravity, but their downward progress could be slowed or even reversed by an electric field lower in the apparatus. By adjusting the electric field strength and making careful measurements and appropriate calculations, Millikan was able to determine the charge on individual drops (Figure **2.2.2**).



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

Figure **2.2.2**: Millikan’s experiment measured the charge of individual oil drops. The tabulated data are examples of a few possible values.

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

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

Scientists had now established that the atom was not indivisible as Dalton had believed, and due to the work of Thomson, Millikan, and others, the charge and mass of the negative, subatomic particles—the electrons—were known. However, the positively charged part of an atom was not yet well understood. In 1904, Thomson proposed the “plum pudding” model of atoms, which described a positively charged mass with an equal amount of negative charge in the form of electrons embedded in it, since all atoms are electrically neutral. A competing model had been proposed in 1903 by Hantaro Nagaoka, who postulated a Saturn-like atom, consisting of a positively charged sphere surrounded by a halo of electrons (Figure **2.2.3**).

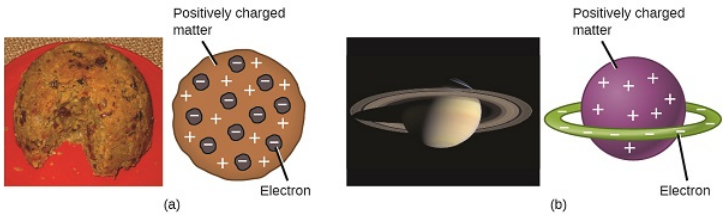


Figure **2.2.3**: (a) Thomson suggested that atoms resembled plum pudding, an English dessert consisting of moist cake with embedded raisins (“plums”). (b) Nagaoka proposed that atoms resembled the planet Saturn, with a ring of electrons surrounding a positive “planet.” (credit a: modification of work by “Man vyi”/Wikimedia Commons; credit b: modification of work by “NASA”/Wikimedia Commons).

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

What did they discover? Most particles passed right through the foil without being deflected at all. However, some were diverted slightly, and a very small number were deflected almost straight back toward the source (Figure **2.2.4**). Rutherford described finding these results: "It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you"[1] (p. 68).

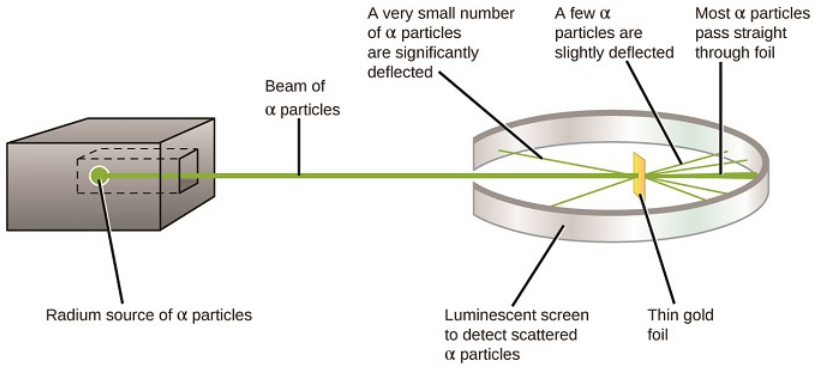


Figure **2.2.4**: Geiger and Rutherford fired α particles at a piece of gold foil and detected where those particles went, as shown in this schematic diagram of their experiment. Most of the particles passed straight through the foil, but a few were deflected slightly and a very small number were significantly deflected.

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

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

This analysis led Rutherford to propose a model in which an atom consists of a very small, positively charged nucleus, in which most of the mass of the atom is concentrated, surrounded by the negatively charged electrons, so that the atom is electrically neutral (Figure **2.2.5**).

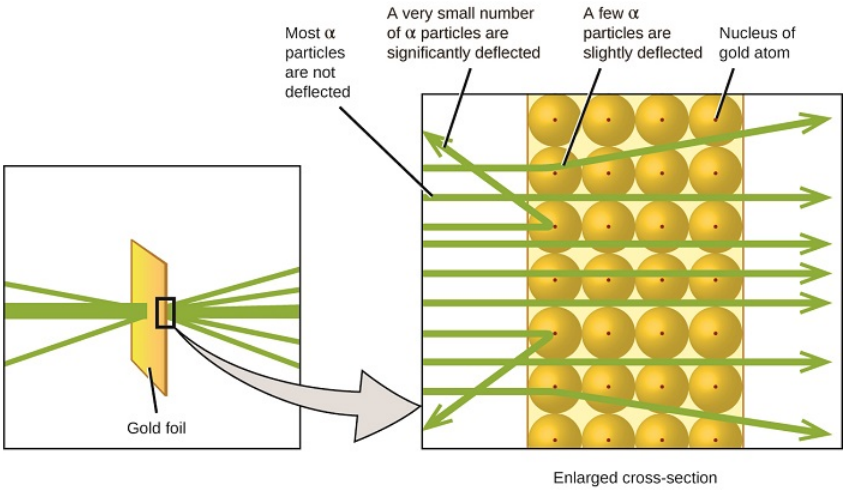


Figure **2.2.5**: The α particles are deflected only when they collide with or pass close to the much heavier, positively charged gold nucleus. Because the nucleus is very small compared to the size of an atom, very few α particles are deflected. Most pass through the relatively large region occupied by electrons, which are too light to deflect the rapidly moving particles.

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

Isotopes

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.

Contributors and Attributions

Summary

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

Footnotes

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

Glossary

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

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

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

neutron
uncharged, subatomic particle located in the nucleus

proton
positively charged, subatomic particle located in the nucleus

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

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: Evolution of Atomic Theory is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

2.3: Atomic Structure and Symbolism

Learning Objectives

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

The development of modern atomic theory revealed much about the inner structure of atoms. It was learned that an atom contains a very small nucleus composed of positively charged protons and uncharged neutrons, surrounded by a much larger volume of space containing negatively charged electrons. The nucleus contains the majority of an atom's mass because protons and neutrons are much heavier than electrons, whereas electrons occupy almost all of an atom's volume. The diameter of an atom is on the order of 10^{-10} m, whereas the diameter of the nucleus is roughly 10^{-15} m—about 100,000 times smaller. For a perspective about their relative sizes, consider this: If the nucleus were the size of a blueberry, the atom would be about the size of a football stadium (Figure **2.3.1**).



Figure **2.3.1**: If an atom could be expanded to the size of a football stadium, the nucleus would be the size of a single blueberry. (credit middle: modification of work by "babyknight"/Wikimedia Commons; credit right: modification of work by Paxson Woelber).

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

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

A proton has a mass of 1.0073 amu and a charge of 1+. A neutron is a slightly heavier particle with a mass 1.0087 amu and a charge of zero; as its name suggests, it is neutral. The electron has a charge of 1− and is a much lighter particle with a mass of about 0.00055 amu (it would take about 1800 electrons to equal the mass of one proton. The properties of these fundamental particles are summarized in Table **2.3.1**. (An observant student might notice that the sum of an atom's subatomic particles does not equal the atom's actual mass: The total mass of six protons, six neutrons, and six electrons is 12.0993 amu, slightly larger than the 12.00 amu of an actual carbon-12 atom. This "missing" mass is known as the mass defect, and you will learn about it in the chapter on nuclear chemistry.)

Table **2.3.1**: Properties of Subatomic Particles

Name	Location	Charge (C)	Unit Charge	Mass (amu)	Mass (g)
electron	outside nucleus	-1.602×10^{-19}	1−	0.00055	0.00091×10^{-24}
proton	nucleus	1.602×10^{-19}	1+	1.00727	1.67262×10^{-24}
neutron	nucleus	0	0	1.00866	1.67493×10^{-24}

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

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

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

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

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

Example 2.3.1: 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 2.3.2).





(a) (b)

Figure **2.3.2**: (a) Insufficient iodine in the diet can cause an enlargement of the thyroid gland called a goiter. (b) The addition of small amounts of iodine to salt, which prevents the formation of goiters, has helped eliminate this concern in the US where salt consumption is high. (credit a: modification of work by "Almazi"/Wikimedia Commons; credit b: modification of work by Mike Mozart)

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

The addition of small amounts of iodine to table salt (iodized salt) has essentially eliminated this health concern in the United States, but as much as 40% of the world's population is still at risk of iodine deficiency. The iodine atoms are added as anions, and each has a 1− charge and a mass number of 127. Determine the numbers of protons, neutrons, and electrons in one of these iodine anions.

Solution

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

? Exercise **2.3.1**

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+

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 **2.3.3**). 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 **2.3.3**: 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 **2.3.2**. 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 **2.3.2**: Some Common Elements and Their Symbols

Element	Symbol	Element	Symbol
aluminum	Al	iron	Fe (from *ferrum*)
bromine	Br	lead	Pb (from *plumbum*)
calcium	Ca	magnesium	Mg
carbon	C	mercury	Hg (from *hydrargyrum*)
chlorine	Cl	nitrogen	N
chromium	Cr	oxygen	O
cobalt	Co	potassium	K (from *kalium*)
copper	Cu (from *cuprum*)	silicon	Si
fluorine	F	silver	Ag (from *argentum*)
gold	Au (from *aurum*)	sodium	Na (from *natrium*)
helium	He	sulfur	S
hydrogen	H	tin	Sn (from *stannum*)
iodine	I	zinc	Zn

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

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 **2.3.4**). 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.

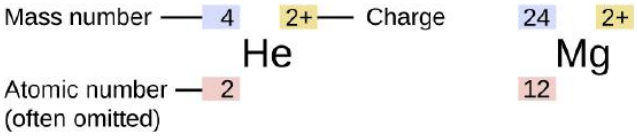


Figure **2.3.4**: The symbol for an atom indicates the element via its usual two-letter symbol, the mass number as a left superscript, the atomic number as a left subscript (sometimes omitted), and the charge as a right superscript.

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

Information about the naturally occurring isotopes of elements with atomic numbers 1 through 10 is given in Table **2.3.2**. 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 **2.3.2**: Nuclear Compositions of Atoms of the Very Light Elements

https://chem.libretexts.org/@go/page/216732

Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (amu)	% Natural Abundance
hydrogen	$^{1}_{1}\mathrm{H}$ (protium)	1	1	0	1.0078	99.989
	$^{2}_{1}\mathrm{H}$ (deuterium)	1	1	1	2.0141	0.0115
	$^{3}_{1}\mathrm{H}$ (tritium)	1	1	2	3.01605	— (trace)
helium	$^{3}_{2}\mathrm{He}$	2	2	1	3.01603	0.00013
	$^{4}_{2}\mathrm{He}$	2	2	2	4.0026	100
lithium	$^{6}_{3}\mathrm{Li}$	3	3	3	6.0151	7.59
	$^{7}_{3}\mathrm{Li}$	3	3	4	7.0160	92.41
beryllium	$^{9}_{4}\mathrm{Be}$	4	4	5	9.0122	100
boron	$^{10}_{5}\mathrm{B}$	5	5	5	10.0129	19.9
	$^{11}_{5}\mathrm{B}$	5	5	6	11.0093	80.1
carbon	$^{12}_{6}\mathrm{C}$	6	6	6	12.0000	98.89
	$^{13}_{6}\mathrm{C}$	6	6	7	13.0034	1.11
	$^{14}_{6}\mathrm{C}$	6	6	8	14.0032	— (trace)
nitrogen	$^{14}_{7}\mathrm{N}$	7	7	7	14.0031	99.63
	$^{15}_{7}\mathrm{N}$	7	7	8	15.0001	0.37
oxygen	$^{16}_{8}\mathrm{O}$	8	8	8	15.9949	99.757
	$^{17}_{8}\mathrm{O}$	8	8	9	16.9991	0.038
	$^{18}_{8}\mathrm{O}$	8	8	10	17.9992	0.205
fluorine	$^{19}_{9}\mathrm{F}$	9	9	10	18.9984	100
neon	$^{20}_{10}\mathrm{Ne}$	10	10	10	19.9924	90.48
	$^{21}_{10}\mathrm{Ne}$	10	10	11	20.9938	0.27
	$^{22}_{10}\mathrm{Ne}$	10	10	12	21.9914	9.25

Atomic Mass

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

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

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

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

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

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

✔ Example 2.3.2: Calculation of Average Atomic Mass

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

Solution

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

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

? Exercise 2.3.2

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

Answer

24.31 amu

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

✔ Example 2.3.3: Calculation of Percent Abundance

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

Solution

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

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

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

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

Substituting this into the average mass equation, we have:

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

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

? Exercise 2.3.3

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

Answer

69.15% Cu-63 and 30.85% Cu-65

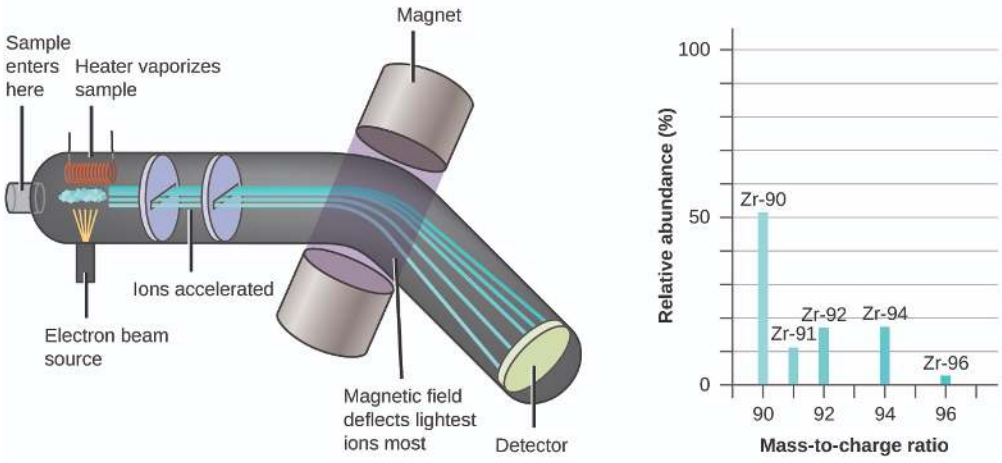


Figure **2.3.5**: Analysis of zirconium in a mass spectrometer produces a mass spectrum with peaks showing the different isotopes of Zr.

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

The occurrence and natural abundances of isotopes can be experimentally determined using an instrument called a mass spectrometer. Mass spectrometry (MS) is widely used in chemistry, forensics, medicine, environmental science, and many other fields to analyze and help identify the substances in a sample of material. In a typical mass spectrometer (Figure **2.3.5**), 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* 2.3.1**: *Watch this video from the Royal Society for Chemistry for a brief description of the rudiments of mass spectrometry.*

Summary

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

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

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

Key Equations

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

Glossary

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

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

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

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

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

chemical symbol

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

Dalton (Da)

alternative unit equivalent to the atomic mass unit

fundamental unit of charge

(also called the elementary charge) equals the magnitude of the charge of an electron (e) with $e = 1.602 \times 10^{-19}$ C

ion

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

mass number (A)

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

unified atomic mass unit (u)

alternative unit equivalent to the atomic mass unit

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

This page titled 2.3: Atomic Structure and Symbolism is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

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

2.4: Chemical Formulas

Learning Objectives

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

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

The structural formula for a compound gives the same information as its molecular formula (the types and numbers of atoms in the molecule) but also shows how the atoms are connected in the molecule. The structural formula for methane contains symbols for one C atom and four H atoms, indicating the number of atoms in the molecule (Figure **2.4.1**). The lines represent bonds that hold the atoms together. (A chemical bond is an attraction between atoms or ions that holds them together in a molecule or a crystal.) We will discuss chemical bonds and see how to predict the arrangement of atoms in a molecule later. For now, simply know that the lines are an indication of how the atoms are connected in a molecule. A ball-and-stick model shows the geometric arrangement of the atoms with atomic sizes not to scale, and a space-filling model shows the relative sizes of the atoms.

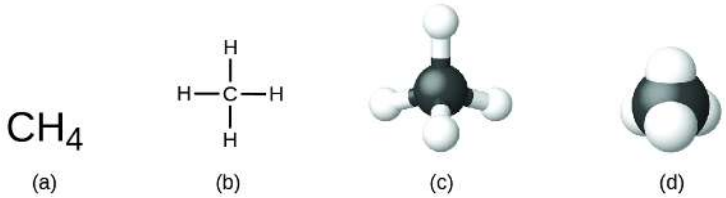


Figure **2.4.1**: A methane molecule can be represented as (a) a molecular formula, (b) a structural formula, (c) a ball-and-stick model, and (d) a space-filling model. Carbon and hydrogen atoms are represented by black and white spheres, respectively.

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

Although many elements consist of discrete, individual atoms, some exist as molecules made up of two or more atoms of the element chemically bonded together. For example, most samples of the elements hydrogen, oxygen, and nitrogen are composed of molecules that contain two atoms each (called diatomic molecules) and thus have the molecular formulas H_2, O_2, and N_2, respectively. Other elements commonly found as diatomic molecules are fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2). The most common form of the element sulfur is composed of molecules that consist of eight atoms of sulfur; its molecular formula is S_8 (Figure **2.4.2**).

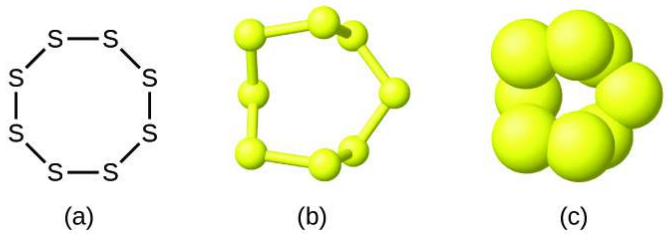


Figure **2.4.2**: A molecule of sulfur is composed of eight sulfur atoms and is therefore written as S_8. It can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. Sulfur atoms are represented by yellow spheres.

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

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

indicates two separate hydrogen atoms that are not combined as a unit. The expression $2H_2$ represents two molecules of diatomic hydrogen (Figure **2.4.3**).

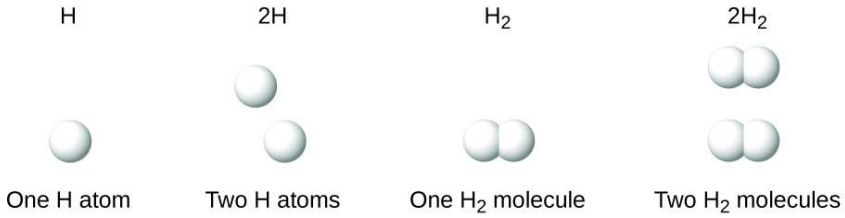


Figure **2.4.3**: The symbols H, 2H, H_2, and $2H_2$ represent very different entities.

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

Compounds are formed when two or more elements chemically combine, resulting in the formation of bonds. For example, hydrogen and oxygen can react to form water, and sodium and chlorine can react to form table salt. We sometimes describe the composition of these compounds with an empirical formula, which indicates the types of atoms present and *the simplest whole-number ratio of the number of atoms (or ions) in the compound*. For example, titanium dioxide (used as pigment in white paint and in the thick, white, blocking type of sunscreen) has an empirical formula of TiO_2. This identifies the elements titanium (Ti) and oxygen (O) as the constituents of titanium dioxide, and indicates the presence of twice as many atoms of the element oxygen as atoms of the element titanium (Figure **2.4.4**).

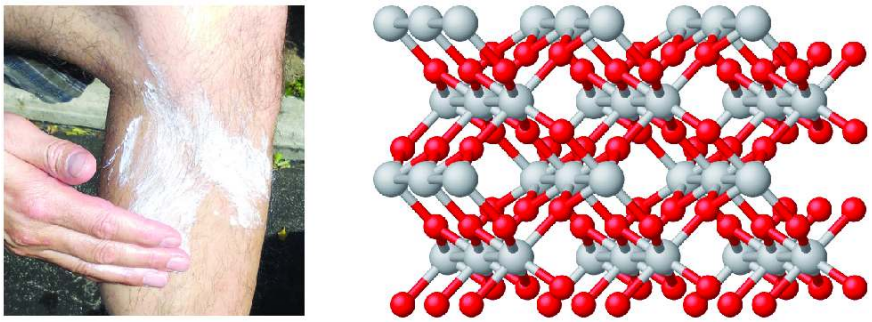


Figure **2.4.4**: (a) The white compound titanium dioxide provides effective protection from the sun. (b) A crystal of titanium dioxide, TiO_2, contains titanium and oxygen in a ratio of 1 to 2. The titanium atoms are gray and the oxygen atoms are red. (credit a: modification of work by “osseous”/Flickr).

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

As discussed previously, we can describe a compound with a molecular formula, in which the subscripts indicate the *actual numbers of atoms* of each element in a molecule of the compound. In many cases, the molecular formula of a substance is derived from experimental determination of both its empirical formula and its molecular mass (the sum of atomic masses for all atoms composing the molecule). For example, it can be determined experimentally that benzene contains two elements, carbon (C) and hydrogen (H), and that for every carbon atom in benzene, there is one hydrogen atom. Thus, the empirical formula is CH. An experimental determination of the molecular mass reveals that a molecule of benzene contains six carbon atoms and six hydrogen atoms, so the molecular formula for benzene is C_6H_6 (Figure **2.4.5**).

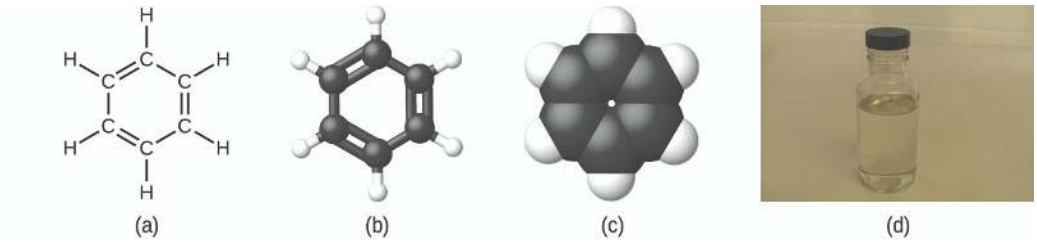


Figure **2.4.5**: Benzene, C_6H_6, is produced during oil refining and has many industrial uses. A benzene molecule can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. (d) Benzene is a clear liquid. (credit d: modification of work by Sahar Atwa).

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

If we know a compound's formula, we can easily determine the empirical formula. (This is somewhat of an academic exercise; the reverse chronology is generally followed in actual practice.) For example, the molecular formula for acetic acid, the component that gives vinegar its sharp taste, is $C_2H_4O_2$. This formula indicates that a molecule of acetic acid (Figure **2.4.6**) contains two carbon atoms, four hydrogen atoms, and two oxygen atoms. The ratio of atoms is 2:4:2. Dividing by the lowest common denominator (2) gives the simplest, whole-number ratio of atoms, 1:2:1, so the empirical formula is CH_2O. Note that a molecular formula is always a whole-number multiple of an empirical formula.

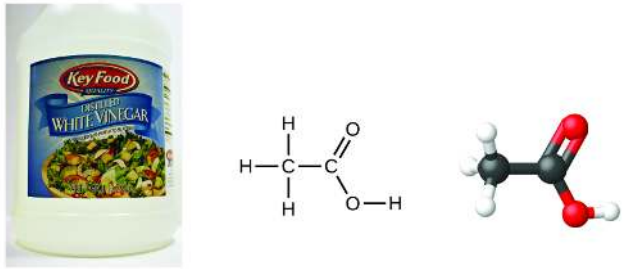


Figure **2.4.6**: (a) Vinegar contains acetic acid, $C_2H_4O_2$, which has an empirical formula of CH_2O. It can be represented as (b) a structural formula and (c) as a ball-and-stick model. (credit a: modification of work by "HomeSpot HQ"/Flickr)

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

✔ Example **2.4.1**: 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 **2.4.1**

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 **2.4.7**). 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.

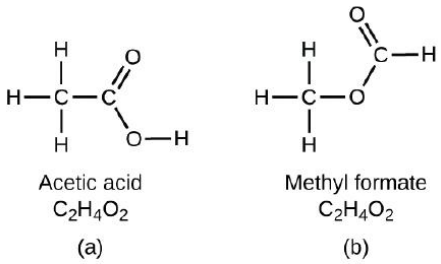


Figure **2.4.7**: Molecules of (a) acetic acid and methyl formate (b) are structural isomers; they have the same formula ($C_2H_4O_2$) but different structures (and therefore different chemical properties).

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

Many types of isomers exist (Figure **2.4.8**). 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.

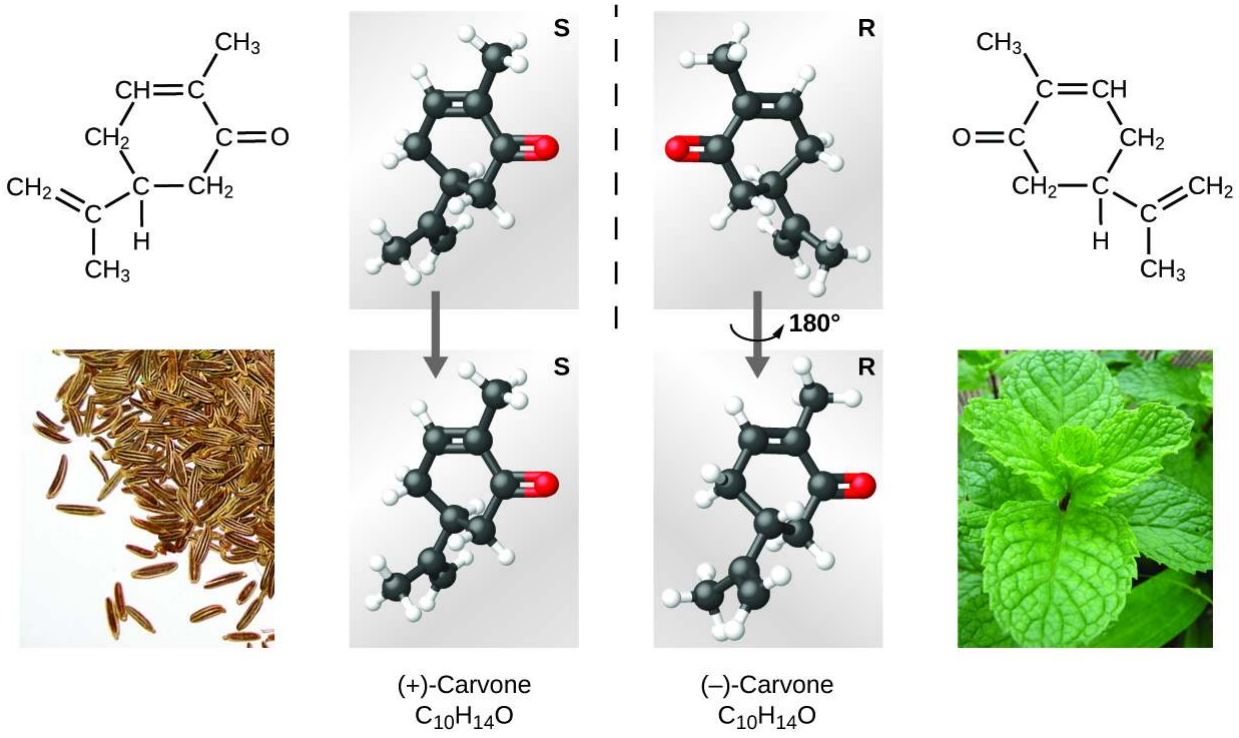


Figure **2.4.8**: Molecules of carvone are spatial isomers; they only differ in the relative orientations of the atoms in space. (credit bottom left: modification of work by "Miansari66"/Wikimedia Commons; credit bottom right: modification of work by Forest & Kim Starr)

Summary

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

Glossary

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

isomers
compounds with the same chemical formula but different structures

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

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

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

structural formula

shows the atoms in a molecule and how they are connected

This page titled 2.4: Chemical Formulas is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

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

2.5: 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.

Formula Mass

In an earlier chapter, we described the development of the 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.

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 **2.5.1** outlines the calculations used to derive the molecular mass of chloroform, which is 119.37 amu.

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

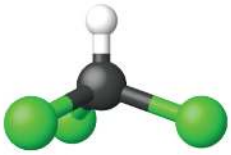


Figure **2.5.1**: The average mass of a chloroform molecule, $CHCl_3$, is 119.37 amu, which is the sum of the average atomic masses of each of its constituent atoms. The model shows the molecular structure of chloroform.

A table and diagram are shown. The table is made up of six columns and five rows. The header row reads: "Element," "Quantity," a blank space, "Average atomic mass (a m u)," a blank space, and "Subtotal (a m u)." The first column contains the symbols "C," "H," "C l" and a blank, merged cell that runs the width of the first five columns. The second column contains the numbers "1," "1," and "3" as well as the merged cell. The third column contains the multiplication symbol in each cell except for the last, merged cell. The fourth column contains the numbers "12.01," "1.008," and "35.45" as well as the merged cell. The fifth column contains the symbol "=" in each cell except for the last, merged cell. The sixth column contains the values "12.01," "1.008," "106.35," and "119.37." There is a thick black line below the number 106.35. The merged cell under the first five columns reads "Molecular mass." To the left of the table is a diagram of a molecule. Three green spheres are attached to a slightly smaller black sphere, which is also attached to a smaller white sphere. The green spheres lie beneath and to the sides of the black sphere while the white sphere is located straight up from the black sphere.

Likewise, the 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 amu (Figure **2.5.2**).

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	9	×	12.01	=	108.09
H	8	×	1.008	=	8.064
O	4	×	16.00	=	64.00
				Molecular mass	180.15

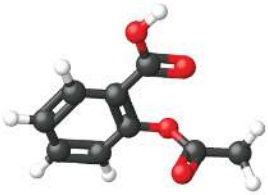


Figure **2.5.2**: The average mass of an aspirin molecule is 180.15 amu. The model shows the molecular structure of aspirin, $C_9H_8O_4$. A table and diagram are shown. The table is made up of six columns and five rows. The header row reads: “Element,” “Quantity,” a blank space, “Average atomic mass (a m u),” a blank space, and “Subtotal (a m u).” The first column contains the symbols “C,” “H,” “O,” and a merged cell. The merged cell runs the length of the first five columns. The second column contains the numbers “9,” “8,” and “4” as well as the merged, cell. The third column contains the multiplication symbol in each cell except for the last, merged cell. The fourth column contains the numbers “12.01,” “1.008,” and “16.00” as well as the merged cell. The fifth column contains the symbol “=” in each cell except for the last, merged cell. The sixth column contains the values: “108.09,” “8.064,” “64.00,” and “180.15.” There is a thick black line below the number 64.00. The merged cell under the first five columns reads “Molecular mass.” To the left of the table is a diagram of a molecule. Six black spheres are located in a six-sided ring and connected by alternating double and single black bonds. Attached to each of the four black spheres is one smaller white sphere. Attached to the farthest right black sphere is a red sphere, connected to two more black spheres, all in a row. Attached to the last black sphere of that row are two more white spheres. Attached to the first black sphere of that row is another red sphere. A black sphere, attached to two red spheres and a white sphere is attached to the black sphere on the top right of the six-sided ring.

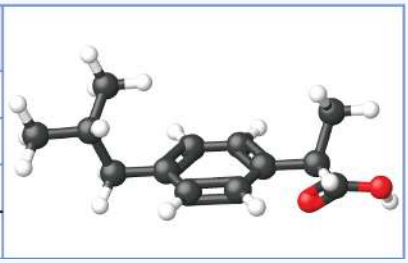
✔ Example 2.5.1: Computing Molecular Mass for a Covalent Compound

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 molecular mass (amu) 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:

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	13	×	12.01	=	156.13
H	18	×	1.008	=	18.114
O	2	×	16.00	=	32.00
				Molecular mass	206.27



? Exercise 2.5.1

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 molecular mass (amu) for this compound?

Answer

151.16 amu

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 formula mass for this compound is

computed as 58.44 amu (Figure **2.5.3**).

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

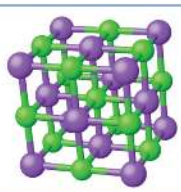


Figure **2.5.3**: Table salt, NaCl, contains an array of sodium and chloride ions combined in a 1:1 ratio. Its formula mass is 58.44 amu.
A table and diagram are shown. The table is made up of six columns and four rows. The header row reads: “Element,” “Quantity,” a blank space, “Average atomic mass (a m u),” a blank space and “Subtotal (a m u).” The first column contains the symbols “N a”, “C l,” and a merged cell. The merged cell runs the length of the first five columns. The second column contains the numbers “1” and “1” as well as the merged cell. The third column contains the multiplication symbol in each cell except for the last, merged cell. The fourth column contains the numbers “22.99” and “35.45” as well as the merged cell. The fifth column contains the symbol “=” in each cell except for the last, merged cell. The sixth column contains the values “22.99,” “35.45,” and “58.44.” There is a thick black line below the number “35.45.” The merged cell under the first five columns reads “Formula mass.” To the left of the table is a diagram of a chemical structure. The diagram shows green and purple spheres placed in an alternating pattern, making up the corners of eight stacked cubes to form one larger cube. The green spheres are slightly smaller than the purple spheres.

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. Even though a sodium cation has a slightly smaller mass than a sodium atom (since it is missing an electron), this difference will be offset by the fact that a chloride anion is slightly more massive than a chloride atom (due to the extra electron). Moreover, the mass of an electron is negligibly small with respect to the mass of a typical atom. Even when calculating the mass of an isolated ion, the missing or additional electrons can generally be ignored, since their contribution to the overall mass is negligible, reflected only in the nonsignificant digits that will be lost when the computed mass is properly rounded. The few exceptions to this guideline are very light ions derived from elements with precisely known atomic masses.

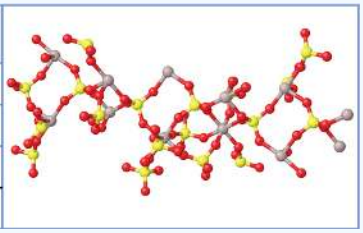
✔ Example 2.5.2: Computing Formula Mass for an Ionic Compound

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 formula mass (amu) of this compound?

Solution

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

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
Al	2	×	26.98	=	53.96
S	3	×	32.06	=	96.18
O	12	×	16.00	=	192.00
				Molecular mass	342.14



? Exercise 2.5.2

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

Answer

310.18 amu

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, $\mathbf{H_2O}$, and hydrogen peroxide, $\mathbf{H_2O_2}$, 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. 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 unit 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. A mole is defined as the amount of substance containing the same number of discrete entities (such as atoms, molecules, and ions) as the number of atoms in a sample of pure ^{12}C weighing exactly 12 g. 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 number of entities composing a mole has been experimentally determined to be $\mathbf{6.02214179 \times 10^{23}}$, 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 “per mole,” a conveniently rounded version being $\mathbf{6.022 \times 10^{23}/mol}$.

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 of an element (or compound) is the mass in grams of 1 mole of that substance, a property expressed in units of grams per mole (g/mol) (Figure **2.5.4**).

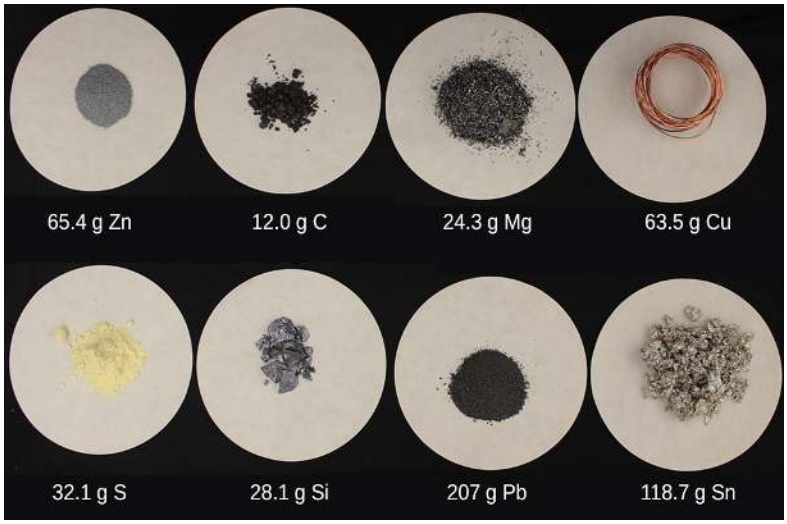
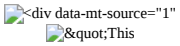


Figure **2.5.4**: Each sample contains $\mathbf{6.022 \times 10^{23}}$ atoms —1.00 mol of atoms. From left to right (top row): 65.4 g zinc, 12.0 g carbon, 24.3 g magnesium, and 63.5 g copper. From left to right (bottom row): 32.1 g sulfur, 28.1 g silicon, 207 g lead, and 118.7 g tin. (credit: modification of work by Mark Ott).

This figure contains eight different substances displayed on white circles. The amount of each substance is visibly different.

Because the definitions of both the mole and the atomic mass unit are based on the same reference substance, ^{12}C, the molar mass of any substance is numerically equivalent to its atomic or formula weight in amu. Per the amu definition, a single ^{12}C atom weighs 12 amu (its atomic mass is 12 amu). According to the definition of the mole, 12 g of ^{12}C contains 1 mole of ^{12}C atoms (its molar mass is 12 g/mol). This relationship holds for all elements, since their atomic masses are measured relative to that of the amu-reference substance, ^{12}C. Extending this principle, the molar mass of a compound in grams is likewise numerically equivalent to its formula mass in amu (Figure **2.5.5**).



" height="292" width="437" src="/@api/deki/files/56173/CNX_Chem_03_02_compound.jpg">

Figure **2.5.5**: Each sample contains $\mathbf{6.022 \times 10^{23}}$ 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 **2.5.1**: Mass of one mole of elements

Element	Average Atomic Mass (amu)	Molar Mass (g/mol)	Atoms/Mole
C	12.01	12.01	$\mathbf{6.022 \times 10^{23}}$
H	1.008	1.008	$\mathbf{6.022 \times 10^{23}}$
O	16.00	16.00	$\mathbf{6.022 \times 10^{23}}$
Na	22.99	22.99	$\mathbf{6.022 \times 10^{23}}$
Cl	33.45	35.45	$\mathbf{6.022 \times 10^{23}}$

While 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 (amu 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 **2.5.1**: The mole is used in chemistry to represent $\mathbf{6.022 \times 10^{23}}$ 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.

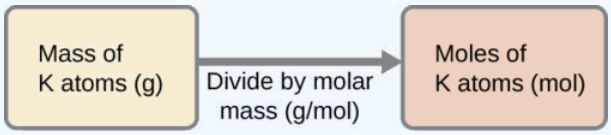
✔ Example **2.5.3**: Deriving Moles from Grams for an Element

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 amu, 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:"

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

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

? Exercise 2.5.3: 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

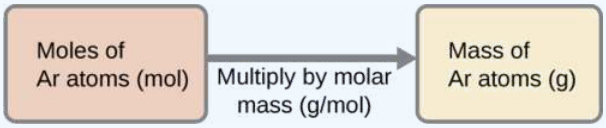
0.360 mol

✓ Example 2.5.4: 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):

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

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

? Exercise 2.5.4

What is the mass of 2.561 mol of gold?

Answer

504.4 g

Example 2.5.6: Deriving Number of Atoms from Mass for an Element

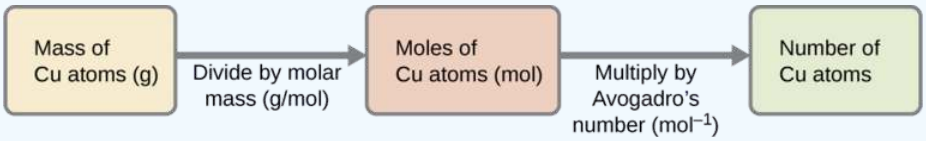
Copper is commonly used to fabricate electrical wire (Figure 2.5.6). How many copper atoms are in 5.00 g of copper wire?



Figure 2.5.6: 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:

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

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

Exercise 2.5.6

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

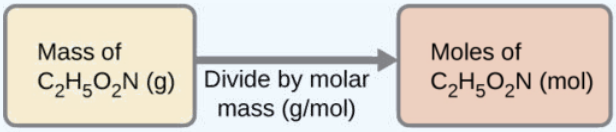
4.586×10^{22} *Au* atoms

Example 2.5.7: 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?

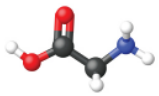
Solution

We can derive the number of moles of a compound from its mass following the same procedure we used for an element in Example 2.5.6:



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



A table is shown that is made up of six columns and six rows. The header row reads: “Element,” “Quantity (mol element / mol compound,” a blank space, “Molar mass (g / mol element),” a blank space, and “Subtotal (a m u).” The first column contains the symbols “C,” “H,” “O,” “N,” and a merged cell. The merged cell runs the width of the first five columns. The second column contains the numbers “2,” “5,” “2,” and “1” as well as the merged cell. The third column contains the multiplication symbol in each cell except for the last, merged cell. The fourth column contains the numbers “12.01,” “1.008,” “16.00,” and “14.007” as well as the merged cell. The fifth column contains the symbol “=” in each cell except for the last, merged cell. The sixth column contains the values “24.02,” “5.040,” “32.00,” “14.007,” and “75.07.” There is a thick black line under the number 14.007. The merged cell under the first five columns reads “Molar mass (g / mol compound). There is a ball-and-stick drawing to the right of this table. It shows a black sphere that forms a double bond with a slightly smaller red sphere, a single bond with another red sphere, and a single bond with another black sphere. The red sphere that forms a single bond with the black sphere also forms a single bond with a smaller, white sphere. The second black sphere forms a single bond with a smaller, white sphere and a smaller blue sphere. The blue sphere forms a single bond with two smaller, white spheres each.

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 2.5.7

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

Answer

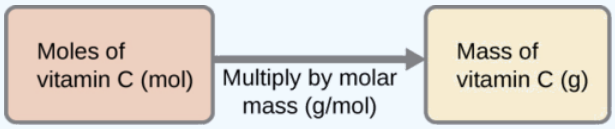
0.073 mol

✔ Example 2.5.8: 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 2.5.8

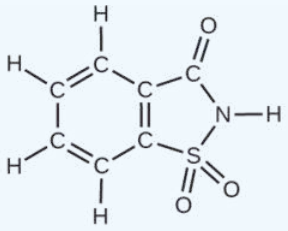
What is the mass of 0.443 mol of hydrazine, N_2H_4?

Answer

14.2 g

Example 2.5.9: Deriving the Number of Molecules from the Compound Mass

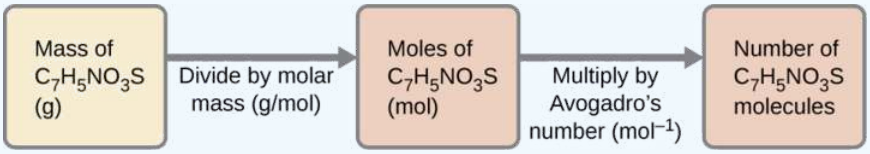
A packet of an artificial sweetener contains 40.0 mg of saccharin ($C_7H_5NO_3S$), which has the structural formula:



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 2.5.8, and then multiplying by Avogadro's number:



Using the provided mass and molar mass for saccharin yields:

$$0.0400\ \cancel{g}\ C_7H_5NO_3S \left(\frac{\cancel{mol}\ C_7H_5NO_3S}{183.18\ \cancel{g}\ C_7H_5NO_3S}\right)\left(\frac{6.022 \times 10^{23}\ C_7H_5NO_3S\ \text{molecules}}{1\ \cancel{mol}\ C_7H_5NO_3S}\right)$$
$$= 1.31 \times 10^{20}\ C_7H_5NO_3S\ \text{molecules}$$

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

$$1.31 \times 10^{20}\ C_7H_5NO_3S\ \text{molecules}\left(\frac{7\ \text{C atoms}}{1\ C_7H_5NO_3S\ \text{molecule}}\right) = 9.20 \times 10^{21}\ \text{C atoms}$$

Exercise 2.5.9

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

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 molecular 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 (amu) and molar mass (g/mol) for any substance are numerically equivalent (for example, one H_2O molecule weighs approximately18 amu and 1 mole of H_2O molecules weighs approximately 18 g).

Footnotes

1. 1 Omiatek, Donna M., Amanda J. Bressler, Ann-Sofie Cans, Anne M. Andrews, Michael L. Heien, and Andrew G. Ewing. "The Real Catecholamine Content of Secretory Vesicles in the CNS Revealed by Electrochemical Cytometry." *Scientific Report* 3 (2013): 1447, accessed January 14, 2015, doi:10.1038/srep01447.

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

This page titled 2.5: Formula Mass and the Mole Concept is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

- **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.

2.6: 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.

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:

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

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

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:

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

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

Example 2.6.1: 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 2.6.1

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

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 formula mass and the atomic masses of its constituent elements. A molecule of NH_3 contains one N atom weighing 14.01 amu and three H atoms weighing a total of (3 × 1.008 amu) = 3.024 amu. The formula mass of ammonia is therefore (14.01 amu + 3.024 amu) = 17.03 amu, and its percent composition is:

$$\%\mathrm{N} = \frac{14.01\ \text{amu N}}{17.03\ \text{amu NH}_3} \times 100\% = 82.27\%$$

$$\%\mathrm{H} = \frac{3.024\ \text{amu N}}{17.03\ \text{amu NH}_3} \times 100\% = 17.76\%$$

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 **2.6.2**. 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 2.6.2: 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:

$$\%\mathrm{C} = \frac{9\ \text{mol C} \times \text{molar mass C}}{\text{molar mass } C_9H_{18}O_4} \times 100$$

$$= \frac{9 \times 12.01\ \text{g/mol}}{180.159\ \text{g/mol}} \times 100 = \frac{108.09\ \text{g/mol}}{180.159\ \text{g/mol}} \times 100$$

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

$$\%\mathrm{H} = \frac{8\ \text{mol H} \times \text{molar mass H}}{\text{molar mass } C_9H_{18}O_4} \times 100$$

$$= \frac{8 \times 1.008\ \text{g/mol}}{180.159\ \text{g/mol}} \times 100 = \frac{8.064\ \text{g/mol}}{180.159\ \text{g/mol}} \times 100$$

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

$$\%\mathrm{O} = \frac{4\ \text{mol O} \times \text{molar mass O}}{\text{molar mass } C_9H_{18}O_4} \times 100$$

$$= \frac{4 \times 16.00\ \text{g/mol}}{180.159\ \text{g/mol}} \times 100 = \frac{64.00\ \text{g/mol}}{180.159\ \text{g/mol}} \times 100$$

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

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

? Exercise 2.6.2

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

Answer

69.9% Fe

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:

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

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

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:

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

(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:

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

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

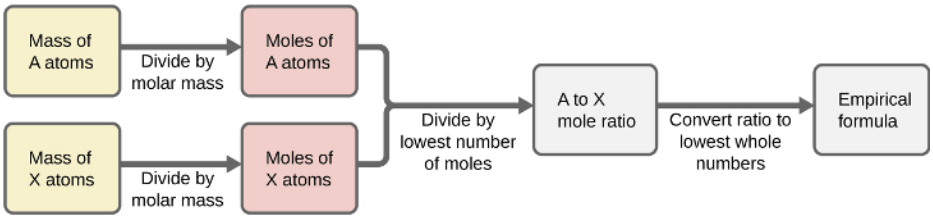


Figure **2.6.1**: The empirical formula of a compound can be derived from the masses of all elements in the sample.

A flow chart is shown that is composed of six boxes, two of which are connected together by a right facing arrow and located above two more that are also connected by a right-facing arrow. These two rows of boxes are connected vertically by a line that leads to a right-facing arrow and the last two boxes, connected by a final right facing arrow. The first two upper boxes have the phrases, “Mass of A atoms” and “Moles of A atoms” respectively, while the arrow that connects them has the phrase, “Divide by molar mass,” written below it. The second two bottom boxes have the phrases, “Mass of X atoms” and “Moles of X atoms” respectively, while the arrow that connects them has the phrase, “Divide by molar mass” written below it. The arrow that connects the upper and lower boxes to the last two boxes has the phrase “Divide by lowest number of moles” written below it. The last two boxes have the phrases, “A to X mole ratio” and “Empirical formula” respectively, while the arrow that connects them has the phrase, “Convert ratio to lowest whole numbers” written below it.

Example **2.6.3**: Determining an Empirical Formula from Masses of Elements

A sample of the black mineral hematite (Figure **2.6.2**), 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 **2.6.2**: 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 $\boldsymbol{Fe_2O_3}$.

? Exercise 2.6.3

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

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 2.6.4: 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 2.6.3). What is the empirical formula for this gas?



Figure 2.6.3: An oxide of carbon is removed from these fermentation tanks through the large copper pipes at the top. (credit: "Dual Freq"/Wikimedia Commons)

A picture is shown of four copper-colored industrial containers with a large pipe connecting to the top of each one.

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:

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

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

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

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

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

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

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

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

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

? Exercise 2.6.4

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. Molecular 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 molecular (or 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*:

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

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:

Double subscripts: use braces to clarify

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

$$\frac{180\ \text{amu/molecule}}{30\ \frac{\text{amu}}{\text{formula unit}}} = 6\ \text{formula units/molecule}$$

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

$$(CH_2O)_6 = C_6H_{12}O_6$$

Note that this same approach may be used when the molar mass (g/mol) instead of the molecular mass (amu) 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 2.6.5: 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:

$$(74.02\ \text{g C})\left(\frac{1\ \text{mol C}}{12.01\ \text{g C}}\right) = 6.163\ \text{mol C} \tag{2.6.1}$$

$$(8.710\ \text{g H})\left(\frac{1\ \text{mol H}}{1.01\ \text{g H}}\right) = 8.624\ \text{mol H} \tag{2.6.2}$$

$$(17.27\ \text{g N})\left(\frac{1\ \text{mol N}}{14.01\ \text{g N}}\right) = 1.233\ \text{mol N} \tag{2.6.3}$$

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 amu/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:

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

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 2.6.5

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 a molecular mass of 194.2 amu?

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

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

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

This page titled 2.6: Determining Empirical and Molecular Formulas is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

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

2.7: Chemical Nomenclature

Learning Objectives

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

Nomenclature, a collection of rules for naming things, is important in science and in many other situations. This module describes an approach that is used to name simple ionic and molecular compounds, such as NaCl, $CaCO_3$, and N_2O_4. The simplest of these are binary compounds, those containing only two elements, but we will also consider how to name ionic compounds containing polyatomic ions, and one specific, very important class of compounds known as acids (subsequent chapters in this text will focus on these compounds in great detail). We will limit our attention here to inorganic compounds, compounds that are composed principally of elements other than carbon, and will follow the nomenclature guidelines proposed by IUPAC. The rules for organic compounds, in which carbon is the principle element, will be treated in a later chapter on organic chemistry.

Ionic Compounds

To name an inorganic compound, we need to consider the answers to several questions. First, is the compound ionic or molecular? If the compound is ionic, does the metal form ions of only one type (fixed charge) or more than one type (variable charge)? Are the ions monatomic or polyatomic? If the compound is molecular, does it contain hydrogen? If so, does it also contain oxygen? From the answers we derive, we place the compound in an appropriate category and then name it accordingly. We will begin with the nomenclature rules for ionic compounds.

Compounds Containing Only Monatomic Ions

The name of a binary compound containing monatomic ions consists of the name of the cation (the name of the metal) followed by the name of the anion (the name of the nonmetallic element with its ending replaced by the suffix –*ide*). Some examples are given in Table **2.7.2**.

Table **2.7.1**: Names of Some Ionic Compounds

NaCl, sodium chloride	Na_2O, sodium oxide
KBr, potassium bromide	CdS, cadmium sulfide
CaI_2, calcium iodide	Mg_3N_2, magnesium nitride
CsF, cesium fluoride	Ca_3P_2, calcium phosphide
LiCl, lithium chloride	Al_4C_3, aluminum carbide

Compounds Containing Polyatomic Ions

Compounds containing polyatomic ions are named similarly to those containing only monatomic ions, except there is no need to change to an –*ide* ending, since the suffix is already present in the name of the anion. Examples are shown in Table **2.7.2**.

CL, ammonium chloride, C a S O subscript 4 calcium sulfate, and M g subscript 3 (P O subscript 4) subscript 2 magnesium phosphate." data-quail-id="54" data-mt-width="1246">

Table **2.7.2**: Names of Some Polyatomic Ionic Compounds

$KC_2H_3O_2$, potassium acetate	$(NH_4)Cl$, ammonium chloride
$NaHCO_3$, sodium bicarbonate	$CaSO_4$, calcium sulfate
$Al_2(CO_3)_3$, aluminum carbonate	$Mg_3(PO_4)_2$, magnesium phosphate

Ionic Compounds in Your Cabinets

Every day you encounter and use a large number of ionic compounds. Some of these compounds, where they are found, and what they are used for are listed in Table **2.7.3**. 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 **2.7.3**: Everyday Ionic Compounds

Ionic Compound	Name	Use
NaCl	sodium chloride	ordinary table salt
KI	potassium iodide	added to “iodized” salt for thyroid health
NaF	sodium fluoride	ingredient in toothpaste
$NaHCO_3$	sodium bicarbonate	baking soda; used in cooking (and in antacids)
Na_2CO_3	sodium carbonate	washing soda; used in cleaning agents
NaOCl	sodium hypochlorite	active ingredient in household bleach
$CaCO_3$	calcium carbonate	ingredient in antacids
$Mg(OH)_2$	magnesium hydroxide	ingredient in antacids
$Al(OH)_3$	aluminum hydroxide	ingredient in antacids
NaOH	sodium hydroxide	lye; used as drain cleaner
K_3PO_4	potassium phosphate	food additive (many purposes)
$MgSO_4$	magnesium sulfate	added to purified water
Na_2HPO_4	sodium hydrogen phosphate	anti-caking agent; used in powdered products
Na_2SO_3	sodium sulfite	preservative

Compounds Containing a Metal Ion with a Variable Charge

Most of the transition metals can form two or more cations with different charges. Compounds of these metals with nonmetals are named with the same method as compounds in the first category, except the charge of the metal ion is specified by a Roman numeral in parentheses after the name of the metal. The charge of the metal ion is determined from the formula of the compound and the charge of the anion. For example, consider binary ionic compounds of iron and chlorine. Iron typically exhibits a charge of either 2+ or 3+, and the two corresponding compound formulas are $FeCl_2$ and $FeCl_3$. The simplest name, “iron chloride,” will, in this case, be ambiguous, as it does not distinguish between these two compounds. In cases like this, the charge of the metal ion is included as a Roman numeral in parentheses immediately following the metal name. These two compounds are then unambiguously named iron(II) chloride and iron(III) chloride, respectively. Other examples are provided in Table **2.7.4**.

Table **2.7.4**: Names of Some Transition Metal Ionic Compounds

Transition Metal Ionic Compound	Name
$FeCl_3$	iron(III) chloride
Hg_2O	mercury(I) oxide
HgO	mercury(II) oxide
$Cu_3(PO_4)_2$	copper(II) phosphate

Out-of-date nomenclature used the suffixes *–ic* and *–ous* to designate metals with higher and lower charges, respectively: Iron(III) chloride, $FeCl_3$, was previously called ferric chloride, and iron(II) chloride, $FeCl_2$, was known as ferrous chloride. Though this naming convention has been largely abandoned by the scientific community, it remains in use by some segments of industry. For example, you may see the words *stannous fluoride* on a tube of toothpaste. This represents the formula SnF_2, which is more properly named tin(II) fluoride. The other fluoride of tin is SnF_4, which was previously called stannic fluoride but is now named tin(IV) fluoride.

Example 2.7.1: 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 2.7.1

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

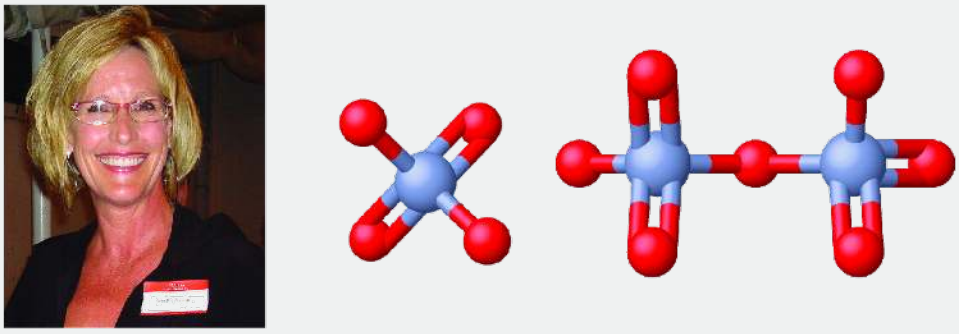
Cu_2O

Answer e

CrF_6

Erin Brokovich and Chromium Contamination

In the early 1990s, legal file clerk Erin Brockovich (Figure **2.7.2**) 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 **2.7.2**: (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.

Molecular (Covalent) Compounds

The bonding characteristics of inorganic molecular compounds are different from ionic compounds, and they are named using a different system as well. The charges of cations and anions dictate their ratios in ionic compounds, so specifying the names of the ions provides sufficient information to determine chemical formulas. However, because covalent bonding allows for significant variation in the combination ratios of the atoms in a molecule, the names for molecular compounds must explicitly identify these ratios.

Compounds Composed of Two Elements

When two nonmetallic elements form a molecular compound, several combination ratios are often possible. For example, carbon and oxygen can form the compounds CO and CO_2. Since these are different substances with different properties, they cannot both have the same name (they cannot both be called carbon oxide). To deal with this situation, we use a naming method that is somewhat similar to that used for ionic compounds, but with added prefixes to specify the numbers of atoms of each element. The name of the more metallic element (the one farther to the left and/or bottom of the periodic table) is first, followed by the name of the more nonmetallic element (the one farther to the right and/or top) with its ending changed to the suffix *–ide*. The numbers of atoms of each element are designated by the Greek prefixes shown in Table **2.7.5**.

Table **2.7.5**: 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 **2.7.6**.

Table **2.7.6**: Names of Some Molecular Compounds Composed of Two Elements

Compound	Name		Compound	Name
SO_2	sulfur dioxide		BCl_3	boron trichloride
SO_3	sulfur trioxide		SF_6	sulfur hexafluoride
NO_2	nitrogen dioxide		PF_5	phosphorus pentafluoride
N_2O_4	dinitrogen tetroxide		P_4O_{10}	tetraphosphorus decaoxide
N_2O_5	dinitrogen pentoxide		IF_7	iodine heptafluoride

There are a few common names that you will encounter as you continue your study of chemistry. For example, although NO is often called nitric oxide, its proper name is nitrogen monoxide. Similarly, N_2O is known as nitrous oxide even though our rules would specify the name dinitrogen monoxide. (And H_2O is usually called water, not dihydrogen monoxide.) You should commit to memory the common names of compounds as you encounter them.

✔ Example 2.7.2: 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 2.7.2

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

Binary Acids

Some compounds containing hydrogen are members of an important class of substances known as acids. The chemistry of these compounds is explored in more detail in later chapters of this text, but for now, it will suffice to note that many acids release hydrogen ions, H^+, when dissolved in water. To denote this distinct chemical property, a mixture of water with an acid is given a name derived from the compound's name. If the compound is a binary acid (comprised of hydrogen and one other nonmetallic element):

1. The word "hydrogen" is changed to the prefix *hydro-*
2. The other nonmetallic element name is modified by adding the suffix *-ic*
3. The word "acid" is added as a second word

For example, when the gas **HCl** (hydrogen chloride) is dissolved in water, the solution is called *hydrochloric acid*. Several other examples of this nomenclature are shown in Table **2.7.7**.

Table **2.7.7**: Names of Some Simple Acids

Name of Gas	Name of Acid
HF(*g*), hydrogen fluoride	HF(*aq*), hydrofluoric acid
HCl(*g*), hydrogen chloride	HCl(*aq*), hydrochloric acid
HBr(*g*), hydrogen bromide	HBr(*aq*), hydrobromic acid
HI(*g*), hydrogen iodide	HI(*aq*), hydroiodic acid
H_2S(*g*), hydrogen sulfide	H_2S(*aq*), hydrosulfuric acid

Oxyacids

Many compounds containing three or more elements (such as organic compounds or coordination compounds) are subject to specialized nomenclature rules that you will learn later. However, we will briefly discuss the important compounds known as oxyacids, compounds that contain hydrogen, oxygen, and at least one other element, and are bonded in such a way as to impart acidic properties to the compound (you will learn the details of this in a later chapter). Typical oxyacids consist of hydrogen combined with a polyatomic, oxygen-containing ion. To name oxyacids:

1. Omit "hydrogen"
2. Start with the root name of the anion
3. Replace *–ate* with *–ic*, or *–ite* with *–ous*
4. Add "acid"

For example, consider H_2CO_3 (which you might be tempted to call “hydrogen carbonate”). To name this correctly, “hydrogen” is omitted; the *–ate* of carbonate is replace with *–ic*; and acid is added—so its name is carbonic acid. Other examples are given in Table **2.7.8**. There are some exceptions to the general naming method (e.g., H_2SO_4 is called sulfuric acid, not sulfic acid, and H_2SO_3 is sulfurous, not sulfous, acid).

Table **2.7.8**: Names of Common Oxyacids

Formula	Anion Name	Acid Name
$HC_2H_3O_2$	acetate	acetic acid
HNO_3	nitrate	nitric acid
HNO_2	nitrite	nitrous acid
$HClO_4$	perchlorate	perchloric acid
H_2CO_3	carbonate	carbonic acid
H_2SO_4	sulfate	sulfuric acid
H_2SO_3	sulfite	sulfurous acid
H_3PO_4	phosphate	phosphoric acid

Summary

Chemists use nomenclature rules to clearly name compounds. Ionic and molecular compounds are named using somewhat-different methods. Binary ionic compounds typically consist of a metal and a nonmetal. The name of the metal is written first, followed by the name of the nonmetal with its ending changed to *–ide*. For example, K_2O is called potassium oxide. If the metal can form ions with different charges, a Roman numeral in parentheses follows the name of the metal to specify its charge. Thus, $FeCl_2$ is iron(II) chloride and $FeCl_3$ is iron(III) chloride. Some compounds contain polyatomic ions; the names of common polyatomic ions should be memorized. Molecular compounds can form compounds with different ratios of their elements, so prefixes are used to specify the numbers of atoms of each element in a molecule of the compound. Examples include SF_6, sulfur hexafluoride, and N_2O_4, dinitrogen tetroxide. Acids are an important class of compounds containing hydrogen and having special nomenclature rules. Binary acids are named using the prefix *hydro-*, changing the *–ide* suffix to *–ic*, and adding “acid;” HCl is hydrochloric acid. Oxyacids are named by changing the ending of the anion (*-ate* to *–ic*, and *-ite* to *-ous*) and adding “acid;” H_2CO_3 is carbonic acid.

Glossary

binary acid
: compound that contains hydrogen and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H^+ ions when dissolved in water)

binary compound
: compound containing two different elements.

oxyacid
: compound that contains hydrogen, oxygen, and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H^+ ions when dissolved in water)

nomenclature
: system of rules for naming objects of interest

This page titled 2.7: Chemical Nomenclature is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

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

https://chem.libretexts.org/@go/page/216734

CHAPTER OVERVIEW

3: 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.

3.1: Electromagnetic Energy

3.2: The Bohr Model

3.3: Electronic Structure of Atoms (Electron Configurations)

3.4: The Periodic Table

3.5: Periodic Variations in Element Properties

3.6: Molecular and Ionic Compounds

3.E: Electronic Structure and Periodic Properties (Exercises)

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: Electronic Structure and Periodic Properties is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

3.1: Electromagnetic Energy

Learning Objectives

- Describe the wave nature of light
- Distinguish between line and continuous emission spectra

The nature of light has been a subject of inquiry since antiquity. In the seventeenth century, Isaac Newton performed experiments with lenses and prisms and was able to demonstrate that white light consists of the individual colors of the rainbow combined together. Newton explained his optics findings in terms of a "corpuscular" view of light, in which light was composed of streams of extremely tiny particles travelling at high speeds according to Newton's laws of motion. Others in the seventeenth century, such as Christiaan Huygens, had shown that optical phenomena such as reflection and refraction could be equally well explained in terms of light as waves travelling at high speed through a medium called "luminiferous aether" that was thought to permeate all space. Early in the nineteenth century, Thomas Young demonstrated that light passing through narrow, closely spaced slits produced interference patterns that could not be explained in terms of Newtonian particles but could be easily explained in terms of waves. Later in the nineteenth century, after James Clerk Maxwell developed his theory of electromagnetic radiation and showed that light was the visible part of a vast spectrum of electromagnetic waves, the particle view of light became thoroughly discredited. By the end of the nineteenth century, scientists viewed the physical universe as roughly comprising two separate domains: matter composed of particles moving according to Newton's laws of motion, and electromagnetic radiation consisting of waves governed by Maxwell's equations. Today, these domains are referred to as classical mechanics and classical electrodynamics (or classical electromagnetism). Although there were a few physical phenomena that could not be explained within this framework, scientists at that time were so confident of the overall soundness of this framework that they viewed these aberrations as puzzling paradoxes that would ultimately be resolved somehow within this framework. As we shall see, these paradoxes led to a contemporary framework that intimately connects particles and waves at a fundamental level called wave-particle duality, which has superseded the classical view.

Visible light and other forms of electromagnetic radiation play important roles in chemistry, since they can be used to infer the energies of electrons within atoms and molecules. Much of modern technology is based on electromagnetic radiation. For example, radio waves from a mobile phone, X-rays used by dentists, the energy used to cook food in your microwave, the radiant heat from red-hot objects, and the light from your television screen are forms of electromagnetic radiation that all exhibit wavelike behavior.

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 **3.1.1**, the wavelength is the distance between two consecutive peaks or troughs in a wave (measured in meters in the SI system). Electromagnetic waves have wavelengths that fall within an enormous range-wavelengths of kilometers (10^3 m) to picometers (10^{-12} m) have been observed. The frequency is the number of wave cycles that pass a specified point in space in a specified amount of time (in the SI system, this is measured in seconds). A cycle corresponds to one complete wavelength. The unit for

frequency, expressed as cycles per second [s^{-1}], is the hertz (Hz). Common multiples of this unit are megahertz, (1 MHz = 1 × 10^6 Hz) and gigahertz (1 GHz = 1 × 10^9 Hz). The amplitude corresponds to the magnitude of the wave's displacement and so, in Figure, this corresponds to one-half the height between the peaks and troughs. The amplitude is related to the intensity of the wave, which for light is the brightness, and for sound is the loudness.

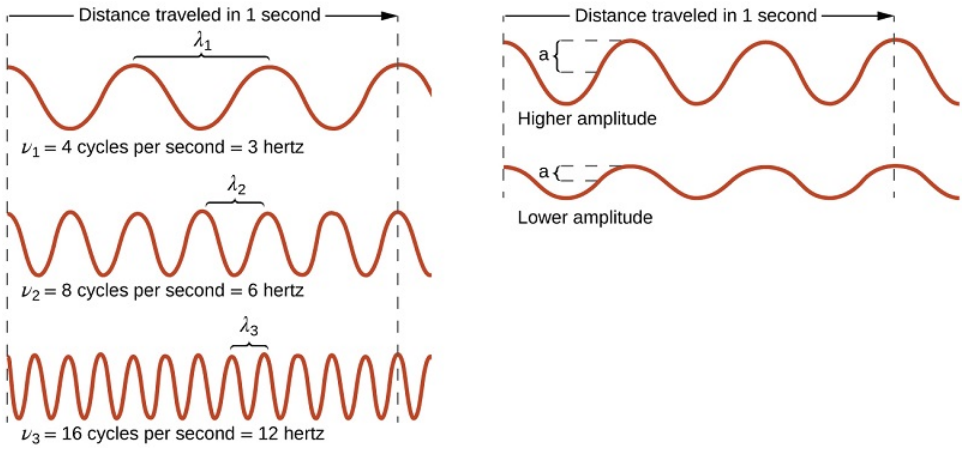


Figure **3.1.1**: One-dimensional sinusoidal waves show the relationship among wavelength, frequency, and speed. The wave with the shortest wavelength has the highest frequency. Amplitude is one-half the height of the wave from peak to trough.

Line Spectra

One paradox within the classical electromagnetic theory that scientists in the late nineteenth century struggled with concerned the light emitted from atoms and molecules. When solids, liquids, or condensed gases are heated sufficiently, they radiate some of the excess energy as light. Photons produced in this manner have a range of energies, and thereby produce a continuous spectrum in which an unbroken series of wavelengths is present. Most of the light generated from stars (including our sun) is produced in this fashion. You can see all the visible wavelengths of light present in sunlight by using a prism to separate them. As can be seen in Figure **3.1.8**, sunlight also contains UV light (shorter wavelengths) and IR light (longer wavelengths) that can be detected using instruments but that are invisible to the human eye. Incandescent (glowing) solids such as tungsten filaments in incandescent lights also give off light that contains all wavelengths of visible light. These continuous spectra can often be approximated by blackbody radiation curves at some appropriate temperature, such as those shown in Figure **3.1.9**.

In contrast to continuous spectra, light can also occur as discrete or line spectra having very narrow line widths interspersed throughout the spectral regions such as those shown in Figure **3.1.5**. 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 **3.1.11**). Each element displays its own characteristic set of lines, as do molecules, although their spectra are generally much more complicated.



Figure **3.1.11**: 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 **3.1.12**.

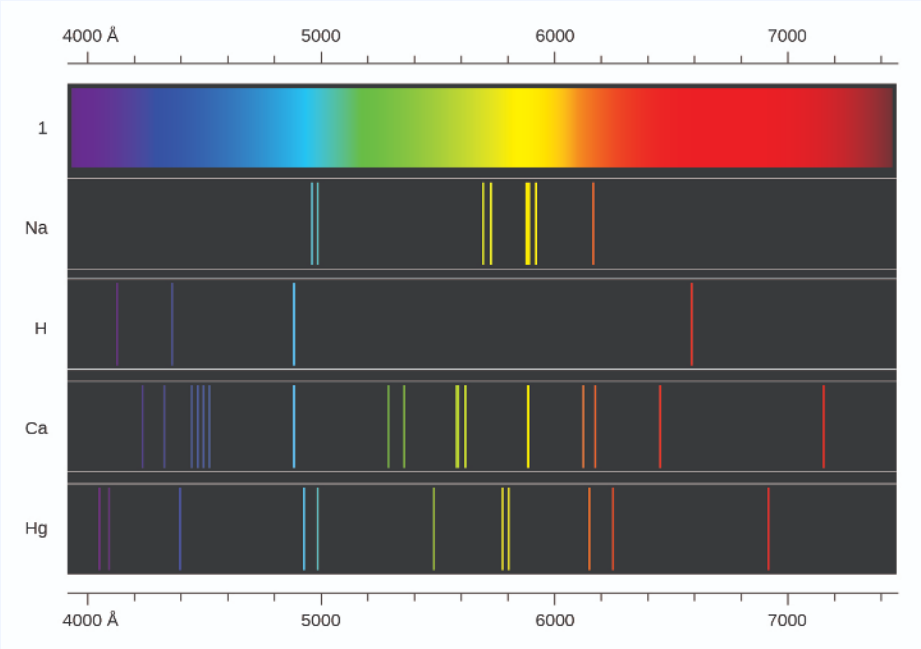


Figure **3.1.12**: Line spectra of select gas. Compare the two types of emission spectra: continuous spectrum of white light (top) and the line spectra of the light from excited sodium, hydrogen, calcium, and mercury atoms.

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:

$$\frac{1}{\lambda} = k\left(\frac{1}{4} - \frac{1}{n^2}\right), \; n = 3,\, 4,\, 5,\, 6 \tag{3.1.1}$$

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 ($1.097 \times 10^7\ \mathrm{m}^{-1}$).

$$\frac{1}{\lambda} = R_\infty \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{3.1.2}$$

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.

You will not need to be able to calculate or use these equations, but these discrete lines will help us understand some of the concepts later in this chapter.

Contributors and Attributions

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 and a wavelength. Light is an example of a travelling wave. Other important wave phenomena include standing waves, periodic oscillations, and vibrations. The emitted light can be either continuous (incandescent sources like the sun) or discrete (from specific types of excited atoms).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.

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)

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

intensity
: property of wave-propagated energy related to the amplitude of the wave, such as brightness of light or loudness of sound

line spectrum
: electromagnetic radiation emitted at discrete wavelengths by a specific atom (or atoms) in an excited state

quantization
: occurring only in specific discrete values, not continuous

wave

oscillation that can transport energy from one point to another in space

wavelength

distance between two consecutive peaks or troughs in a wave

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 3.1: Electromagnetic Energy is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

3.2: The Bohr Model

Learning Objectives

- Describe the Bohr model of the hydrogen atom

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. The electrostatic force attracting the electron to the proton depends only on the distance between the two particles.

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.

The lowest few energy levels are shown in Figure **3.2.1**. 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 electronic state (or simply 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 electronic state (or simply an excited state) with a higher energy. When an electron transitions from an excited state (higher energy orbit) to a less excited state, or 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.

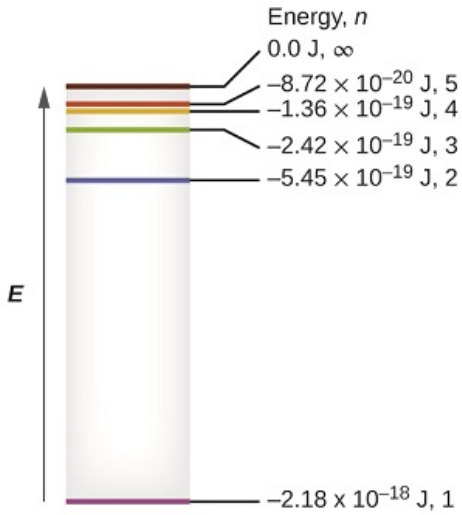


Figure **3.2.1**: Quantum numbers and energy levels in a hydrogen atom. The more negative the calculated value, the lower the energy.

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 **3.2.2**). 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).

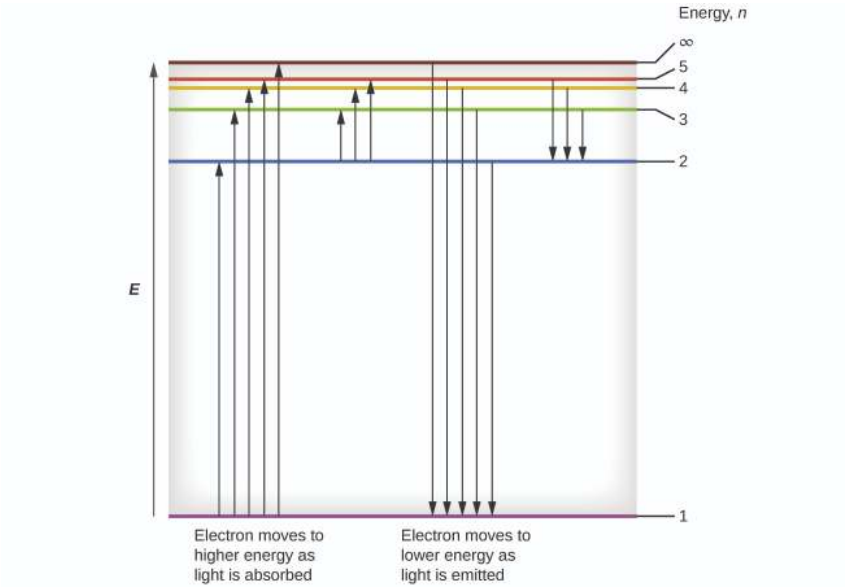


Figure **3.2.2**: The horizontal lines show the relative energy of orbits in the Bohr model of the hydrogen atom, and the vertical arrows depict the energy of photons absorbed (left) or emitted (right) as electrons move between these orbits.

Bohr's model of the hydrogen atom provides insight into the behavior of matter at the microscopic level. It introduces 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. Later in this chapter, we will examine how these specific energy levels relate to the periods (rows) of the Periodic Table and structure of larger atoms.

Summary

The Bohr model of the hydrogen atom helps to determine why atoms produce line spectra instead of continuous spectrums. It also helps to lay the foundation for how electrons are organized in an atom into discrete levels.

Glossary

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.

excited state
state having an energy greater than the ground-state energy

ground state
state in which the electrons in an atom, ion, or molecule have the lowest energy possible

quantum number
integer number having only specific allowed values and used to characterize the arrangement of electrons in an 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 3.2: The Bohr Model is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

3.3: 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.

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 **3.3.1** depicts how these two trends in increasing energy relate. The figure also shows how many orbitals there are for each subshell. Notice there is one 1 for each "s" subshell, but there are 3 for each "p" subshell. Each orbital can only hold 2 electrons, meaning that an "s" subshell can only hold 2 electrons total, while the "p" subshell can hold 6 electrons (2 in each orbital). 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. We will focus on s and p orbitals in this course, but it is important to remember that higher level orbitals exist.

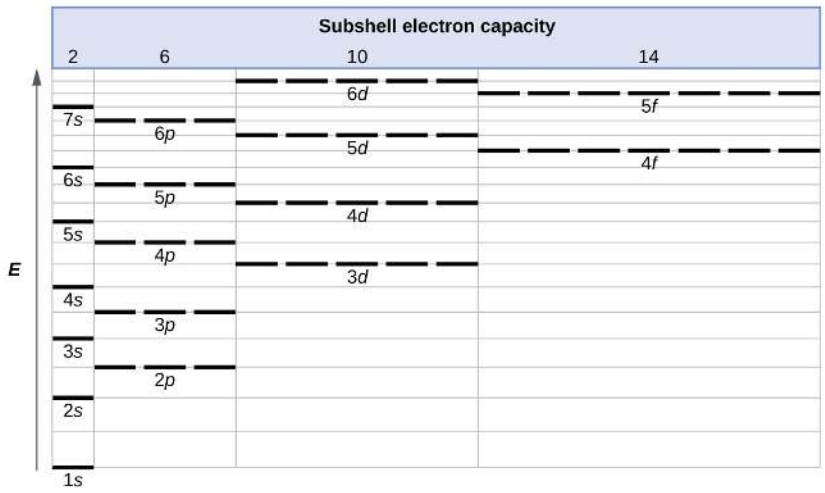


Figure **3.3.1**: Generalized energy-level diagram for atomic orbitals in an atom with two or more electrons (not to scale).

Electrons in successive atoms on the periodic table tend to fill low-energy orbitals first.

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 **3.3.2**):

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 $n = 3$.

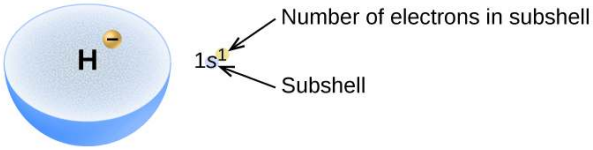


Figure **3.3.2**: The diagram of an electron configuration specifies the subshell (n and l value, with letter symbol) and superscript number of electrons.

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 **3.3.3**), 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 **3.3.3** illustrates the traditional way to remember the filling order for atomic orbitals.

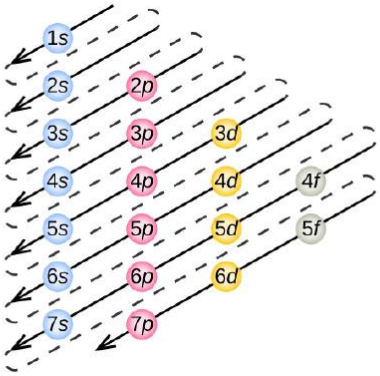


Figure **3.3.3**: The arrow leads through each subshell in the appropriate filling order for electron configurations. This chart is straightforward to construct. Simply make a column for all the s orbitals with each n shell on a separate row. Repeat for p, d, and f. Be sure to only include orbitals allowed 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 **3.3.4** 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.

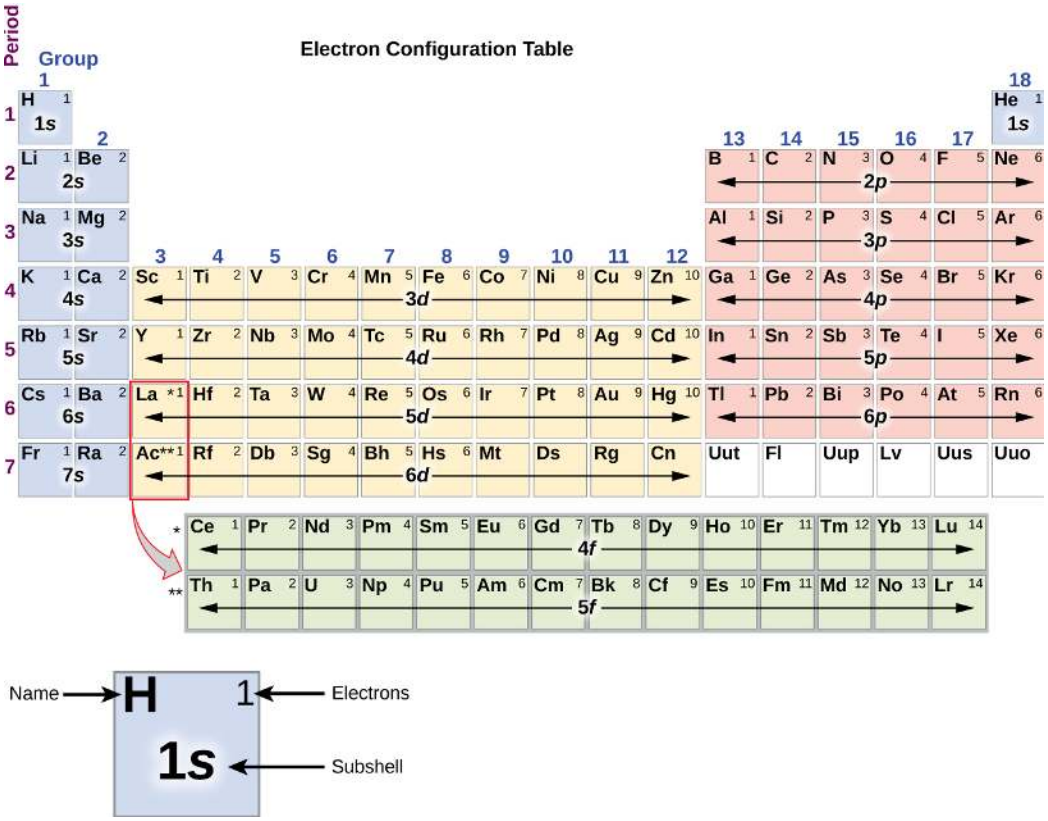
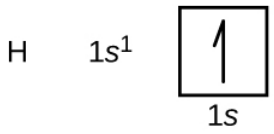
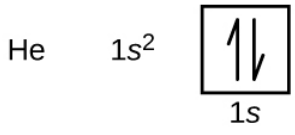


Figure **3.3.4**: This periodic table shows the electron configuration for each subshell. By "building up" from hydrogen, this table can be used to determine the electron configuration for any atom on the periodic table.

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 **3.3.3** or **3.3.4**, 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:



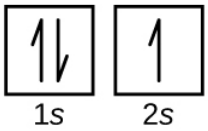
Following hydrogen is the noble gas helium, which has an atomic number of 2. The helium atom contains two protons and two electrons. The first electron has the same four quantum numbers as the hydrogen atom electron (n = 1, l = 0, m_l = 0, $m_s = +\frac{1}{2}$). The second electron also goes into the 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.

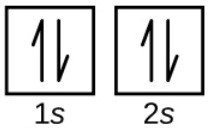
The next atom is the alkali metal lithium with an atomic number of 3. The first two electrons in lithium fill the 1*s* orbital and have the same sets of four quantum numbers as the two electrons in helium. The remaining electron must occupy the orbital of next lowest energy, the 2*s* orbital (Figure **3.3.3** or **3.3.4**). Thus, the electron configuration and orbital diagram of lithium are:

Li $1s^2 2s^1$



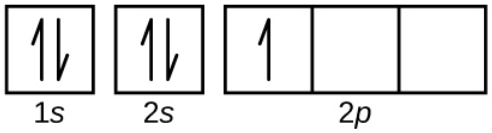
An atom of the alkaline earth metal beryllium, with an atomic number of 4, contains four protons in the nucleus and four electrons surrounding the nucleus. The fourth electron fills the remaining space in the 2*s* orbital.

Be $1s^2 2s^2$



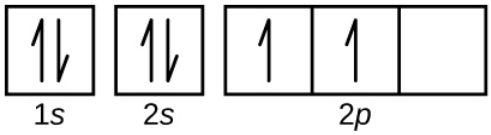
An atom of boron (atomic number 5) contains five electrons. The $n = 1$ shell is filled with two electrons and three electrons will occupy the $n = 2$ shell. Because any *s* subshell can contain only two electrons, the fifth electron must occupy the next energy level, which will be a 2*p* orbital. There 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:

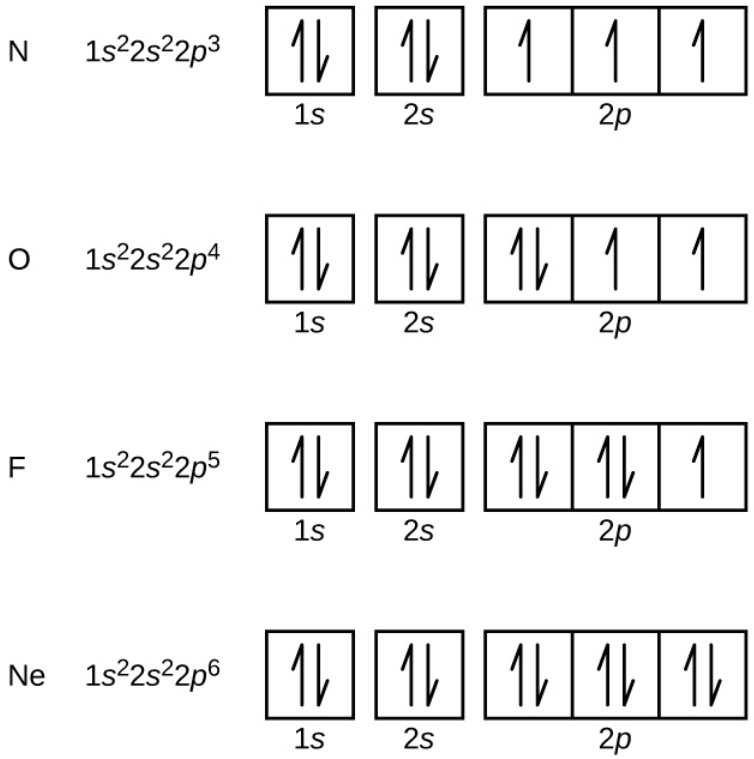


Figure **3.3.5**: Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [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 \PageIndex5\PageIndex5). Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, ($1s^2 2s^2 2p^6$) and our abbreviated or condensed configuration is [Ne]$3s^1$.

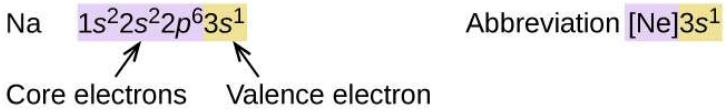


Figure **3.3.5**: A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

Similarly, the abbreviated configuration of lithium can be represented as [He]$2s^1$, where [He] represents the configuration of the helium atom, which is identical to that of the filled inner shell of lithium. Writing the configurations in this way emphasizes the similarity of the configurations of lithium and sodium. Both atoms, which are in the alkali metal family, have only one electron in a valence *s* subshell outside a filled set of inner shells.

$$\begin{aligned} \textbf{Li} &: \textbf{[He]}\, 2s^1 \\ \textbf{Na} &: \textbf{[Ne]}\, 3s^1 \end{aligned} \qquad (3.3.1)$$

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 **3.3.6** shows the lowest energy, or ground-state, electron configuration for these elements as well as that for atoms of each of the known elements.

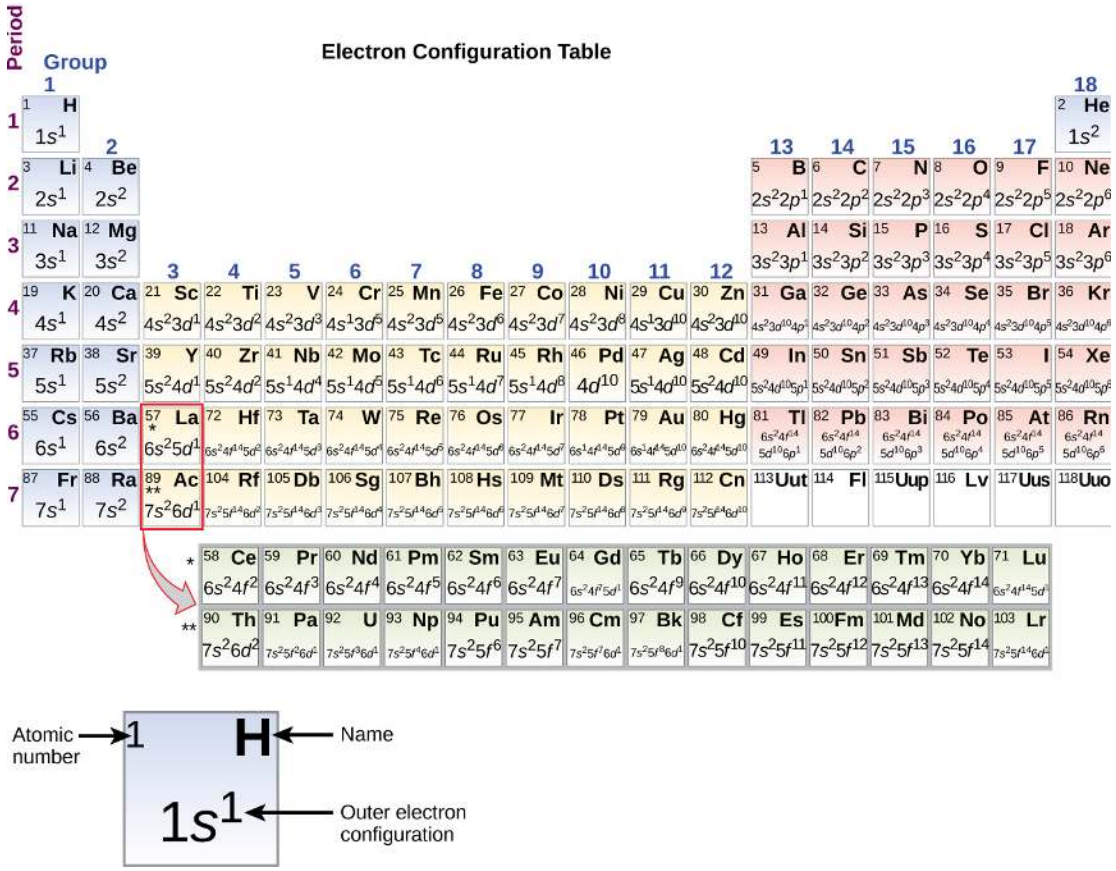


Figure **3.3.6**: This version of the periodic table shows the outer-shell electron configuration of each element. Note that down each group, the configuration is often similar.

When we come to the next element in the periodic table, the alkali metal potassium (atomic number 19), we might expect that we would begin to add electrons to the 3*d* subshell. However, all available chemical and physical evidence indicates that potassium is like lithium and sodium, and that the next electron is not added to the 3*d* level but is, instead, added to the 4*s* level (Figure **3.3.3** or **3.3.4**). 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.

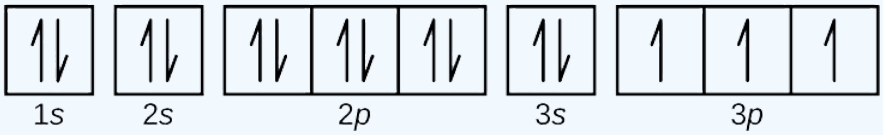
Example 3.3.1: Quantum Numbers and Electron Configurations

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 3.3.1

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. However, we do find exceptions to the order of filling of orbitals that are shown in Figure **3.3.3** or **3.3.4**. For instance, the electron configurations of the transition metals chromium (Cr; atomic number 24) and copper (Cu; atomic number 29), among others, are not those we would expect. In general, such exceptions involve subshells with very similar energy, and small effects can lead to changes in the order of filling.

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 **3.3.6**), 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 **3.3.6**, 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 **3.3.6** 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 **3.3.6**. 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. The official IUPAC definition of transition elements specifies those with partially filled *d* orbitals. Thus, the elements with completely filled orbitals (Zn, Cd, Hg, as well as Cu, Ag, and Au in Figure **3.3.6**) are not technically transition elements. However, the term is frequently used to refer to the entire *d* block (colored yellow in Figure **3.3.6**), and we will adopt this usage in this textbook.
3. **Inner transition elements** are metallic elements in which the last electron added occupies an *f* orbital. They are shown in green in Figure **3.3.6**. 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.

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 **3.3.2**: Predicting Electron Configurations of Ions

What is the electron configuration and orbital diagram of:

a. Na^+
b. P^{3-}
c. Al^{2+}

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: $1s^22s^22p^63s^1$. Sodium cation loses one electron, so Na^+: $1s^22s^22p^63s^1 = Na^+$: $1s^22s^22p^6$.
b. P: $1s^22s^22p^63s^23p^3$. Phosphorus trianion gains three electrons, so P^{3-}: $1s^22s^22p^63s^23p^6$.
c. Al: $1s^22s^22p^63s^23p^1$. Aluminum dication loses two electrons Al^{2+}: $1s^22s^22p^63s^23p^1 = Al^{2+}$: $1s^22s^22p^63s^1$.

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

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 3.3: Electronic Structure of Atoms (Electron Configurations) is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

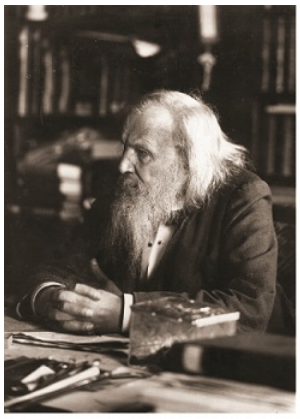
3.4: The Periodic Table

Learning Objectives

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

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

Dimitri Mendeleev in Russia (1869) and Lothar Meyer in Germany (1870) independently recognized that there was a periodic relationship among the properties of the elements known at that time. Both published tables with the elements arranged according to increasing atomic mass. But Mendeleev went one step further than Meyer: He used his table to predict the existence of elements that would have the properties similar to aluminum and silicon, but were yet unknown. The discoveries of gallium (1875) and germanium (1886) provided great support for Mendeleev's work. Although Mendeleev and Meyer had a long dispute over priority, Mendeleev's contributions to the development of the periodic table are now more widely recognized (Figure **3.4.1**).



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

(a) (b)

Figure **3.4.1**: (a) Dimitri Mendeleev is widely credited with creating (b) the first periodic table of the elements. (credit a: modification of work by Serge Lachinov; credit b: modification of work by “Den fjättrade ankan”/Wikimedia Commons)

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

By the twentieth century, it became apparent that the periodic relationship involved atomic numbers rather than atomic masses. The modern statement of this relationship, the periodic law, is as follows: *the properties of the elements are periodic functions of their atomic numbers*. A modern periodic table arranges the elements in increasing order of their atomic numbers and groups atoms with similar properties in the same vertical column (Figure **3.4.2**). Each box represents an element and contains its atomic number, symbol, average atomic mass, and (sometimes) name. The elements are arranged in seven horizontal rows, called periods or series, and 18 vertical columns, called groups. Groups are labeled at the top of each column. In the United States, the labels traditionally were numerals with capital letters. However, IUPAC recommends that the numbers 1 through 18 be used, and these labels are more common. For the table to fit on a single page, parts of two of the rows, a total of 14 columns, are usually written below the main body of the table.

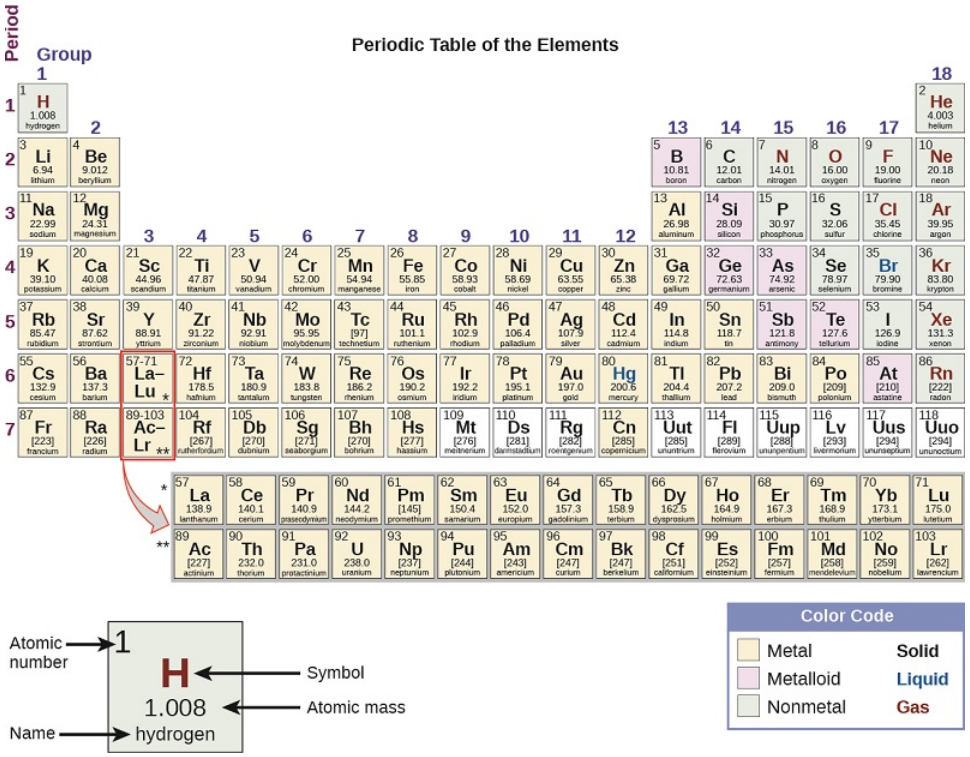


Figure 3.4.2: Elements in the periodic table are organized according to their properties.

https://chem.libretexts.org/@go/page/216739

The Periodic Table of Elements is shown. The 18 columns are labeled “Group” and the 7 rows are labeled “Period.” Below the table to the right is a box labeled “Color Code” with different colors for metals, metalloids, and nonmetals, as well as solids, liquids, and gases. To the left of this box is an enlarged picture of the upper-left most box on the table. The number 1 is in its upper-left hand corner and is labeled “Atomic number.” The letter “H” is in the middle in red indicating that it is a gas. It is labeled “Symbol.” Below that is the number 1.008 which is labeled “Atomic Mass.” Below that is the word hydrogen which is labeled “name.” The color of the box indicates that it is a nonmetal. Each element will be described in this order: atomic number; name; symbol; whether it is a metal, metalloid, or nonmetal; whether it is a solid, liquid, or gas; and atomic mass. Beginning at the top left of the table, or period 1, group 1, is a box containing “1; hydrogen; H; nonmetal; gas; and 1.008.” There is only one other element box in period 1, group 18, which contains “2; helium; H e; nonmetal; gas; and 4.003.” Period 2, group 1 contains “3; lithium; L i; metal; solid; and 6.94” Group 2 contains “4; beryllium; B e; metal; solid; and 9.012.” Groups 3 through 12 are skipped and group 13 contains “5; boron; B; metalloid; solid; 10.81.” Group 14 contains “6; carbon; C; nonmetal; solid; and 12.01.” Group 15 contains “7; nitrogen; N; nonmetal; gas; and 14.01.” Group 16 contains “8; oxygen; O; nonmetal; gas; and 16.00.” Group 17 contains “9; fluorine; F; nonmetal; gas; and 19.00.” Group 18 contains “10; neon; N e; nonmetal; gas; and 20.18.” Period 3, group 1 contains “11; sodium; N a; metal; solid; and 22.99.” Group 2 contains “12; magnesium; M g; metal; solid; and 24.31.” Groups 3 through 12 are skipped again in period 3 and group 13 contains “13; aluminum; A l; metal; solid; and 26.98.” Group 14 contains “14; silicon; S i; metalloid; solid; and 28.09.” Group 15 contains “15; phosphorous; P; nonmetal; solid; and 30.97.” Group 16 contains “16; sulfur; S; nonmetal; solid; and 32.06.” Group 17 contains “17; chlorine; C l; nonmetal; gas; and 35.45.” Group 18 contains “18; argon; A r; nonmetal; gas; and 39.95.” Period 4, group 1 contains “19; potassium; K; metal; solid; and 39.10.” Group 2 contains “20; calcium; C a; metal; solid; and 40.08.” Group 3 contains “21; scandium; S c; metal; solid; and 44.96.” Group 4 contains “22; titanium; T i; metal; solid; and 47.87.” Group 5 contains “23; vanadium; V; metal; solid; and 50.94.” Group 6 contains “24; chromium; C r; metal; solid; and 52.00.” Group 7 contains “25; manganese; M n; metal; solid; and 54.94.” Group 8 contains “26; iron; F e; metal; solid; and 55.85.” Group 9 contains “27; cobalt; C o; metal; solid; and 58.93.” Group 10 contains “28; nickel; N i; metal; solid; and 58.69.” Group 11 contains “29; copper; C u; metal; solid; and 63.55.” Group 12 contains “30; zinc; Z n; metal; solid; and 65.38.” Group 13 contains “31; gallium; G a; metal; solid; and 69.72.” Group 14 contains “32; germanium; G e; metalloid; solid; and 72.63.” Group 15 contains “33; arsenic; A s; metalloid; solid; and 74.92.” Group 16 contains “34; selenium; S e; nonmetal; solid; and 78.97.” Group 17 contains “35; bromine; B r; nonmetal; liquid; and 79.90.” Group 18 contains “36; krypton; K r; nonmetal; gas; and 83.80.” Period 5, group 1 contains “37; rubidium; R b; metal; solid; and 85.47.” Group 2 contains “38; strontium; S r; metal; solid; and 87.62.” Group 3 contains “39; yttrium; Y; metal; solid; and 88.91.” Group 4 contains “40; zirconium; Z r; metal; solid; and 91.22.” Group 5 contains “41; niobium; N b; metal; solid; and 92.91.” Group 6 contains “42; molybdenum; M o; metal; solid; and 95.95.” Group 7 contains “43; technetium; T c; metal; solid; and 97.” Group 8 contains “44; ruthenium; R u; metal; solid; and 101.1.” Group 9 contains “45; rhodium; R h; metal; solid; and 102.9.” Group 10 contains “46; palladium; P d; metal; solid; and 106.4.” Group 11 contains “47; silver; A g; metal; solid; and 107.9.” Group 12 contains “48; cadmium; C d; metal; solid; and 112.4.” Group 13 contains “49; indium; I n; metal; solid; and 114.8.” Group 14 contains “50; tin; S n; metal; solid; and 118.7.” Group 15 contains “51; antimony; S b; metalloid; solid; and 121.8.” Group 16 contains “52; tellurium; T e; metalloid; solid; and 127.6.” Group 17 contains “53; iodine; I; nonmetal; solid; and 126.9.” Group 18 contains “54; xenon; X e; nonmetal; gas; and 131.3.” Period 6, group 1 contains “55; cesium; C s; metal; solid; and 132.9.” Group 2 contains “56; barium; B a; metal; solid; and 137.3.” Group 3 breaks the pattern. The box has a large arrow pointing to a row of elements below the table with atomic numbers ranging from 57-71. In sequential order by atomic number, the first box in this row contains “57; lanthanum; L a; metal; solid; and 138.9.” To its right, the next is “58; cerium; C e; metal; solid; and 140.1.” Next is “59; praseodymium; P r; metal; solid; and 140.9.” Next is “60; neodymium; N d; metal; solid; and 144.2.” Next is “61; promethium; P m; metal; solid; and 145.” Next is “62; samarium; S m; metal; solid; and 150.4.” Next is “63; europium; E u; metal; solid; and 152.0.” Next is “64; gadolinium; G d; metal; solid; and 157.3.” Next is “65; terbium; T b; metal; solid; and 158.9.” Next is “66; dysprosium; D y; metal; solid; and 162.5.” Next is “67; holmium; H o; metal; solid; and 164.9.” Next is “68; erbium; E r; metal; solid; and 167.3.” Next is “69; thulium; T m; metal; solid; and 168.9.” Next is “70; ytterbium; Y b; metal; solid; and 173.1.” The last in this special row is “71; lutetium; L u; metal; solid; and 175.0.” Continuing in period 6, group 4 contains “72; hafnium; H f; metal; solid; and 178.5.” Group 5 contains “73; tantalum; T a; metal; solid; and 180.9.” Group 6 contains “74; tungsten; W; metal; solid; and 183.8.” Group 7 contains “75; rhenium; R e; metal; solid; and 186.2.” Group 8 contains “76; osmium; O s; metal; solid; and 190.2.” Group 9 contains “77; iridium; I r; metal; solid; and 192.2.” Group 10 contains “78; platinum; P t; metal; solid; and 195.1.” Group 11 contains “79; gold; A u; metal; solid; and 197.0.” Group 12 contains “80; mercury; H g; metal; liquid; and 200.6.” Group 13 contains “81; thallium; T l; metal; solid; and 204.4.” Group 14 contains “82; lead; P b; metal; solid; and 207.2.” Group 15 contains “83; bismuth; B i; metal; solid; and 209.0.” Group 16 contains “84; polonium; P o; metal; solid; and 209.” Group 17 contains “85; astatine; A t; metalloid; solid; and 210.” Group 18 contains “86; radon; R n; nonmetal; gas; and 222.” Period 7, group 1 contains “87; francium; F r; metal; solid; and 223.” Group 2 contains “88; radium; R a; metal; solid; and 226.” Group 3 breaks the pattern much like what occurs in period 6. A large arrow points from the box in period 7, group 3 to a special row containing the elements with atomic numbers ranging from 89-103, just below the row which contains atomic numbers 57-71. In sequential order by atomic number, the first box in this row contains “89; actinium; A c; metal; solid; and 227.” To its right, the next is “90; thorium; T h; metal; solid; and 232.0.” Next is “91; protactinium; P a; metal; solid; and 231.0.” Next is “92; uranium; U; metal; solid; and 238.0.” Next is “93; neptunium; N p; metal; solid; and N p.” Next is “94; plutonium; P u; metal; solid; and 244.” Next is “95; americium; A m; metal; solid; and 243.” Next is “96; curium; C m; metal; solid; and 247.” Next is “97; berkelium; B k; metal; solid; and 247.” Next is “98; californium; C f; metal; solid; and 251.” Next is “99; einsteinium; E s; metal; solid; and 252.” Next is “100; fermium; F m; metal; solid; and 257.” Next is “101; mendelevium; M d; metal; solid; and 258.” Next is “102; nobelium; N o; metal; solid; and 259.” The last in this special row is “103; lawrencium; L r; metal; solid; and 262.” Continuing in period 7, group 4 contains “104; rutherfordium; R f; metal; solid; and 267.” Group 5 contains “105; dubnium; D b; metal; solid; and 270.” Group 6 contains “106; seaborgium; S g; metal; solid; and 271.” Group 7 contains “107; bohrium; B h; metal; solid; and 270.” Group 8 contains “108; hassium; H s; metal; solid; and 277.” Group 9 contains “109; meitnerium; M t; not

indicated; solid; and 276.” Group 10 contains “110; darmstadtium; D s; not indicated; solid; and 281.” Group 11 contains “111; roentgenium; R g; not indicated; solid; and 282.” Group 12 contains “112; copernicium; C n; metal; liquid; and 285.” Group 13 contains “113; ununtrium; U u t; not indicated; solid; and 285.” Group 14 contains “114; flerovium; F l; not indicated; solid; and 289.” Group 15 contains “115; ununpentium; U u p; not indicated; solid; and 288.” Group 16 contains “116; livermorium; L v; not indicated; solid; and 293.” Group 17 contains “117; ununseptium; U u s; not indicated; solid; and 294.” Group 18 contains “118; ununoctium; U u o; not indicated; solid; and 294.”

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

The elements can also be classified into the main-group elements (or representative elements) in the columns labeled 1, 2, and 13–18; the transition metals in the columns labeled 3–12; and inner transition metals in the two rows at the bottom of the table (the top-row elements are called lanthanides and the bottom-row elements are actinides; Figure **3.4.3**). The elements can be subdivided further by more specific properties, such as the composition of the compounds they form. For example, the elements in group 1 (the first column) form compounds that consist of one atom of the element and one atom of hydrogen. These elements (except hydrogen) are known as alkali metals, and they all have similar chemical properties. The elements in group 2 (the second column) form compounds consisting of one atom of the element and two atoms of hydrogen: These are called alkaline earth metals, with similar properties among members of that group. Other groups with specific names are the pnictogens (group 15), chalcogens (group 16), halogens (group 17), and the noble gases (group 18, also known as inert gases). The groups can also be referred to by the first element of the group: For example, the chalcogens can be called the oxygen group or oxygen family. Hydrogen is a unique, nonmetallic element with properties similar to both group 1 and group 17 elements. For that reason, hydrogen may be shown at the top of both groups, or by itself.

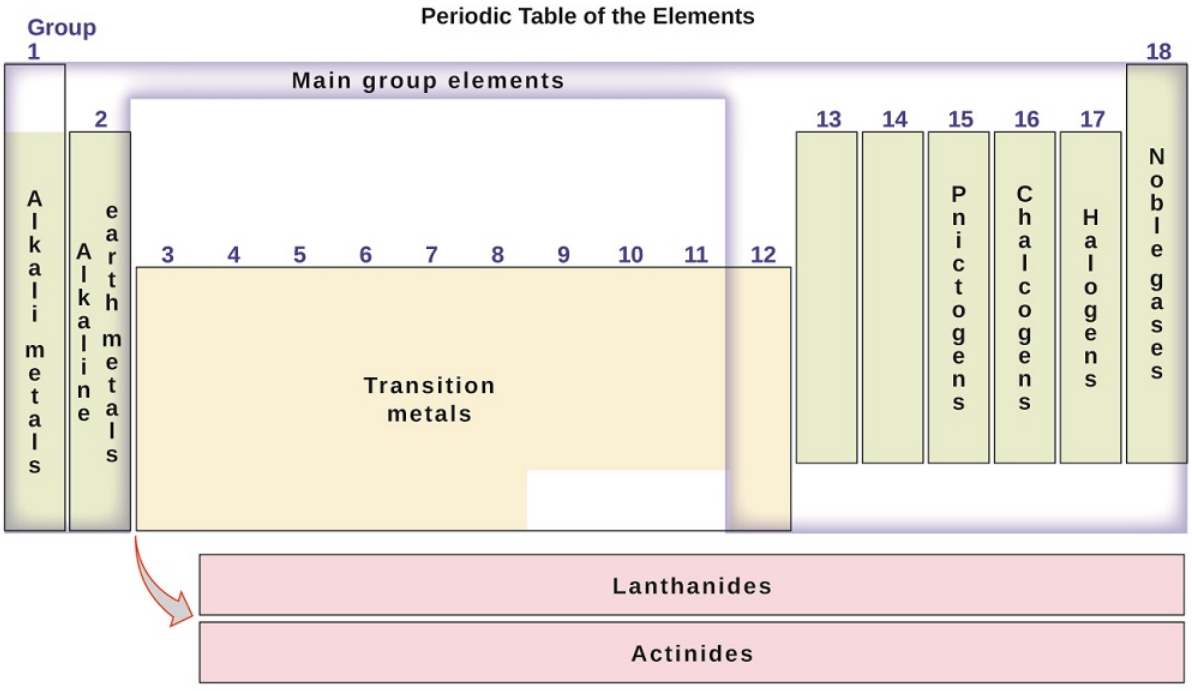


Figure **3.4.3**: The periodic table organizes elements with similar properties into groups.

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

Example 3.4.1: Naming Groups of Elements

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

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

Solution

The family names are as follows:

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

Exercise 3.4.1

Give the group name for each of the following elements:

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

Answer a

noble gas

Answer b

chalcogen

Answer c

alkaline earth metal

Answer d

alkali metal

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

Summary

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

Glossary

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

alkali metal
element in group 1

alkaline earth metal
element in group 2

chalcogen
element in group 16

group
vertical column of the periodic table

halogen
element in group 17

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

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

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

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

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

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

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

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

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

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

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

pnictogen

element in group 15

representative element

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

transition metal

element in columns 3–11

series

(also, period) horizontal row of the period table

This page titled 3.4: The Periodic Table is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

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

3.5: Periodic Variations in Element Properties

Learning Objectives

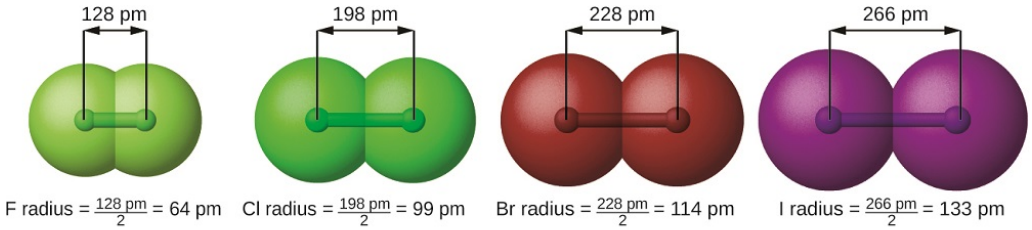
- Describe and explain the observed trends in atomic size, ionization energy, and electron affinity of the elements

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.

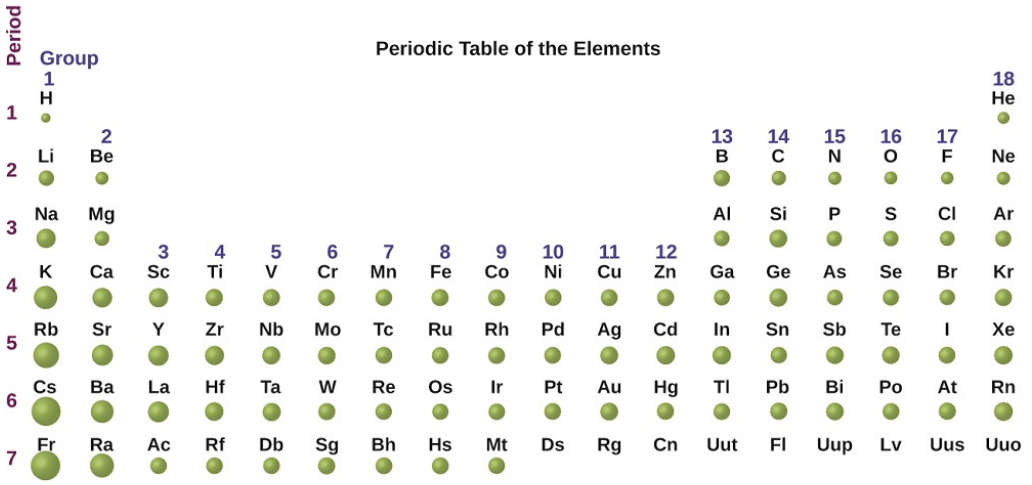
As we go across a period from left to right, we add a proton to the nucleus and an electron to the valence shell with each successive element. As we go down the elements in a group, the number of electrons in the valence shell remains constant, but the principal quantum number increases by one each time. 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.

Variation in Covalent Radius

The quantum mechanical picture makes it difficult to establish a definite size of an atom. However, there are several practical ways to define the radius of atoms and, thus, to determine their relative sizes that give roughly similar values. We will use the covalent radius (Figure **3.5.1**), 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 **3.5.1**: (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.

This figure has two parts: a and b. In figure a, 4 diatomic molecules are shown to illustrate the method of determining the atomic radius of an atom. The first model, in light green, is used to find the F atom radius. Two spheres are pushed very tightly together. The distance between the centers of the two atoms is indicated above the diagram with a double headed arrow labeled, “128 p m.” The endpoints of this arrow connect to line segments that extend to the atomic radii below. Beneath the molecule is the label, “F radius equals 128 p m divided by 2 equals 64 p m.” The next three models are similarly used to show the atomic radii of additional atoms. The second diatomic molecule is in a darker shade of green. The distance between the radii is 198 p m. Beneath the molecule is the label, “C l radius equals 198 p m divided by 2 equals 99 pm.” The third diatomic molecule is in red. The distance between the radii is 228 p m. Beneath the molecule is the label, “B r radius equals 228 p m divided by 2 equals 114 pm.” The fourth diatomic molecule is in purple. The distance between the radii is 266 p m. Beneath the molecule is the label, “I radius equals 266 p m divided by 2 equals 133 p m.” In figure b, a periodic table layout is used to compare relative sizes of atoms using green spheres. No spheres are provided for the noble or inert gas, group 18 elements. General trends noted are increasing circle size moving from top to bottom in a group, with a general tendency toward increasing atomic radii toward the lower left corner of the periodic table.

We know that as we scan down a group, the principal quantum number, *n*, increases by one for each element. Thus, the electrons are being added to a region of space that is increasingly distant from the nucleus. Consequently, the size of the atom (and its covalent radius) must increase as we increase the distance of the outermost electrons from the nucleus. This trend is illustrated for the covalent radii of the halogens in Table **3.5.1** and Figure **3.5.1**. The trends for the entire periodic table can be seen in Figure **3.5.2**.

Table **3.5.1**: Covalent Radii of the Halogen Group Elements

Atom	Covalent radius (pm)	Nuclear charge
F	64	+9
Cl	99	+17
Br	114	+35
I	133	+53
At	148	+85

As shown in Figure **3.5.2**, 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.

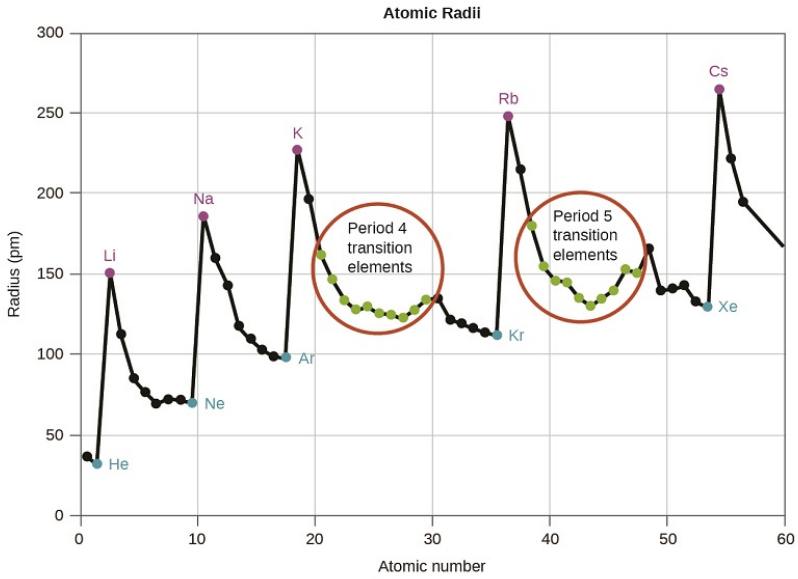


Figure **3.5.2**: Within each period, the trend in atomic radius decreases as Z increases; for example, from K to Kr. Within each group (e.g., the alkali metals shown in purple), the trend is that atomic radius increases as Z increases.

This graph is labeled Atomic Number on the horizontal axis and Radius (p m) on the vertical axis. A black jagged line connects the radii values for elements with atomic numbers 1 through 60 on the graph. Peaks are evident at the locations of the alkali metals: L i, N a, K, R b, and C s. Similarly, minima exist at the locations of noble or inert gases: H e, N e, A r, K r, X e, and R n. The locations of period 4 and period 5 transition elements are provided with green dots.

Thus, as we would expect, the outermost or valence electrons are easiest to remove because they have the highest energies, are shielded more, and are farthest from the nucleus. As a general rule, when the representative elements form cations, they do so by the loss of the *ns* or *np* electrons that were added last in the Aufbau process. The transition elements, on the other hand, lose the *ns* electrons before they begin to lose the $(n - 1)d$ electrons, even though the *ns* electrons are added first, according to the Aufbau principle.

✔ Example **3.5.1**: Sorting Atomic Radii

Predict the order of increasing covalent radius for Ge, Fl, Br, Kr.

Solution

Radius increases as we move down a group, so Ge < Fl (Note: Fl is the symbol for flerovium, element 114, NOT fluorine). Radius decreases as we move across a period, so Kr < Br < Ge. Putting the trends together, we obtain Kr < Br < Ge < Fl.

? Exercise 3.5.1

Give an example of an atom whose size is smaller than fluorine.

Answer

Ne or He

Variation in Ionic Radii

Ionic radius is the measure used to describe the size of an ion. A cation always has fewer electrons and the same number of protons as the parent atom; it is smaller than the atom from which it is derived (Figure **3.5.3**). 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 **3.5.3**: 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.

The figure includes spheres in green to represent the relative sizes of A l and S atoms. Beneath each of these spheres is a red sphere. The red sphere represents the ionic states of aluminum and sulfur respectively. While radius for the aluminum cation is smaller than aluminum, the sulfur anion has a greater radius than sulfur.

Cations with larger charges are smaller than cations with smaller charges (e.g., V^{2+} has an ionic radius of 79 pm, while that of V^{3+} is 64 pm). Proceeding down the groups of the periodic table, we find that cations of successive elements with the same charge generally have larger radii, corresponding to an increase in the principal quantum number, *n*.

An anion (negative ion) is formed by the addition of one or more electrons to the valence shell of an atom. This results in a greater repulsion among the electrons and a decrease in Z_{eff} per electron. Both effects (the increased number of electrons and the decreased Z_{eff}) cause the radius of an anion to be larger than that of the parent atom (Figure **3.5.3**). 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.

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:

$$\mathbf{X}(g) \longrightarrow \mathbf{X}^+(g) + \mathbf{e}^- \quad \mathbf{IE_1}$$

The energy required to remove the second most loosely bound electron is called the second ionization energy (IE_2).

$$\mathbf{X}^+(g) \longrightarrow \mathbf{X}^{2+}(g) + \mathbf{e}^- \quad \mathbf{IE_2}$$

The energy required to remove the third electron is the third ionization energy, and so on. Energy is always required to remove electrons from atoms or ions, so ionization processes are endothermic and IE values are always positive. For larger atoms, the most loosely bound electron is located farther from the nucleus and so is easier to remove. Thus, as size (atomic radius) increases, the

ionization energy should decrease. Relating this logic to what we have just learned about radii, we would expect first ionization energies to decrease down a group and to increase across a period.

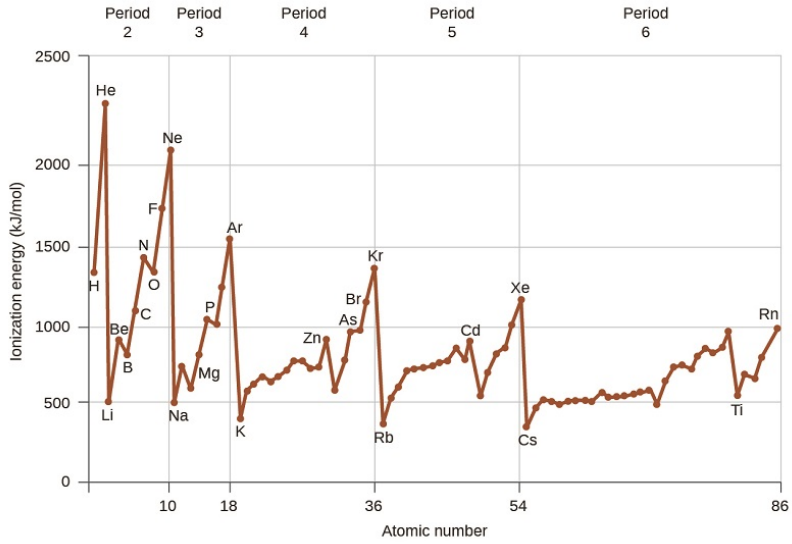


Figure 3.5.4: The first ionization energy of the elements in the first five periods are plotted against their atomic number.

This figure includes Atomic Number on the horizontal axis and, Ionization Energy (k J divided by mol) on the vertical axis. A red jagged line connects the ionization energies for elements with atomic numbers 1 through 86 on the graph. Peaks are evident at the locations of the noble or inert gases: H e, N e, A r, K r, X e, and R n. Similarly, minima exist at the locations of the alkali metals: L i, N a, K, R b, and C s.

Figure 3.5.4 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 ($[He]2s^2$) is an s electron, whereas the electron removed during the ionization of boron ($[He]2s^22p^1$) is a p electron; this results in a lower first ionization energy for boron, even though its nuclear charge is greater by one proton. Thus, we see a small deviation from the predicted trend occurring each time a new subshell begins.

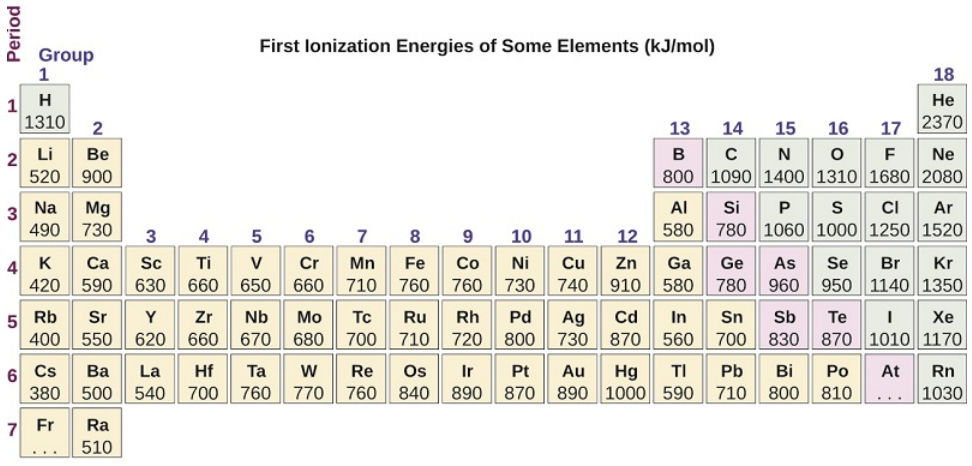
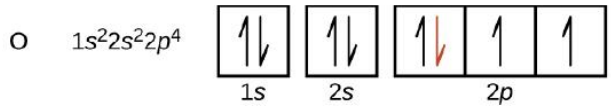


Figure 3.5.5: This version of the periodic table shows the first ionization energy of (IE: $_1$), in kJ/mol, of selected elements.

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 **3.5.4**.



The electronic configuration for oxygen is 1s superscript 2, 2s superscript, 2p superscript 4. An orbital diagram shows 2 squares each filled with a pair of opposite pointing arrows to represent the 1s ans 2s orbitals. Each of the three connected square which represents the 2p orbitals are filled with one arrow respectively with the addition of 1 red arrow in the first of the three squares.

Removing an electron from a cation is more difficult than removing an electron from a neutral atom because of the greater electrostatic attraction to the cation. Likewise, removing an electron from a cation with a higher positive charge is more difficult than removing an electron from an ion with a lower charge. Thus, successive ionization energies for one element always increase. As seen in Table **3.5.2**, there is a large increase in the ionization energies (color change) for each element. This jump corresponds to removal of the core electrons, which are harder to remove than the valence electrons. For example, Sc and Ga both have three valence electrons, so the rapid increase in ionization energy occurs after the third ionization.

Table 3.5.2: Successive Ionization Energies for Selected Elements (kJ/mol)

Element	IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7
K	418.8	3051.8	4419.6	5876.9	7975.5	9590.6	11343
Ca	589.8	1145.4	4912.4	6490.6	8153.0	10495.7	12272.9
Sc	633.1	1235.0	2388.7	7090.6	8842.9	10679.0	13315.0
Ga	578.8	1979.4	2964.6	6180	8298.7	10873.9	13594.8
Ge	762.2	1537.5	3302.1	4410.6	9021.4	Not available	Not available
As	944.5	1793.6	2735.5	4836.8	6042.9	12311.5	Not available

✔ Example 3.5.2: 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

$$\mathbf{Al} \quad (\mathbf{Al^{2+} \longrightarrow Al^{3+} + e^-})$$

requires more energy because the cation Al^{2+} exerts a stronger pull on the electron than the neutral Al atom, so $IE_1(Al) < IE_3(Al)$. The second ionization energy for sodium removes a core electron, which is a much higher energy process than removing valence electrons. Putting this all together, we obtain:

$$IE_1(Tl) < IE_1(Al) < IE_3(Al) < IE_2(Na).$$

? Exercise 3.5.2

Which has the lowest value for IE_1: O, Po, Pb, or Ba?

Answer

Ba

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 **3.5.6**. 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.

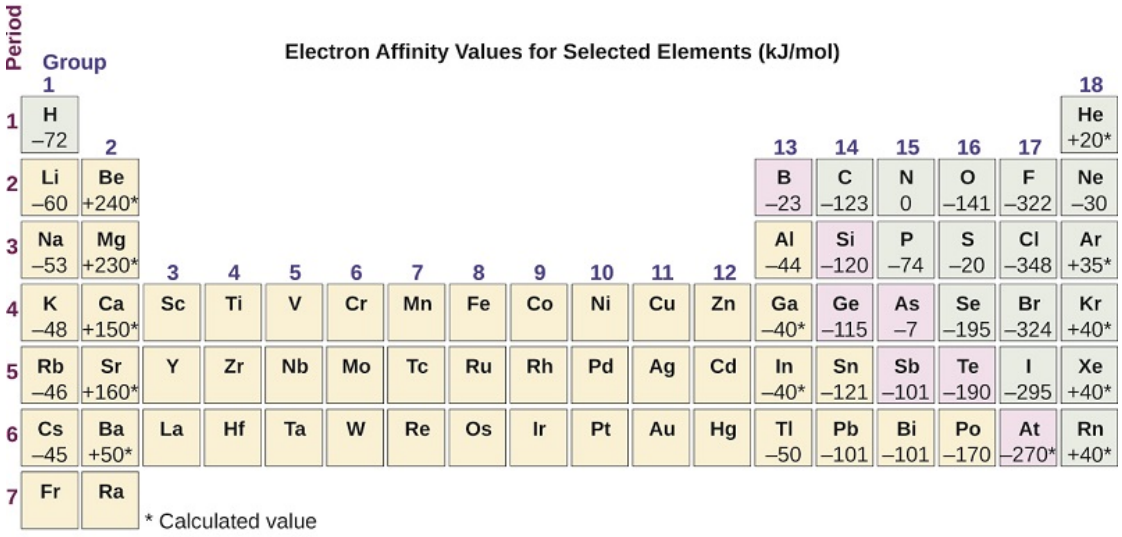


Figure **3.5.6**: This version of the periodic table displays the electron affinity values (in kJ/mol) for selected elements.:
The trend for electron affinity values across periods and down groups is shown in this version of the periodic table. Values are not shown for groups 3 to 12 as well as period 7.

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.

Summary

Electron configurations allow us to understand many periodic trends. Covalent radius increases as we move down a group because the *n* level (orbital size) increases. Covalent radius mostly decreases as we move left to right across a period because the effective nuclear charge experienced by the electrons increases, and the electrons are pulled in tighter to the nucleus. Anionic radii are larger than the parent atom, while cationic radii are smaller, because the number of valence electrons has changed while the nuclear charge has remained constant. Ionization energy (the energy associated with forming a cation) decreases down a group and mostly increases across a period because it is easier to remove an electron from a larger, higher energy orbital. Electron affinity (the energy associated with forming an anion) is more favorable (exothermic) when electrons are placed into lower energy orbitals, closer to the nucleus. Therefore, electron affinity becomes increasingly negative as we move left to right across the periodic table and decreases as we move down a group. For both IE and electron affinity data, there are exceptions to the trends when dealing with completely filled or half-filled subshells.

Glossary

covalent radius
: one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond

effective nuclear charge
: charge that leads to the Coulomb force exerted by the nucleus on an electron, calculated as the nuclear charge minus shielding

electron affinity
: energy required to add an electron to a gaseous atom to form an anion

ionization energy
: energy required to remove an electron from a gaseous atom or ion. The associated number (e.g., second ionization energy) corresponds to the charge of the ion produced (X^{2+})

isoelectronic
: group of ions or atoms that have identical electron configurations

This page titled 3.5: Periodic Variations in Element Properties is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

- **6.5: Periodic Variations in Element Properties** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

3.6: Molecular and Ionic Compounds

Learning Objectives

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

In ordinary chemical reactions, the nucleus of each atom (and thus the identity of the element) remains unchanged. Electrons, however, can be added to atoms by transfer from other atoms, lost by transfer to other atoms, or shared with other atoms. The transfer and sharing of electrons among atoms govern the chemistry of the elements. During the formation of some compounds, atoms gain or lose electrons, and form electrically charged particles called ions (Figure **3.6.1**).

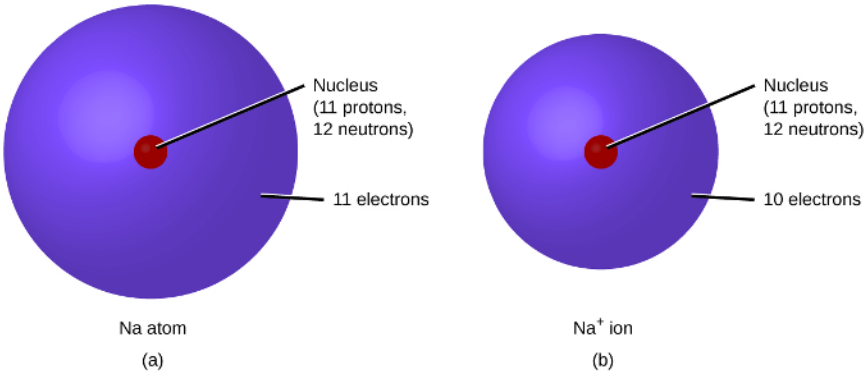


Figure **3.6.1**: (a) A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. (b) A sodium cation (Na^+) has lost an electron, so it has one more proton (11) than electrons (10), giving it an overall positive charge, signified by a superscripted plus sign.

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

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

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

Note the usefulness of the periodic table in predicting likely ion formation and charge (Figure **3.6.2**). Moving from the far left to the right on the periodic table, main-group elements tend to form cations with a charge equal to the group number. That is, group 1 elements form 1+ ions; group 2 elements form 2+ ions, and so on. Moving from the far right to the left on the periodic table, elements often form anions with a negative charge equal to the number of groups moved left from the noble gases. For example, group 17 elements (one group left of the noble gases) form 1− ions; group 16 elements (two groups left) form 2− ions, and so on. This trend can be used as a guide in many cases, but its predictive value decreases when moving toward the center of the periodic

table. In fact, transition metals and some other metals often exhibit variable charges that are not predictable by their location in the table. For example, copper can form ions with a 1+ or 2+ charge, and iron can form ions with a 2+ or 3+ charge.

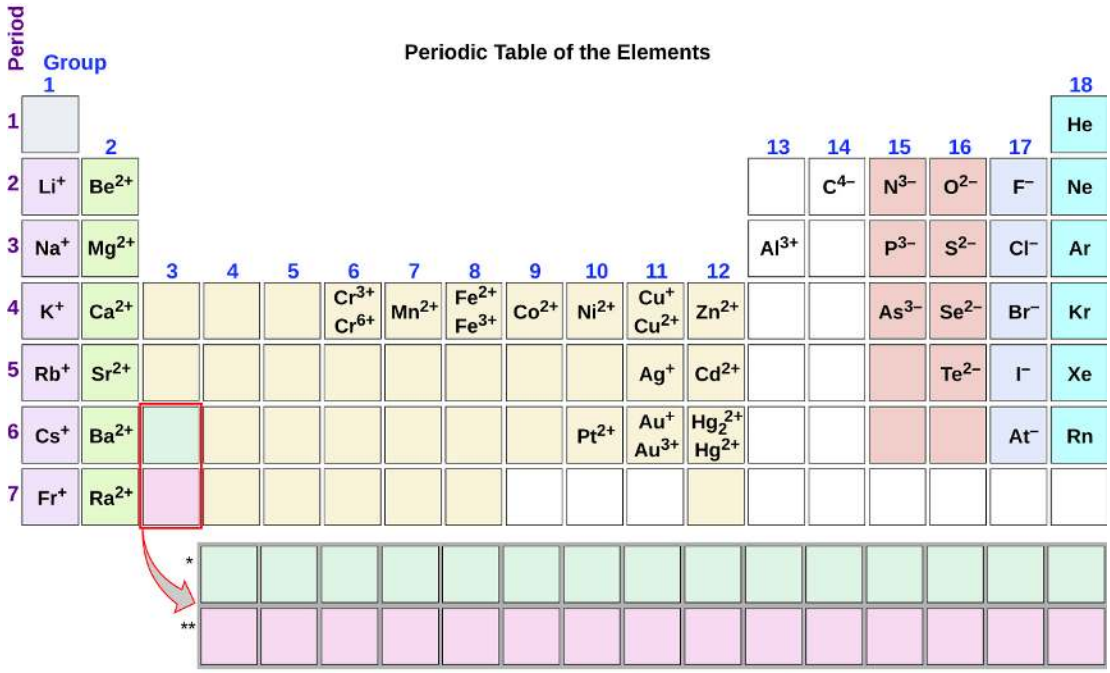


Figure **3.6.2**: Some elements exhibit a regular pattern of ionic charge when they form ions.

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

✔ Example **3.6.1**: Composition of Ions

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

Solution

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

? Exercise **3.6.1**

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

Answer

Se^{2-}, the selenide ion

✔ Example **3.6.2**: Formation of Ions

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

Solution

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

Nitrogen's position in the periodic table (group 15) reveals that it is a nonmetal. Nonmetals form negative ions (anions). A nitrogen atom must gain three electrons to have the same number of electrons as an atom of the following noble gas, neon. Thus, a nitrogen atom will form an anion with three more electrons than protons and a charge of 3−. The symbol for the ion is N^{3-}, and it is called a nitride ion.

? Exercise 3.6.2

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

Answer

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

The ions that we have discussed so far are called monatomic ions, that is, they are ions formed from only one atom. We also find many polyatomic ions. These ions, which act as discrete units, are electrically charged molecules (a group of bonded atoms with an overall charge). Some of the more important polyatomic ions are listed in Table **3.6.1**. 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 **3.6.1**: Common Polyatomic Ions

Name	Formula	Related Acid	Formula
ammonium	NH_4^+		
hydronium	H_3O^+		
oxide	O^{2-}		
peroxide	O_2^{2-}		
hydroxide	OH^-		
acetate	CH_3COO^-	acetic acid	CH_3COOH
cyanide	CN^-	hydrocyanic acid	HCN
azide	N_3^-	hydrazoic acid	HN_3
carbonate	CO_3^{2-}	carbonic acid	H_2CO_3
bicarbonate	HCO_3^-		
nitrate	NO_3^-	nitric acid	HNO_3
nitrite	NO_2^-	nitrous acid	HNO_2
sulfate	SO_4^{2-}	sulfuric acid	H_2SO_4
hydrogen sulfate	HSO_4^-		
sulfite	SO_3^{2-}	sulfurous acid	H_2SO_3
hydrogen sulfite	HSO_3^-		
phosphate	PO_4^{3-}	phosphoric acid	H_3PO_4
hydrogen phosphate	HPO_4^{2-}		
dihydrogen phosphate	$H_2PO_4^-$		
perchlorate	ClO_4^-	perchloric acid	$HClO_4$
chlorate	ClO_3^-	chloric acid	$HClO_3$
chlorite	ClO_2^-	chlorous acid	$HClO_2$
hypochlorite	ClO^-	hypochlorous acid	$HClO$
chromate	CrO_4^{2-}	chromic acid	H_2CrO_4
dichromate	$Cr_2O_7^{2-}$	dichromic acid	$H_2Cr_2O_7$
permanganate	MnO_4^-	permanganic acid	$HMnO_4$

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

The nature of the attractive forces that hold atoms or ions together within a compound is the basis for classifying chemical bonding. When electrons are transferred and ions form, ionic bonds result. Ionic bonds are electrostatic forces of attraction, that is, the attractive forces experienced between objects of opposite electrical charge (in this case, cations and anions). When electrons are “shared” and molecules form, covalent bonds result. Covalent bonds are the attractive forces between the positively charged nuclei

of the bonded atoms and one or more pairs of electrons that are located between the atoms. Compounds are classified as ionic or molecular (covalent) on the basis of the bonds present in them.

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 **3.6.3**).

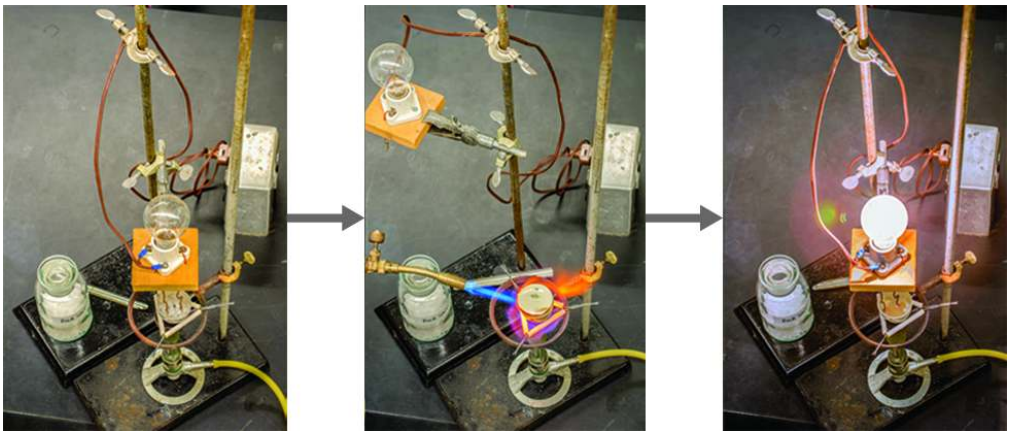


Figure **3.6.3**: Sodium chloride melts at 801 °C and conducts electricity when molten. (credit: modification of work by Mark Blaser and Matt Evans)

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

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

Example **3.6.3**: Predicting the Formula of an Ionic Compound

The gemstone sapphire (Figure **3.6.4**) 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 **3.6.4**: 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 3.6.3

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 **3.6.1**) 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 ($\mathbf{PO_4^{3-}}$) groups. The $\mathbf{PO_4^{3-}}$ 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 3.6.4: 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 $\mathbf{H_2PO_4^-}$. 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 $\mathbf{H_2PO_4^-}$ 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 3.6.4

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

Answer

Li_2O_2

Because an ionic compound is not made up of single, discrete molecules, it may not be properly symbolized using a *molecular* formula. Instead, ionic compounds must be symbolized by a formula indicating the *relative numbers* of its constituent ions. For compounds containing only monatomic ions (such as NaCl) and for many compounds containing polyatomic ions (such as $CaSO_4$), these formulas are just the empirical formulas introduced earlier in this chapter. However, the formulas for some ionic compounds containing polyatomic ions are not empirical formulas. For example, the ionic compound sodium oxalate is comprised of Na^+ and

$C_2O_4^{2-}$ ions combined in a 2:1 ratio, and its formula is written as $Na_2C_2O_4$. The subscripts in this formula are not the smallest-possible whole numbers, as each can be divided by 2 to yield the empirical formula, $NaCO_2$. This is not the accepted formula for sodium oxalate, however, as it does not accurately represent the compound's polyatomic anion, $C_2O_4^{2-}$.

Molecular Compounds

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

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

✔ Example 3.6.5: 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 3.6.5

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

a. SO_2
b. CaF_2
c. N_2H_4
d. $Al_2(SO_4)_3$

Answer a

molecular

Answer b

ionic

Answer c

molecular

Answer d

ionic

Summary

Metals (particularly those in groups 1 and 2) tend to lose the number of electrons that would leave them with the same number of electrons as in the preceding noble gas in the periodic table. By this means, a positively charged ion is formed. Similarly, nonmetals (especially those in groups 16 and 17, and, to a lesser extent, those in Group 15) can gain the number of electrons needed to provide atoms with the same number of electrons as in the next noble gas in the periodic table. Thus, nonmetals tend to form negative ions. Positively charged ions are called cations, and negatively charged ions are called anions. Ions can be either monatomic (containing only one atom) or polyatomic (containing more than one atom).

Compounds that contain ions are called ionic compounds. Ionic compounds generally form from metals and nonmetals. Compounds that do not contain ions, but instead consist of atoms bonded tightly together in molecules (uncharged groups of atoms that behave as a single unit), are called covalent compounds. Covalent compounds usually form from two or more nonmetals.

Glossary

covalent bond
attractive force between the nuclei of a molecule's atoms and pairs of electrons between the atoms

covalent compound
(also, molecular compound) composed of molecules formed by atoms of two or more different elements

ionic bond
electrostatic forces of attraction between the oppositely charged ions of an ionic compound

ionic compound
compound composed of cations and anions combined in ratios, yielding an electrically neutral substance

molecular compound
(also, covalent compound) composed of molecules formed by atoms of two or more different elements

monatomic ion
ion composed of a single atom

polyatomic ion
ion composed of more than one atom

oxyanion
polyatomic anion composed of a central atom bonded to oxygen atoms

This page titled 3.6: Molecular and Ionic Compounds is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

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

3.E: Electronic Structure and Periodic Properties (Exercises)

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

General Chemistry

These are homework exercises to accompany the Textmap created for "Chemistry" by OpenStax. Complementary General Chemistry question banks can be found for other Textmaps and can be accessed here. In addition to these publicly available questions, access to private problems bank for use in exams and homework is available to faculty only on an individual basis; please contact Delmar Larsen for an account with access permission.

6.1: Electromagnetic Energy

Q6.1.1

The light produced by a red neon sign is due to the emission of light by excited neon atoms. Qualitatively describe the spectrum produced by passing light from a neon lamp through a prism.

S6.1.1

The spectrum consists of colored lines, at least one of which (probably the brightest) is red.

S6.1.2

1.) Convert 614.5 nm into meters

$6.145nm = 6.145 \times 10^{-7}m$

6.2: The Bohr Model

Q6.2.1

Why is the electron in a Bohr hydrogen atom bound less tightly when it has a quantum number of 3 than when it has a quantum number of 1?

Q6.2.2

What does it mean to say that the energy of the electrons in an atom is quantized?

S6.2.2

Quantized energy means that the electrons can possess only certain discrete energy values; values between those quantized values are not permitted.

Q6.2.3

The spectra of hydrogen and of calcium are shown in[link]. What causes the lines in these spectra? Why are the colors of the lines different? Suggest a reason for the observation that the spectrum of calcium is more complicated than the spectrum of hydrogen

S6.2.3

Both involve a relatively heavy nucleus with electrons moving around it, although strictly speaking, the Bohr model works only for one-electron atoms or ions. According to classical mechanics, the Rutherford model predicts a miniature “solar system” with electrons moving about the nucleus in circular or elliptical orbits that are confined to planes. If the requirements of classical electromagnetic theory that electrons in such orbits would emit electromagnetic radiation are ignored, such atoms would be stable,

having constant energy and angular momentum, but would not emit any visible light (contrary to observation). If classical electromagnetic theory is applied, then the Rutherford atom would emit electromagnetic radiation of continually increasing frequency (contrary to the observed discrete spectra), thereby losing energy until the atom collapsed in an absurdly short time (contrary to the observed long-term stability of atoms). The Bohr model retains the classical mechanics view of circular orbits confined to planes having constant energy and angular momentum, but restricts these to quantized values dependent on a single quantum number, n. The orbiting electron in Bohr's model is assumed not to emit any electromagnetic radiation while moving about the nucleus in its stationary orbits, but the atom can emit or absorb electromagnetic radiation when the electron changes from one orbit to another. Because of the quantized orbits, such "quantum jumps" will produce discrete spectra, in agreement with observations.

6.3: Development of Quantum Theory

Q6.3.1

Answer the following questions:

a. Without using quantum numbers, describe the differences between the shells, subshells, and orbitals of an atom.
b. How do the quantum numbers of the shells, subshells, and orbitals of an atom differ?

Q6.3.2

Identify the subshell in which electrons with the following quantum numbers are found:

a. $n = 2$, $l = 1$
b. $n = 4$, $l = 2$
c. $n = 6$, $l = 0$

S6.3.2

(a) 2*p*; (b) 4*d*; (c) 6*s*

6.4: Electronic Structure of Atoms (Electron Configurations)

Q6.4.1

Read the labels of several commercial products and identify monatomic ions of at least four transition elements contained in the products. Write the complete electron configurations of these cations.

Q6.4.2

Read the labels of several commercial products and identify monatomic ions of at least six main group elements contained in the products. Write the complete electron configurations of these cations and anions.

S6.4.2

For example, Na^+: $1s^2 2s^2 2p^6$; Ca^{2+}: $1s^2 2s^2 2p^6$; Sn^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2$; F^-: $1s^2 2s^2 2p^6$; O^{2-}: $1s^2 2s^2 2p^6$; Cl^-: $1s^2 2s^2 2p^6 3s^2 3p^6$.

Q6.4.3

Using complete subshell notation (not abbreviations, $1s^2 2s^2 2p^6$, and so forth), predict the electron configuration of each of the following atoms:

a. C
b. P

S6.4.3

a.) $1s^2 2s^2 2p^2$

b.) $1s^2 2s^2 2p^6 3s^2 3p^3$

Q6.4.4

Using complete subshell notation ($1s^2 2s^2 2p^6$, and so forth), predict the electron configuration of each of the following atoms:

a. N
b. Si

S6.4.4

a. $1s^2 2s^2 2p^3$;
b. $1s^2 2s^2 2p^6 3s^2 3p^2$;

Q6.4.5

Is $1s^2 2s^2 2p^6$ the symbol for a macroscopic property or a microscopic property of an element? Explain your answer.

Q6.4.6

What additional information do we need to answer the question "Which ion has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6$"?

S6.4.6

The charge on the ion.

Q6.4.7

Draw the orbital diagram for the valence shell of each of the following atoms:

a. C
b. P

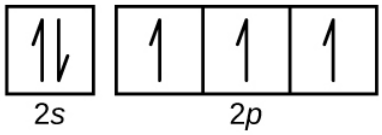
Q6.4.8

Use an orbital diagram to describe the electron configuration of the valence shell of each of the following atoms:

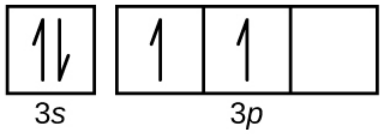
a. N
b. Si

S6.4.8

(a)



(b)



Q6.4.9

Using complete subshell notation ($1s^2 2s^2 2p^6$, and so forth), predict the electron configurations of the following ions.

a. N^{3-}
b. Ca^{2+}
c. S^{-}

Q6.4.10

Which atom has the electron configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^2$? Hint - how many electrons are in this atom?

S6.4.10

Zr

Q6.4.11

Which atom has the electron configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$?

S6.4.11

Co ; Cobalt

Q6.4.12

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?

S6.4.12

Rb^{+}, Se^{2-}

Q6.4.13

Which of the following atoms contains only three valence electrons: Li, B, N, F, Ne?

S6.4.13

B ; Boron

Q6.4.14

Which of the following has two unpaired electrons?

a. Mg
b. Si
c. S
d. Both Mg and S
e. Both Si and S.

S6.4.14

Although both (b) and (c) are correct, (e) encompasses both and is the best answer.

Q6.4.15

Which atom would be expected to have a half-filled 6*p* subshell?

S6.4.15

Bi ; Bismuth

Q6.4.16

Which atom would be expected to have a half-filled 4*s* subshell?

S6.4.16

K

Q6.4.17

In one area of Australia, the cattle did not thrive despite the presence of suitable forage. An investigation showed the cause to be the absence of sufficient cobalt in the soil. Cobalt forms cations in two oxidation states, Co^{2+} and Co^{3+}. How many electrons are in each of these ions? How many protons?

Q6.4.18

Thallium was used as a poison in the Agatha Christie mystery story “The Pale Horse.” Thallium has two possible cationic forms, +1 and +3. The +1 compounds are the more stable. How many electrons are in each of these ions? How many protons?

Q6.4.19

Write the electron configurations for the following atoms or ions:

a. B^{3+}
b. O^{-}
c. Cl^{3-}

Q6.4.20

Cobalt–60 and iodine–131 are radioactive isotopes commonly used in nuclear medicine. How many protons, neutrons, and electrons are in atoms of these isotopes?

S6.4.20

Co has 27 protons, 27 electrons, and 33 neutrons.

I has 53 protons, 53 electrons, and 78 neutrons.

6.5: Periodic Variations in Element Properties

Q6.5.1

Based on their positions in the periodic table, predict which has the smallest atomic radius: Mg, Sr, Si, Cl, I.

S6.5.1

Cl

Q6.5.2

Based on their positions in the periodic table, predict which has the largest atomic radius: Li, Rb, N, F, I.

Q6.5.3

Based on their positions in the periodic table, predict which has the largest first ionization energy: Mg, Ba, B, O, Te.

S6.5.3

O

Q6.5.4

Based on their positions in the periodic table, predict which has the smallest first ionization energy: Li, Cs, N, F, I.

Q6.5.5

Based on their positions in the periodic table, rank the following atoms in order of increasing first ionization energy: F, Li, N, Rb

S6.5.5

Rb < Li < N < F

Q6.5.6

Based on their positions in the periodic table, rank the following atoms or compounds in order of increasing first ionization energy: Mg, O, S, Si

Q6.5.7

Atoms of which group in the periodic table have a valence shell electron configuration of ns^2np^3?

S6.5.7

5A

Q6.5.8

Atoms of which group in the periodic table have a valence shell electron configuration of ns^2?

Q6.5.9

Based on their positions in the periodic table, list the following atoms in order of increasing radius: Mg, Ca, Rb, Cs.

S6.5.9

Mg < Ca < Rb < Cs

Q6.5.10

Based on their positions in the periodic table, list the following atoms in order of increasing radius: Sr, Ca, Si, Cl.

Q6.5.11

Based on their positions in the periodic table, list the following ions in order of increasing radius: K^+, Ca^{2+}, Al^{3+}, Si^{4+}.

S6.5.11

$Si^{4+} < Al^{3+} < Ca^{2+} < K^+$

Q6.5.12

List the following ions in order of increasing radius: Li^+, Mg^{2+}, Br^-, Te^{2-}.

Q6.5.15

Compare both the numbers of protons and electrons present in each to rank the following ions in order of increasing radius: As^{3-}, Br^-, K^+, Mg^{2+}.

S6.5.15

$Mg^{2+} < K^+ < Br^- < As^{3-}$

Q6.5.18

The ionic radii of the ions S^{2-}, Cl^-, and K^+ are 184, 181, 138 pm respectively. Explain why these ions have different sizes even though they contain the same number of electrons.

This page titled 3.E: Electronic Structure and Periodic Properties (Exercises) is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

CHAPTER OVERVIEW

4: Chemical Bonding and Molecular Geometry

A general chemistry Libretexts Textmap organized around the textbook
General Chemistry -Atoms First
By OpenStax

I II III IV V VI VII VIII IX X XI XII XIII XIV XV XVI XVII XVIII XIX XX XXI ● **Homework**

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.

4.1: Ionic Bonding

4.2: Covalent Bonding

4.3: Lewis Symbols and Structures

4.4: Molecular Structure and Polarity

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: Chemical Bonding and Molecular Geometry is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

4.1: Ionic Bonding

Learning Objectives

- Explain the formation of cations, anions, and ionic compounds
- Predict the charge of common metallic and nonmetallic elements, and write their electron configurations

As you have learned, ions are atoms or molecules bearing an electrical charge. A cation (a positive ion) forms when a neutral atom loses one or more electrons from its valence shell, and an anion (a negative ion) forms when a neutral atom gains one or more electrons in its valence shell.

Compounds composed of ions are called ionic compounds (or salts), and their constituent ions are held together by ionic bonds: electrostatic forces of attraction between oppositely charged cations and anions. The properties of ionic compounds shed some light on the nature of ionic bonds. Ionic solids exhibit a crystalline structure and tend to be rigid and brittle; they also tend to have high melting and boiling points, which suggests that ionic bonds are very strong. Ionic solids are also poor conductors of electricity for the same reason—the strength of ionic bonds prevents ions from moving freely in the solid state. Most ionic solids, however, dissolve readily in water. Once dissolved or melted, ionic compounds are excellent conductors of electricity and heat because the ions can move about freely.

Neutral atoms and their associated ions have very different physical and chemical properties. Sodium *atoms* form sodium metal, a soft, silvery-white metal that burns vigorously in air and reacts explosively with water. Chlorine *atoms* form chlorine gas, Cl_2, a yellow-green gas that is extremely corrosive to most metals and very poisonous to animals and plants. The vigorous reaction between the elements sodium and chlorine forms the white, crystalline compound sodium chloride, common table salt, which contains sodium *cations* and chloride *anions* (Figure Figure **4.1.1**). The compound composed of these ions exhibits properties entirely different from the properties of the elements sodium and chlorine. Chlorine is poisonous, but sodium chloride is essential to life; sodium atoms react vigorously with water, but sodium chloride simply dissolves in water.



Figure **4.1.1**: (a) Sodium is a soft metal that must be stored in mineral oil to prevent reaction with air or water. (b) Chlorine is a pale yellow-green gas. (c) When combined, they form white crystals of sodium chloride (table salt). (credit a: modification of work by "Jurii"/Wikimedia Commons)

The Formation of Ionic Compounds

Binary ionic compounds are composed of just two elements: a metal (which forms the cations) and a nonmetal (which forms the anions). For example, NaCl is a binary ionic compound. We can think about the formation of such compounds in terms of the periodic properties of the elements. Many metallic elements have relatively low ionization potentials and lose electrons easily. These elements lie to the left in a period or near the bottom of a group on the periodic table. Nonmetal atoms have relatively high electron affinities and thus readily gain electrons lost by metal atoms, thereby filling their valence shells. Nonmetallic elements are found in the upper-right corner of the periodic table.

As all substances must be electrically neutral, the total number of positive charges on the cations of an ionic compound must equal the total number of negative charges on its anions. The formula of an ionic compound represents the simplest ratio of the numbers of ions necessary to give identical numbers of positive and negative charges. For example, the formula for aluminum oxide, Al_2O_3, indicates that this ionic compound contains two aluminum cations, Al^{3+}, for every three oxide anions, O^{2-} [thus, $(2 \times +3) + (3 \times -2) = 0$].

It is important to note, however, that the formula for an ionic compound does *not* represent the physical arrangement of its ions. It is incorrect to refer to a sodium chloride (NaCl) "molecule" because there is not a single ionic bond, per se, between any specific pair of sodium and chloride ions. The attractive forces between ions are isotropic—the same in all directions—meaning that any particular ion is equally attracted to all of the nearby ions of opposite charge. This results in the ions arranging themselves into a tightly bound, three-dimensional lattice structure. Sodium chloride, for example, consists of a regular arrangement of equal numbers of Na^+ cations and Cl^- anions (Figure Figure **4.1.2**).



Figure **4.1.2**: The atoms in sodium chloride (common table salt) are arranged to (a) maximize opposite charges interacting. The smaller spheres represent sodium ions, the larger ones represent chloride ions. In the expanded view (b), the geometry can be seen more clearly. Note that each ion is "bonded" to all of the surrounding ions—six in this case.

Two diagrams are shown and labeled "a" and "b." Diagram a shows a cube made up of twenty-seven alternating purple and green spheres. The purple spheres are smaller than the green spheres. Diagram b shows the same spheres, but this time, they are spread out and connected in three dimensions by white rods. The purple spheres are labeled "N superscript postive sign" while the green are labeled "C l superscript negative sign."

The strong electrostatic attraction between Na^+ and Cl^- ions holds them tightly together in solid NaCl. It requires 769 kJ of energy to dissociate one mole of solid NaCl into separate gaseous Na^+ and Cl^- ions:

$$\mathrm{NaCl}(s) \longrightarrow \mathrm{Na}^+(g) + \mathrm{Cl}^-(g) \quad \Delta H = 769\ \mathrm{kJ}$$

Electronic Structures of Cations

When forming a cation, an atom of a main group element tends to lose all of its valence electrons, thus assuming the electronic structure of the noble gas that precedes it in the periodic table. For groups 1 (the alkali metals) and 2 (the alkaline earth metals), the group numbers are equal to the numbers of valence shell electrons and, consequently, to the charges of the cations formed from atoms of these elements when all valence shell electrons are removed. For example, calcium is a group 2 element whose neutral atoms have 20 electrons and a ground state electron configuration of $1s^22s^22p^63s^23p^64s^2$. When a Ca atom loses both of its valence electrons, the result is a cation with 18 electrons, a 2+ charge, and an electron configuration of $1s^22s^22p^63s^23p^6$. The Ca^{2+} ion is therefore isoelectronic with the noble gas Ar.

For groups 12–17, the group numbers exceed the number of valence electrons by 10 (accounting for the possibility of full *d* subshells in atoms of elements in the fourth and greater periods). Thus, the charge of a cation formed by the loss of all valence electrons is equal to the group number minus 10. For example, aluminum (in group 13) forms 3+ ions (Al^{3+}).

Exceptions to the expected behavior involve elements toward the bottom of the groups. In addition to the expected ions Tl^{3+}, Sn^{4+}, Pb^{4+}, and Bi^{5+}, a partial loss of these atoms' valence shell electrons can also lead to the formation of Tl^+, Sn^{2+}, Pb^{2+}, and Bi^{3+} ions. The formation of these 1+, 2+, and 3+ cations is ascribed to the inert pair effect, which reflects the relatively low energy of the valence *s*-electron pair for atoms of the heavy elements of groups 13, 14, and 15. Mercury (group 12) also exhibits an unexpected behavior: it forms a diatomic ion, $\mathrm{Hg_2}^{2+}$ (an ion formed from two mercury atoms, with an Hg-Hg bond), in addition to the expected monatomic ion Hg^{2+} (formed from only one mercury atom).

Transition and inner transition metal elements behave differently than main group elements. Most transition metal cations have 2+ or 3+ charges that result from the loss of their outermost *s* electron(s) first, sometimes followed by the loss of one or two *d* electrons from the next-to-outermost shell. For example, iron ($1s^22s^22p^63s^23p^63d^64s^2$) forms the ion Fe^{2+} ($1s^22s^22p^63s^23p^63d^6$) by the loss of the 4*s* electrons and the ion Fe^{3+} ($1s^22s^22p^63s^23p^63d^5$) by the loss of the 4*s* electrons and one of the 3*d* electrons. Although the *d* orbitals of the transition elements are—according to the Aufbau principle—the last to fill when building up electron configurations, the outermost *s* electrons are the first to be lost when these atoms ionize. When the inner transition metals form ions, they usually have a 3+ charge, resulting from the loss of their outermost *s* electrons and a *d* or *f* electron.

✔ Example **4.1.1**: Determining the Electronic Structures of Cations

There are at least 14 elements categorized as "essential trace elements" for the human body. They are called "essential" because they are required for healthy bodily functions, "trace" because they are required only in small amounts, and "elements" in spite of the fact that they are really ions. Two of these essential trace elements, chromium and zinc, are required as Cr^{3+} and Zn^{2+}. Write the electron configurations of these cations.

Solution

First, write the electron configuration for the neutral atoms:

- Zn: [Ar]$3d^{10}4s^2$
- Cr: [Ar]$3d^5 4s^1$

Next, remove electrons from the highest energy orbital. For the transition metals, electrons are removed from the *s* orbital first and then from the *d* orbital. For the *p*-block elements, electrons are removed from the *p* orbitals and then from the *s* orbital. Zinc is a member of group 12, so it should have a charge of 2+, and thus loses only the two electrons in its *s* orbital. Chromium is a transition element and should lose its *s* electrons and then its *d* electrons when forming a cation. Thus, we find the following electron configurations of the ions:

- Zn^{2+}: [Ar]$3d^{10}$
- Cr^{3+}: [Ar]$3d^3$

? Exercise 4.1.1

Potassium and magnesium are required in our diet. Write the electron configurations of the ions expected from these elements.

Answer

K^+: [Ar], Mg^{2+}: [Ne]

Electronic Structures of Anions

Most monatomic anions form when a neutral nonmetal atom gains enough electrons to completely fill its outer *s* and *p* orbitals, thereby reaching the electron configuration of the next noble gas. Thus, it is simple to determine the charge on such a negative ion: The charge is equal to the number of electrons that must be gained to fill the *s* and *p* orbitals of the parent atom. Oxygen, for example, has the electron configuration $1s^2 2s^2 2p^4$, whereas the oxygen anion has the electron configuration of the noble gas neon (Ne), $1s^2 2s^2 2p^6$. The two additional electrons required to fill the valence orbitals give the oxide ion the charge of 2– (O^{2-}).

✓ Example 4.1.2: Determining the Electronic Structure of Anions

Selenium and iodine are two essential trace elements that form anions. Write the electron configurations of the anions.

Solution

Se^{2-}: [Ar]$3d^{10}4s^2 4p^6$

I^-: [Kr]$4d^{10}5s^2 5p^6$

? Exercise 4.1.2

Write the electron configurations of a phosphorus atom and its negative ion. Give the charge on the anion.

Answer

P: [Ne]$3s^2 3p^3$

P^{3-}: [Ne]$3s^2 3p^6$

Summary

Atoms gain or lose electrons to form ions with particularly stable electron configurations. The charges of cations formed by the representative metals may be determined readily because, with few exceptions, the electronic structures of these ions have either a

noble gas configuration or a completely filled electron shell. The charges of anions formed by the nonmetals may also be readily determined because these ions form when nonmetal atoms gain enough electrons to fill their valence shells.

Glossary

inert pair effect

tendency of heavy atoms to form ions in which their valence *s* electrons are not lost

ionic bond

strong electrostatic force of attraction between cations and anions in an ionic compound

---

This page titled 4.1: Ionic Bonding is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

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

4.2: Covalent Bonding

Learning Objectives

- Describe the formation of covalent bonds
- Define electronegativity and assess the polarity of covalent bonds

In ionic compounds, electrons are transferred between atoms of different elements to form ions. But this is not the only way that compounds can be formed. Atoms can also make chemical bonds by sharing electrons between each other. Such bonds are called covalent bonds. Covalent bonds are formed between two atoms when both have similar tendencies to attract electrons to themselves (i.e., when both atoms have identical or fairly similar ionization energies and electron affinities). For example, two hydrogen atoms bond covalently to form an H_2 molecule; each hydrogen atom in the H_2 molecule has two electrons stabilizing it, giving each atom the same number of valence electrons as the noble gas He.

Compounds that contain covalent bonds exhibit different physical properties than ionic compounds. Because the attraction between molecules, which are electrically neutral, is weaker than that between electrically charged ions, covalent compounds generally have much lower melting and boiling points than ionic compounds. In fact, many covalent compounds are liquids or gases at room temperature, and, in their solid states, they are typically much softer than ionic solids. Furthermore, whereas ionic compounds are good conductors of electricity when dissolved in water, most covalent compounds, being electrically neutral, are poor conductors of electricity in any state.

Formation of Covalent Bonds

Nonmetal atoms frequently form covalent bonds with other nonmetal atoms. For example, the hydrogen molecule, H_2, contains a covalent bond between its two hydrogen atoms. Figure **4.2.1** illustrates why this bond is formed. Starting on the far right, we have two separate hydrogen atoms with a particular potential energy, indicated by the red line. Along the *x*-axis is the distance between the two atoms. As the two atoms approach each other (moving left along the *x*-axis), their valence orbitals (1*s*) begin to overlap. The single electrons on each hydrogen atom then interact with both atomic nuclei, occupying the space around both atoms. The strong attraction of each shared electron to both nuclei stabilizes the system, and the potential energy decreases as the bond distance decreases. If the atoms continue to approach each other, the positive charges in the two nuclei begin to repel each other, and the potential energy increases. The bond length is determined by the distance at which the lowest potential energy is achieved.

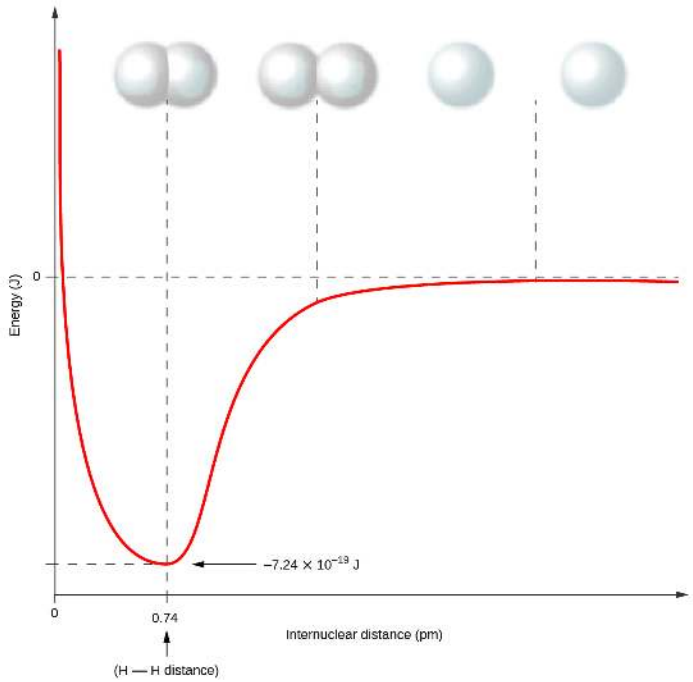


Figure **4.2.1**: *The potential energy of two separate hydrogen atoms (right) decreases as they approach each other, and the single electrons on each atom are shared to form a covalent bond. The bond length is the internuclear distance at which the lowest potential energy is achieved.*

It is essential to remember that energy must be added to break chemical bonds (an endothermic process), whereas forming chemical bonds releases energy (an exothermic process). In the case of H_2, the covalent bond is very strong; a large amount of energy, 436 kJ, must be added to break the bonds in one mole of hydrogen molecules and cause the atoms to separate:

$$\mathrm{H_2}(g) \longrightarrow 2\,\mathrm{H}(g) \quad \Delta H = 436\ \mathrm{kJ}$$

Conversely, the same amount of energy is released when one mole of H_2 molecules forms from two moles of H atoms:

$$2\,\mathrm{H}(g) \longrightarrow \mathrm{H_2}(g) \quad \Delta H = -436\ \mathrm{kJ}$$

Pure vs. Polar Covalent Bonds

If the atoms that form a covalent bond are identical, as in H_2, Cl_2, and other diatomic molecules, then the electrons in the bond must be shared equally. We refer to this as a pure covalent bond. Electrons shared in pure covalent bonds have an equal probability of being near each nucleus. In the case of Cl_2, each atom starts off with seven valence electrons, and each Cl shares one electron with the other, forming one covalent bond:

$$\mathrm{Cl} + \mathrm{Cl} \longrightarrow \mathrm{Cl_2}$$

The total number of electrons around each individual atom consists of six nonbonding electrons and two shared (i.e., bonding) electrons for eight total electrons, matching the number of valence electrons in the noble gas argon. Since the bonding atoms are identical, Cl_2 also features a pure covalent bond.

When the atoms linked by a covalent bond are different, the bonding electrons are shared, but no longer equally. Instead, the bonding electrons are more attracted to one atom than the other, giving rise to a shift of electron density toward that atom. This unequal distribution of electrons is known as a polar covalent bond, characterized by a partial positive charge on one atom and a partial negative charge on the other. The atom that attracts the electrons more strongly acquires the partial negative charge and vice versa. For example, the electrons in the H–Cl bond of a hydrogen chloride molecule spend more time near the chlorine atom than near the hydrogen atom. Thus, in an HCl molecule, the chlorine atom carries a partial negative charge and the hydrogen atom has a partial positive charge. Figure **4.2.2** shows the distribution of electrons in the H–Cl bond. Note that the shaded area around Cl is much larger than it is around H. Compare this to Figure **4.2.1**, which shows the even distribution of electrons in the H_2 nonpolar bond.

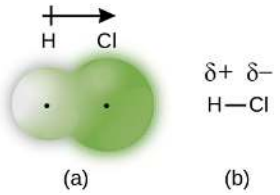


Figure **4.2.2**: (a) The distribution of electron density in the HCl molecule is uneven. The electron density is greater around the chlorine nucleus. The small, black dots indicate the location of the hydrogen and chlorine nuclei in the molecule. (b) Symbols δ+ and δ– indicate the polarity of the H–Cl bond.

We sometimes designate the positive and negative atoms in a polar covalent bond using a lowercase Greek letter "delta," δ, with a plus sign or minus sign to indicate whether the atom has a partial positive charge (δ+) or a partial negative charge (δ–). This symbolism is shown for the H–Cl molecule in Figure **4.2.2***b*.

Electronegativity

Whether a bond is nonpolar or polar covalent is determined by a property of the bonding atoms called electronegativity. Electronegativity is a measure of the tendency of an atom to attract electrons (or electron density) towards itself. It determines how the shared electrons are distributed between the two atoms in a bond. The more strongly an atom attracts the electrons in its bonds, the larger its electronegativity. Electrons in a polar covalent bond are shifted toward the more electronegative atom; thus, the more electronegative atom is the one with the partial negative charge. The greater the difference in electronegativity, the more polarized the electron distribution and the larger the partial charges of the atoms.

Figure **4.2.3** shows the electronegativity values of the elements as proposed by one of the most famous chemists of the twentieth century: Linus Pauling. In general, electronegativity increases from left to right across a period in the periodic table and decreases down a group. Thus, the nonmetals, which lie in the upper right, tend to have the highest electronegativities, with fluorine the most electronegative element of all (EN = 4.0). Metals tend to be less electronegative elements, and the group 1 metals have the lowest electronegativities. Note that noble gases are excluded from this figure because these atoms usually do not share electrons with others atoms since they have a full valence shell. (While noble gas compounds such as XeO_2 do exist, they can only be formed under extreme conditions, and thus they do not fit neatly into the general model of electronegativity.)

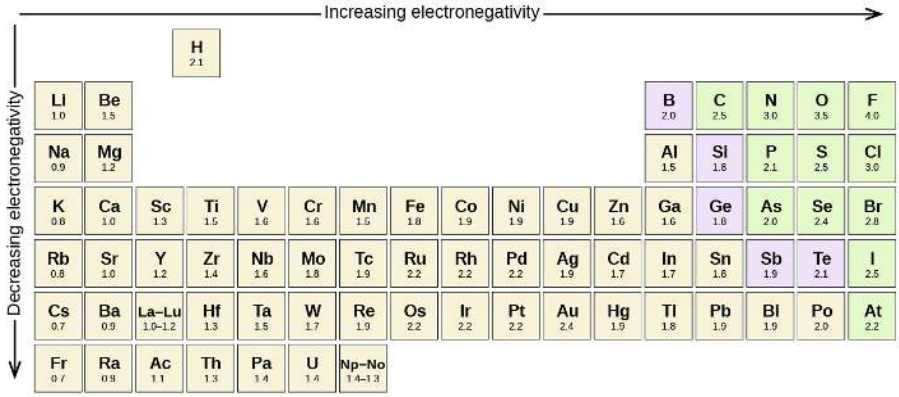


Figure **4.2.3**: The electronegativity values derived by Pauling follow predictable periodic trends with the higher electronegativities toward the upper right of the periodic table.

Linus Pauling

Linus Pauling is the only person to have received two unshared (individual) Nobel Prizes: one for chemistry in 1954 for his work on the nature of chemical bonds and one for peace in 1962 for his opposition to weapons of mass destruction. He developed many of the theories and concepts that are foundational to our current understanding of chemistry, including electronegativity and resonance structures.



Linus Pauling (1901–1994) made many important contributions to the field of chemistry. He was also a prominent activist, publicizing issues related to health and nuclear weapons.

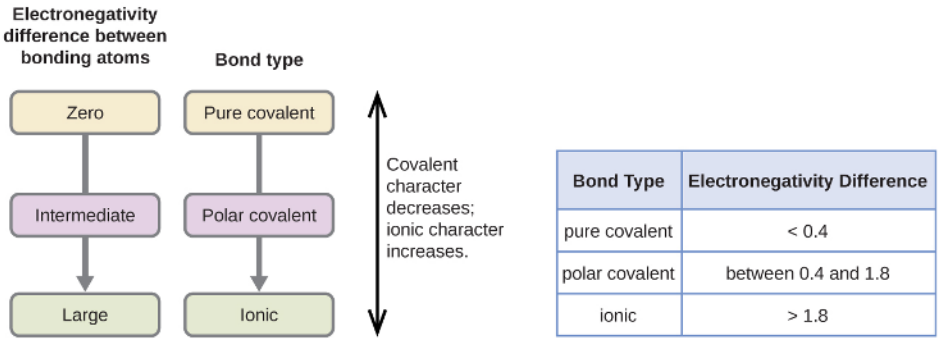
Pauling also contributed to many other fields besides chemistry. His research on sickle cell anemia revealed the cause of the disease—the presence of a genetically inherited abnormal protein in the blood—and paved the way for the field of molecular genetics. His work was also pivotal in curbing the testing of nuclear weapons; he proved that radioactive fallout from nuclear testing posed a public health risk.

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.

Electronegativity and Bond Type

The absolute value of the difference in electronegativity (ΔEN) of two bonded atoms provides a rough measure of the polarity to be expected in the bond and, thus, the bond type. When the difference is very small or zero, the bond is covalent and nonpolar. When it is large, the bond is polar covalent or ionic. The absolute values of the electronegativity differences between the atoms in the bonds H–H, H–Cl, and Na–Cl are 0 (nonpolar), 0.9 (polar covalent), and 2.1 (ionic), respectively. The degree to which electrons are shared between atoms varies from completely equal (pure covalent bonding) to not at all (ionic bonding). Figure **4.2.4** shows the relationship between electronegativity difference and bond type.



Bond Type	Electronegativity Difference
pure covalent	< 0.4
polar covalent	between 0.4 and 1.8
ionic	> 1.8

Figure **4.2.4**: As the electronegativity difference increases between two atoms, the bond becomes more ionic.

A rough approximation of the electronegativity differences associated with covalent, polar covalent, and ionic bonds is shown in Figure **4.2.4**. This table is just a general guide, however, with many exceptions. For example, the H and F atoms in HF have an electronegativity difference of 1.9, and the N and H atoms in NH_3 a difference of 0.9, yet both of these compounds form bonds that are considered polar covalent. Likewise, the Na and Cl atoms in NaCl have an electronegativity difference of 2.1, and the Mn and I atoms in MnI_2 have a difference of 1.0, yet both of these substances form ionic compounds.

The best guide to the covalent or ionic character of a bond is to consider the types of atoms involved and their relative positions in the periodic table. Bonds between two nonmetals are generally covalent; bonding between a metal and a nonmetal is often ionic.

Some compounds contain both covalent and ionic bonds. The atoms in polyatomic ions, such as OH^-, NO_3^-, and NH_4^+, are held together by polar covalent bonds. However, these polyatomic ions form ionic compounds by combining with ions of opposite charge. For example, potassium nitrate, KNO_3, contains the K^+ cation and the polyatomic NO_3^- anion. Thus, bonding in potassium nitrate is ionic, resulting from the electrostatic attraction between the ions K^+ and NO_3^-, as well as covalent between the nitrogen and oxygen atoms in NO_3^-.

Example 4.2.1: Electronegativity and Bond Polarity

Bond polarities play an important role in determining the structure of proteins. Using the electronegativity values in Table A2, arrange the following covalent bonds—all commonly found in amino acids—in order of increasing polarity. Then designate the positive and negative atoms using the symbols δ+ and δ–:

C–H, C–N, C–O, N–H, O–H, S–H

Solution

The polarity of these bonds increases as the absolute value of the electronegativity difference increases. The atom with the δ– designation is the more electronegative of the two. Table 4.2.1 shows these bonds in order of increasing polarity.

Table 4.2.1: 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 4.2.1

Silicones are polymeric compounds containing, among others, the following types of covalent bonds: Si–O, Si–C, C–H, and C–C. Using the electronegativity values in Figure 4.2.3, 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	$\overset{\delta-}{C}-\overset{\delta+}{H}$
Si–C	0.7	$\overset{\delta+}{Si}-\overset{\delta-}{C}$
Si–O	1.7	$\overset{\delta+}{Si}-\overset{\delta-}{O}$

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

---

This page titled 4.2: Covalent Bonding is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

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

4.3: 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.

Lewis Symbols

We use Lewis symbols to describe valence electron configurations of atoms and monatomic ions. A Lewis symbol consists of an elemental symbol surrounded by one dot for each of its valence electrons:



Figure **4.3.1** shows the Lewis symbols for the elements of the third period of the periodic table. Electron dots are typically arranged in four pairs located on the four "sides" of the atomic symbol.

Atoms	Electronic Configuration	Lewis Symbol
sodium	$[Ne]3s^1$	Na ·
magnesium	$[Ne]3s^2$	· Mg ·
aluminum	$[Ne]3s^23p^1$	· Al ·
silicon	$[Ne]3s^23p^2$	· Si ·
phosphorus	$[Ne]3s^23p^3$	· P ·
sulfur	$[Ne]3s^23p^4$	: S ·
chlorine	$[Ne]3s^23p^5$	: Cl ·
argon	$[Ne]3s^23p^6$	: Ar :

Figure **4.3.1**: Lewis symbols illustrating the number of valence electrons for each element in the third period of the periodic table.

Lewis symbols can be used to illustrate the formation of cations from atoms, as shown here for sodium and calcium:



Likewise, they can be used to show the formation of anions from atoms, as shown here for chlorine and sulfur:



Figure **4.3.2** demonstrates the use of Lewis symbols to show the transfer of electrons during the formation of ionic compounds.

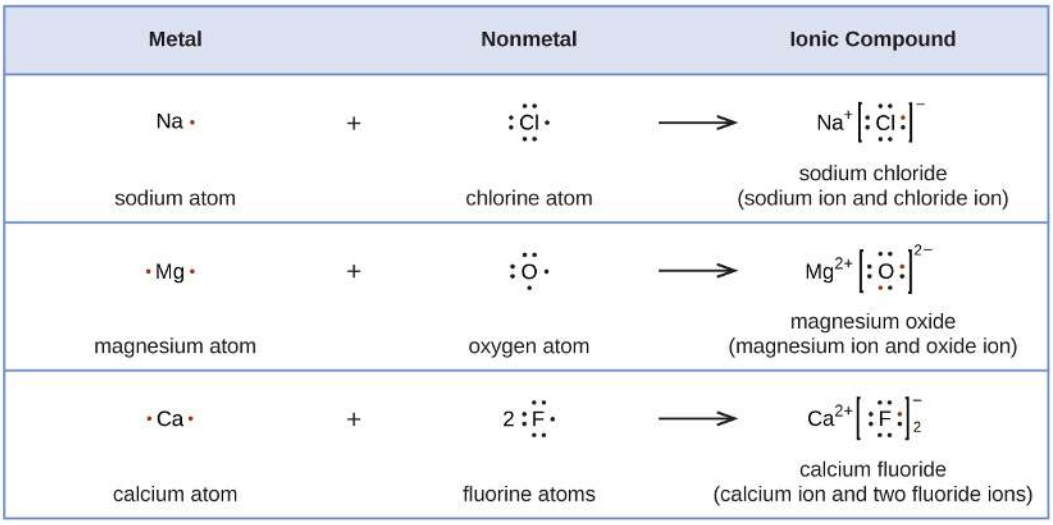
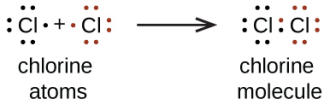


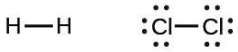
Figure **4.3.2**: Cations are formed when atoms lose electrons, represented by fewer Lewis dots, whereas anions are formed by atoms gaining electrons. The total number of electrons does not change.

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:

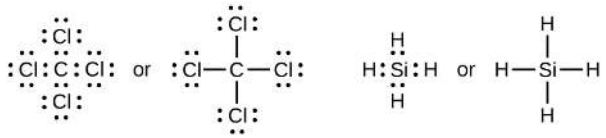


In the Lewis model, a single shared pair of electrons is a single bond. Each Cl atom interacts with eight valence electrons total: the six in the lone pairs and the two in the single bond.

The Octet Rule

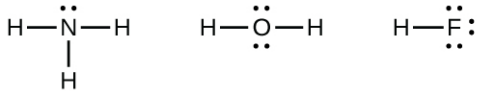
The other halogen molecules (F_2, Br_2, I_2, and At_2) form bonds like those in the chlorine molecule: one single bond between atoms and three lone pairs of electrons per atom. This allows each halogen atom to have a noble gas electron configuration. The tendency of main group atoms to form enough bonds to obtain eight valence electrons is known as the octet rule.

The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons); this is especially true of the nonmetals of the second period of the periodic table (C, N, O, and F). For example, each atom of a group 14 element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming four covalent bonds, as illustrated here for carbon in CCl_4 (carbon tetrachloride) and silicon in SiH_4 (silane). Because hydrogen only needs two electrons to fill its valence shell, it is an exception to the octet rule and only needs to form one bond. The transition elements and inner transition elements also do not follow the octet rule since they have d and f electrons involved in their valence shells.



carbon tetrachloride silane

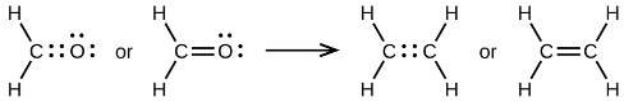
Group 15 elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form three covalent bonds, as in NH_3 (ammonia). Oxygen and other atoms in group 16 obtain an octet by forming two covalent bonds:



ammonia Water hydrogen fluoride

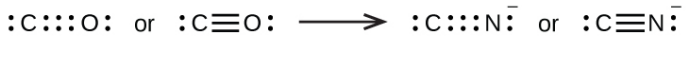
Double and Triple Bonds

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

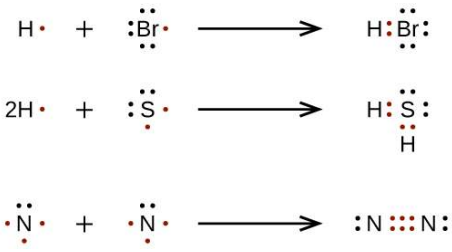
A triple bond forms when three electron pairs are shared by a pair of atoms, as in carbon monoxide (CO) and the cyanide ion (CN^-):



carbon monoxide cyanide ion

Writing Lewis Structures with the Octet Rule

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



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

1. Determine the total number of valence (outer shell) electrons among all the atoms. For cations, subtract one electron for each positive charge. For anions, add one electron for each negative charge.
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom. (Generally, the least electronegative element should be placed in the center.) Connect each atom to the central atom with a single bond (one electron pair).

3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen), completing an octet around each atom.
4. Place all remaining electrons on the central atom.
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

Let us determine the Lewis structures of SiH_4, CHO_2^-, NO^+, and OF_2 as examples in following this procedure:

1. Determine the total number of valence (outer shell) electrons in the molecule or ion.
   - For a molecule, we add the number of valence electrons on each atom in the molecule:

$$\begin{aligned} &SiH_4 && (4.3.1)\\ &\text{Si: 4 valence electrons/atom} \times \text{1 atom} = 4 && (4.3.2)\\ &+\text{H: 1 valence electron/atom} \times \text{4 atoms} = 4 && (4.3.3)\\ &\qquad = \text{8 valence electrons} && (4.3.4)\end{aligned}$$

   - 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):

$$\begin{aligned} &CHO_2^-\\ &\text{C: 4 valence electrons/atom} \times \text{1 atom} = 4\\ &\text{H: 1 valence electron/atom} \times \text{1 atom} = 1\\ &\text{O: 6 valence electrons/atom} \times \text{2 atoms} = 12\\ &+ \qquad \text{1 additional electron} = 1\\ &\qquad = \text{18 valence electrons}\end{aligned}$$

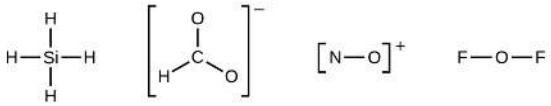
   - For a *positive ion*, such as NO^+, we add the number of valence electrons on the atoms in the ion and then subtract the number of positive charges on the ion (one electron is lost for each single positive charge) from the total number of valence electrons:

$$\begin{aligned} &NO^+\\ &\text{N: 5 valence electrons/atom} \times \text{1 atom} = 5\\ &\text{O: 6 valence electron/atom} \times \text{1 atom} = 6\\ &+ -1 \text{ electron (positive charge)} \quad = -1\\ &\qquad = \text{10 valence electrons}\end{aligned}$$

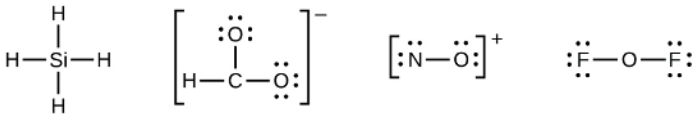
   - Since OF_2 is a neutral molecule, we simply add the number of valence electrons:

$$\begin{aligned} &OF_2\\ &\text{O: 6 valence electrons/atom} \times \text{1 atom} = 6\\ &+ \text{F: 7 valence electrons/atom} \times \text{2 atoms} = 14\\ &\qquad = \text{20 valence electrons}\end{aligned}$$

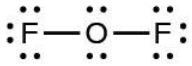
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond. (Note that we denote ions with brackets around the structure, indicating the charge outside the brackets:)



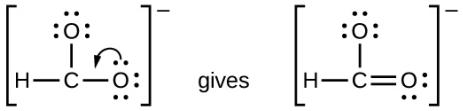
3. When several arrangements of atoms are possible, as for CHO_2^-, we must use experimental evidence to choose the correct one. In general, the less electronegative elements are more likely to be central atoms. In CHO_2^-, the less electronegative carbon atom occupies the central position with the oxygen and hydrogen atoms surrounding it. Other examples include P in $POCl_3$, S in SO_2, and Cl in ClO_4^-. An exception is that hydrogen is almost never a central atom. As the most electronegative element, fluorine also cannot be a central atom.
4. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.
   - There are no remaining electrons on SiH_4, so it is unchanged:



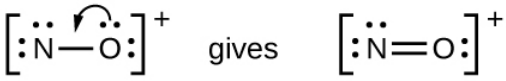
5. Place all remaining electrons on the central atom.
   - For SiH_4, CHO_2^-, and NO^+, there are no remaining electrons; we already placed all of the electrons determined in Step 1.
   - For OF_2, we had 16 electrons remaining in Step 3, and we placed 12, leaving 4 to be placed on the central atom:



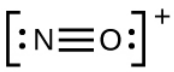
6. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.
   - SiH_4: Si already has an octet, so nothing needs to be done.
   - CHO_2^-: We have distributed the valence electrons as lone pairs on the oxygen atoms, but the carbon atom lacks an octet:



- NO^+: For this ion, we added eight outer electrons, but neither atom has an octet. We cannot add any more electrons since we have already used the total that we found in Step 1, so we must move electrons to form a multiple bond:



- This still does not produce an octet, so we must move another pair, forming a triple bond:



- In OF_2, each atom has an octet as drawn, so nothing changes.

Example 4.3.1: Writing Lewis Structures

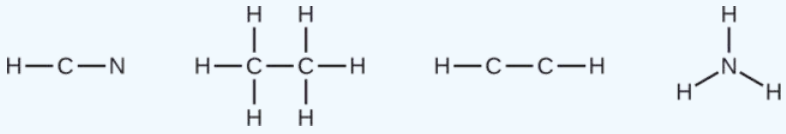
NASA's Cassini-Huygens mission detected a large cloud of toxic hydrogen cyanide (HCN) on Titan, one of Saturn's moons. Titan also contains ethane (H_3CCH_3), acetylene (HCCH), and ammonia (NH_3). What are the Lewis structures of these molecules?

Solution

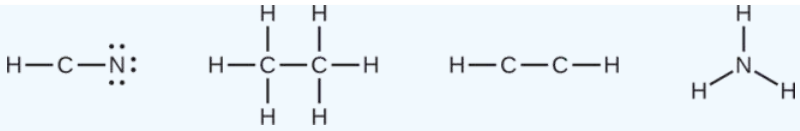
Calculate the number of valence electrons.

- HCN: (1 × 1) + (4 × 1) + (5 × 1) = 10
- H_3CCH_3: (1 × 3) + (2 × 4) + (1 × 3) = 14
- HCCH: (1 × 1) + (2 × 4) + (1 × 1) = 10
- NH_3: (5 × 1) + (3 × 1) = 8

Draw a skeleton and connect the atoms with single bonds. Remember that H is never a central atom:

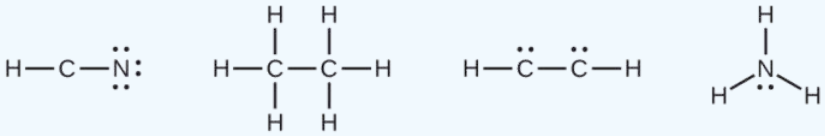


Where needed, distribute electrons to the terminal atoms:



- HCN: six electrons placed on N
- H_3CCH_3: no electrons remain
- HCCH: no terminal atoms capable of accepting electrons
- NH_3: no terminal atoms capable of accepting electrons

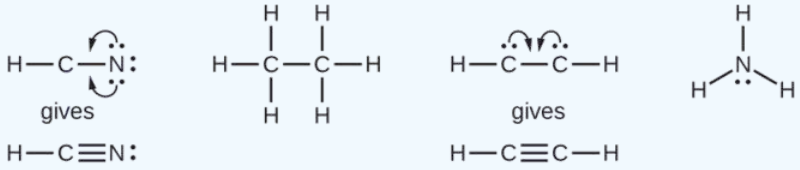
Where needed, place remaining electrons on the central atom:



- HCN: no electrons remain
- H_3CCH_3: no electrons remain
- HCCH: four electrons placed on carbon
- NH_3: two electrons placed on nitrogen

Where needed, rearrange electrons to form multiple bonds in order to obtain an octet on each atom:

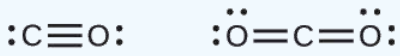
- HCN: form two more C–N bonds
- H_3CCH_3: all atoms have the correct number of electrons
- HCCH: form a triple bond between the two carbon atoms
- NH_3: all atoms have the correct number of electrons



Exercise 4.3.1

Both carbon monoxide, CO, and carbon dioxide, CO_2, are products of the combustion of fossil fuels. Both of these gases also cause problems: CO is toxic and CO_2 has been implicated in global climate change. What are the Lewis structures of these two molecules?

Answer



Fullerene Chemistry

Carbon soot has been known to man since prehistoric times, but it was not until fairly recently that the molecular structure of the main component of soot was discovered. In 1996, the Nobel Prize in Chemistry was awarded to Richard Smalley, Robert Curl, and Harold Kroto for their work in discovering a new form of carbon, the C_{60} buckminsterfullerene molecule. An entire class of compounds, including spheres and tubes of various shapes, were discovered based on C_{60}. This type of molecule, called a fullerene, consists of a complex network of single- and double-bonded carbon atoms arranged in such a way that each carbon atom obtains a full octet of electrons. Because of their size and shape, fullerenes can encapsulate other molecules, so they have shown potential in various applications from hydrogen storage to targeted drug delivery systems. They also possess unique electronic and optical properties that have been put to good use in solar powered devices and chemical sensors.

Exceptions to the Octet Rule

Many covalent molecules have central atoms that do not have eight electrons in their Lewis structures. We will focus on structures that follow the octet rule for this course, but do be aware that there are structures that follow different rules. This can make online searches of structures incorrect, so do be careful! 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.

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. Hydrogen only needs 2 electrons to obey the "octet rule." 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 4.3: Lewis Symbols and Structures is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

4.4: 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 **4.4.1**). A bond angle is the angle between any two bonds that include a common atom, usually measured in degrees. A bond distance (or bond length) is the distance between the nuclei of two bonded atoms along the straight line joining the nuclei. Bond distances are measured in Ångstroms (1 Å = 10^{-10} m) or picometers (1 pm = 10^{-12} m, 100 pm = 1 Å).

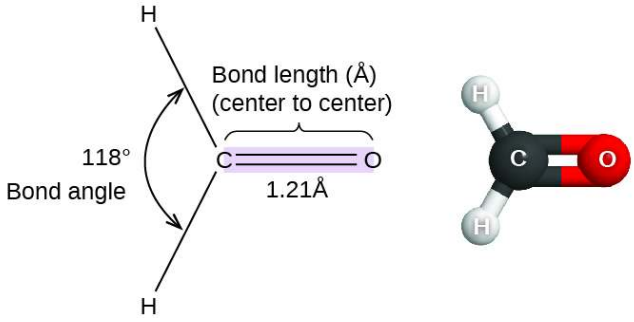


Figure **4.4.1**: Bond distances (lengths) and angles are shown for the formaldehyde molecule, H_2CO.

VSEPR Theory

Valence shell electron-pair repulsion theory (VSEPR theory) enables us to predict the molecular structure, including approximate bond angles around a central atom, of a molecule from an examination of the number of bonds and lone electron pairs in its Lewis structure. The VSEPR model assumes that electron pairs in the valence shell of a central atom will adopt an arrangement that minimizes repulsions between these electron pairs by maximizing the distance between them. The electrons in the valence shell of a central atom form either bonding pairs of electrons, located primarily between bonded atoms, or lone pairs. The electrostatic repulsion of these electrons is reduced when the various regions of high electron density assume positions as far from each other as possible.

VSEPR theory predicts the arrangement of electron pairs around each central atom and, usually, the correct arrangement of atoms in a molecule. We should understand, however, that the theory only considers electron-pair repulsions. Other interactions, such as nuclear-nuclear repulsions and nuclear-electron attractions, are also involved in the final arrangement that atoms adopt in a particular molecular structure.

As a simple example of VSEPR theory, let us predict the structure of a gaseous BeF_2 molecule. The Lewis structure of BeF_2 (Figure **4.4.2**) shows only two electron pairs around the central beryllium atom. With two bonds and no lone pairs of electrons on the central atom, the bonds are as far apart as possible, and the electrostatic repulsion between these regions of high electron density is reduced to a minimum when they are on opposite sides of the central atom. The bond angle is 180° (Figure **4.4.2**).

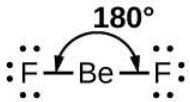


Figure **4.4.2**: The BeF_2 molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the Be atom.

Figure **4.4.3** illustrates this and other electron-pair geometries that minimize the repulsions among regions of high electron density (bonds and/or lone pairs). Two regions of electron density around a central atom in a molecule form a linear geometry; three regions form a trigonal planar geometry; four regions form a tetrahedral geometry; five regions form a trigonal bipyramidal geometry; and six regions form an octahedral geometry.

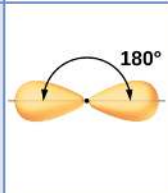
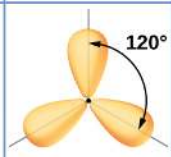
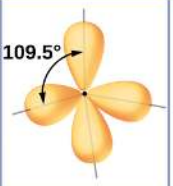
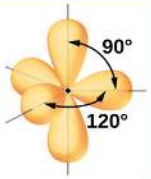
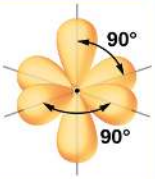
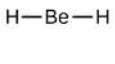
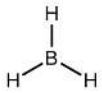
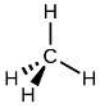
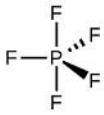
Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions of high electron density (bonds and/or unshared pairs)
Spatial arrangement					
Line-dash-wedge notation					
Electron pair geometry	Linear; 180° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angles of 90° or 120° An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).	Octahedral; all angles 90° or 180°

Figure **4.4.3**: The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs).

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 **4.4.3** 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 will be the same as the molecular structures when there are no lone electron pairs around the central atom, but they will be different when there are lone pairs present on the central atom.

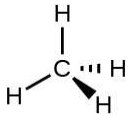


Figure **4.4.4**: The molecular structure of the methane molecule, CH_4, is shown with a tetrahedral arrangement of the hydrogen atoms. VSEPR structures like this one are often drawn using the wedge and dash notation, in which solid lines represent bonds in the plane of the page, solid wedges represent 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 **4.4.4**). 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 **4.4.5**).

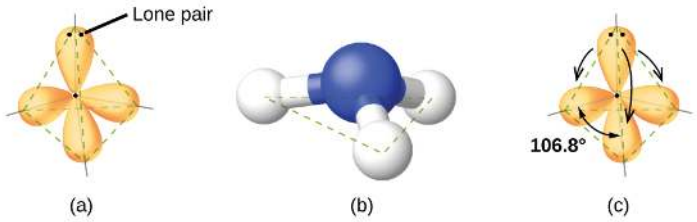


Figure **4.4.5**: (a) The electron-pair geometry for the ammonia molecule is tetrahedral with one lone pair and three single bonds. (b) The trigonal pyramidal molecular structure is determined from the electron-pair geometry. (c) The actual bond angles deviate slightly from the idealized angles because 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°.

Small distortions from the ideal angles in Figure **4.4.5** can result from differences in repulsion between various regions of electron density. VSEPR theory predicts these distortions by establishing an order of repulsions and an order of the amount of space occupied by different kinds of electron pairs. The order of electron-pair repulsions from greatest to least repulsion is:

lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair

This order of repulsions determines the amount of space occupied by different regions of electrons. A lone pair of electrons occupies a larger region of space than the electrons in a triple bond; in turn, electrons in a triple bond occupy more space than those in a double bond, and so on. The order of sizes from largest to smallest is:

lone pair > triple bond > double bond > single bond

Consider formaldehyde, H_2CO, which is used as a preservative for biological and anatomical specimens. This molecule has regions of high electron density that consist of two single bonds and one double bond. The basic geometry is trigonal planar with 120° bond angles, but we see that the double bond causes slightly larger angles (121°), and the angle between the single bonds is slightly smaller (118°).

In the ammonia molecule, the three hydrogen atoms attached to the central nitrogen are not arranged in a flat, trigonal planar molecular structure, but rather in a three-dimensional trigonal pyramid (Figure **4.4.6**) with the nitrogen atom at the apex and the three hydrogen atoms forming the base. The ideal bond angles in a trigonal pyramid are based on the tetrahedral electron pair geometry. Notice that since we are only examining compounds that obey the octet rule, we'll only be using rows 2, 3, and 4 in this figure. The ideal molecular structures are predicted based on the electron-pair geometries for various combinations of lone pairs and bonding pairs.

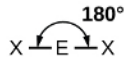
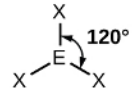
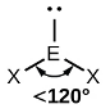
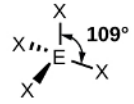
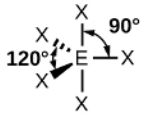
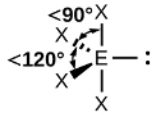
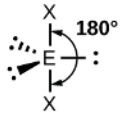
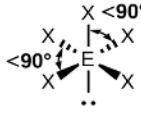
Number of electron pairs	Electron pair geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal planar	 Bent or angular			
4	 Tetrahedral	 Trigonal pyramid	 Bent or angular		
5	 Trigonal bipyramid	 Sawhorse or seesaw	 T-shape	 Linear	
6	 Octahedral	 Square pyramid	 Square planar	 T-shape	 Linear

Figure **4.4.6**: 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.

According to VSEPR theory, the terminal atom locations (Xs in Figure **4.4.7**) 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 to convert positions.

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 **4.4.7**, first column).
4. Use the number of lone pairs to determine the molecular structure (Figure **4.4.7**). 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.

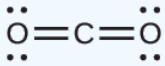
Example 4.4.1: Predicting Electron-pair Geometry and Molecular Structure

Predict the electron-pair geometry and molecular structure for the following:

a. carbon dioxide, CO_2, a molecule produced by the combustion of fossil fuels

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.

Exercise 4.4.1

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 4.4.2: 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:

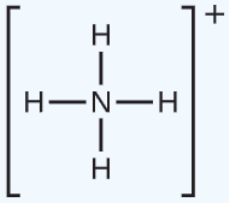


Figure 4.4.7).

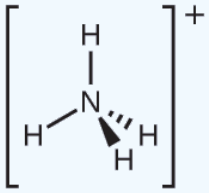


Figure 4.4.8: *The ammonium ion displays a tetrahedral electron-pair geometry as well as a tetrahedral molecular structure.*

The next several examples illustrate the effect of lone pairs of electrons on molecular structure.

Example 4.4.3: 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:

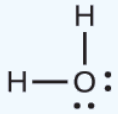


Figure 4.4.9. Thus, the electron-pair geometry is tetrahedral and the molecular structure is bent with an angle slightly less than 109.5°. In fact, the bond angle is 104.5°.

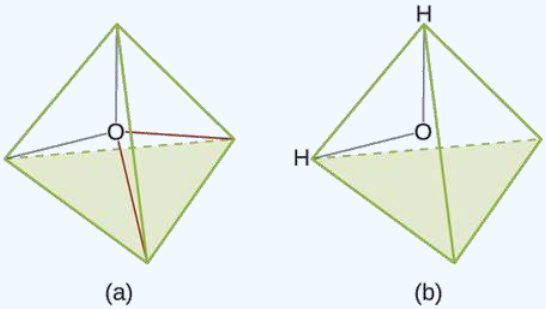


Figure 4.4.9: (a) H_2O has four regions of electron density around the central atom, so it has a tetrahedral electron-pair geometry. (b) Two of the electron regions are lone pairs, so the molecular structure is bent.

Exercise 4.4.3

The hydronium ion, H_3O^+, forms when acids are dissolved in water. Predict the electron-pair geometry and molecular structure of this cation.

Answer

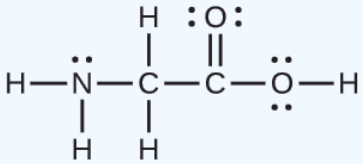
electron pair geometry: tetrahedral; molecular structure: trigonal pyramidal

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.

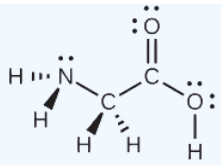
Example 4.4.5: Predicting Structure in Multicenter Molecules

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

https://chem.libretexts.org/@go/page/216747



Consider each central atom independently. The electron-pair geometries:

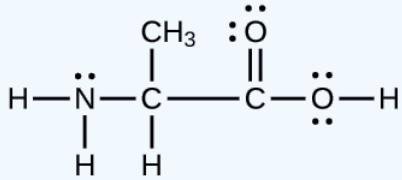
- nitrogen—four regions of electron density; tetrahedral
- carbon ($\underline{C}H_2$)—four regions of electron density; tetrahedral
- carbon ($\underline{C}O_2$)—three regions of electron density; trigonal planar
- oxygen ($\underline{O}H$)—four regions of electron density; tetrahedral

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 4.4.5

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 ($\underline{C}H$)—tetrahedral; carbon ($\underline{C}H_3$)—tetrahedral; carbon ($\underline{C}O_2$)—trigonal planar; oxygen ($\underline{O}H$)—tetrahedral; local structures: nitrogen—trigonal pyramidal; carbon ($\underline{C}H$)—tetrahedral; carbon ($\underline{C}H_3$)—tetrahedral; carbon ($\underline{C}O_2$)—trigonal planar; oxygen ($\underline{O}H$)—bent (109°)

Example 4.4.6: 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:

$$\mathbf{H–C\equiv N}$$

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 4.4.6

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.

Molecular Polarity and Dipole Moment

As discussed previously, polar covalent bonds connect two atoms with differing electronegativities, leaving one atom with a partial positive charge (δ+) and the other atom with a partial negative charge (δ–), as the electrons are pulled toward the more electronegative atom. This separation of charge gives rise to a bond dipole moment. The magnitude of a bond dipole moment is represented by the Greek letter mu (μ).

This bond moment can be represented as a vector, a quantity having both direction and magnitude (Figure **4.4.12**). 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.

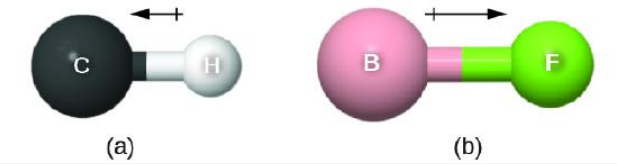


Figure **4.4.12**: (a) There is a small difference in electronegativity between C and H, represented as a short vector. (b) The electronegativity difference between B and F is much larger, so the vector representing the bond moment is much longer.

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 **4.4.13*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 **4.4.13*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).

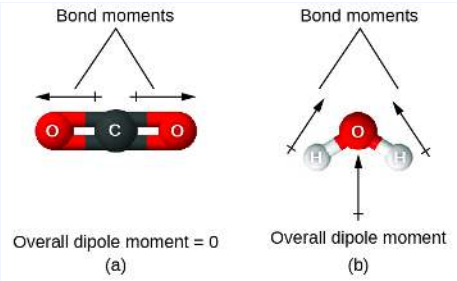
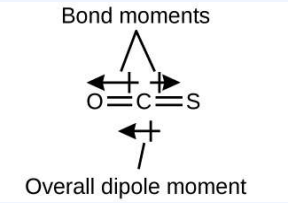


Figure 4.4.13: The overall dipole moment of a molecule depends on the individual bond dipole moments and how they are arranged. (a) Each CO bond has a bond dipole moment, but they point in opposite directions so that the net CO_2 molecule is nonpolar. (b) In contrast, water is polar because the OH bond 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:

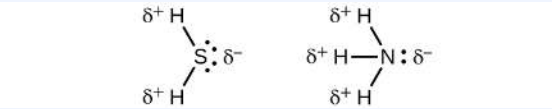


The C–O bond is considerably polar. Although C and S have very similar electronegativity values, S is slightly more electronegative than C, and so the C-S bond is just slightly polar. Because oxygen is more electronegative than sulfur, the oxygen end of the molecule is the negative end.

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.

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 4.4.14). 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.

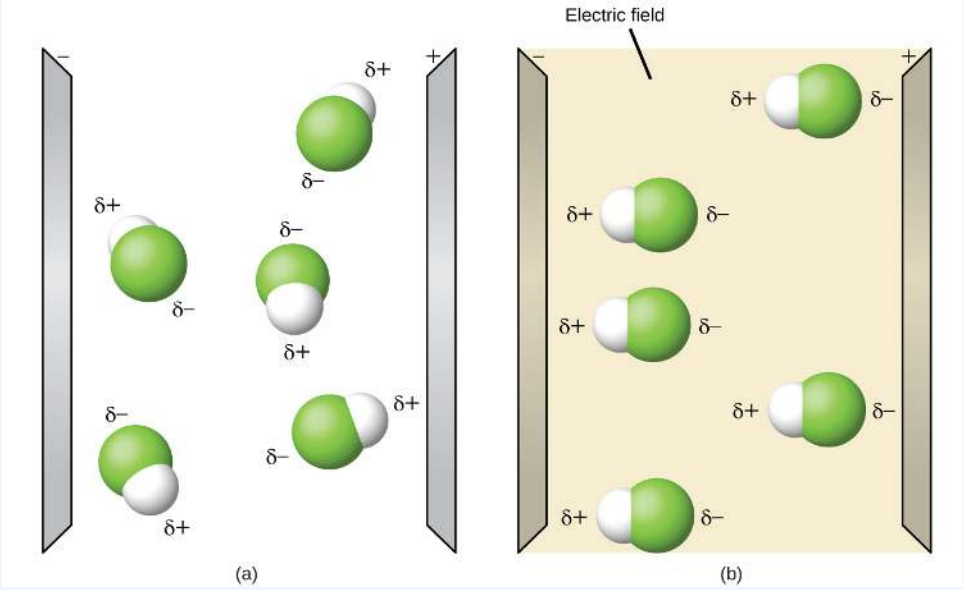


Figure 4.4.14: (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction.

Example 4.4.7: 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 4.4.14.

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 4.4.7

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

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)

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

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 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

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: Molecular Structure and Polarity is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

CHAPTER OVERVIEW

5: Chemical Reactions

Template:HideTOC

5.1: Evidence of a Chemical Reaction
5.2: Chemical Equations
5.3: How to Write Balanced Chemical Equations
5.4: Aqueous Solutions and Solubility - Compounds Dissolved in Water
5.5: Precipitation Reactions
5.6: Writing Chemical Equations for Reactions in Solution- Molecular, Complete Ionic, and Net Ionic Equations
5.7: Acid–Base and Gas Evolution Reactions
5.8: Oxidation–Reduction Reactions
5.9: Classifying Chemical Reactions

Template:HideTOC

5: Chemical Reactions is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

5.1: Evidence of a Chemical Reaction

Learning Objectives

- Identify the evidence for chemical reactions.

In a chemical change, new substances are formed. In order for this to occur, the chemical bonds of the substances break, and the atoms that compose them separate and rearrange themselves into new substances with new chemical bonds. When this process occurs, we call it a chemical reaction. A **chemical reaction** is the process in which one or more substances are changed into one or more new substances.

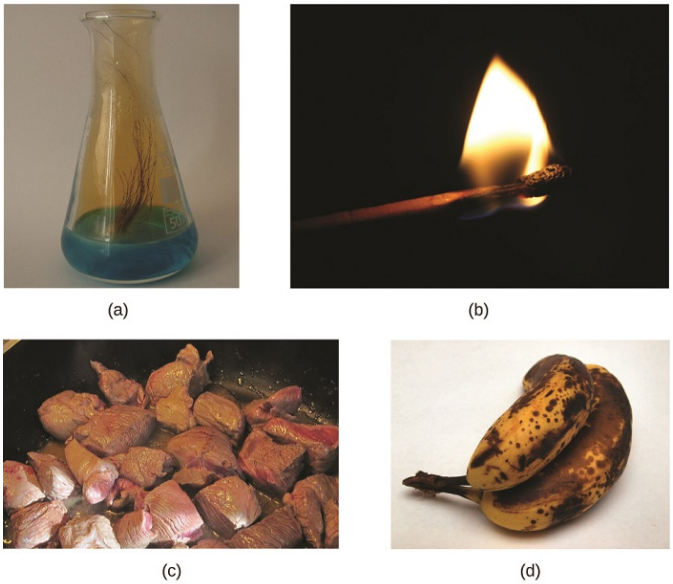


Figure **5.1.1**: (a) Copper and nitric acid undergo a chemical change to form copper nitrate and brown, gaseous nitrogen dioxide. (b) During the combustion of a match, cellulose in the match and oxygen from the air undergo a chemical change to form carbon dioxide and water vapor. (c) Cooking red meat 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.)

To identify a chemical reaction, 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 **5.1.1**).



Video **5.1.1*:*** *Evidence of a Chemical Reaction*

Example 5.1.1: Evidence of a Chemical Reaction

Which of the following is a chemical reaction?

a. Freezing liquid mercury.
b. Adding yellow to blue to make green.
c. Cutting a piece of paper into two pieces.
d. Dropping a sliced orange into a vat of sodium dydroxide.
e. Filling a balloon with natural air.

Solution

A, B, C, & E involve only physical changes. A sliced orange has acid (citric acid) that can react with sodium hydroxide, so the answer is D.

Exercise 5.1.1

Which of the following is a chemical reaction?

a. Painting a wall blue.
b. A bicycle rusting.
c. Ice cream melting.
d. Scratching a key across a desk.
e. Making a sand castle.

Answer

B

Example 5.1.2: Evidence of a Chemical Reaction

Which of the following is not a chemical reaction?

a. Shattering glass with a baseball.
b. Corroding metal.
c. Fireworks exploding.
d. Lighting a match.
e. Baking a cake.

Solution

Shattering glass with a baseball results in glass broken into many pieces but no chemical change happens, so the answer is A.

? Exercise 5.1.2

Which of the following is NOT a chemical reaction?

a. Frying an egg.
b. Slicing carrots.
c. A Macbook falling out of a window.
d. Creating ATP in the human body.
e. Dropping a fizzy tablet into a glass of water.

Answer

B and C

Summary

Chemical reactions can be identified via a wide range of different observable factors including change in color, energy change (temperature change or light produced), gas production, formation of precipitate and change in properties.

5.1: Evidence of a Chemical Reaction is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **7.2: Evidence of a Chemical Reaction** by Henry Agnew, Marisa Alviar-Agnew is licensed CC BY 4.0. Original source: https://www.ck12.org/c/chemistry/.

5.2: Chemical Equations

Learning Objectives

- Identify the reactants and products in any chemical reaction.
- Convert word equations into chemical equations.
- Use the common symbols, (s), (l), (g), (aq), and $\rightarrow$ appropriately when writing a chemical reaction.

In a chemical change, new substances are formed. In order for this to occur, the chemical bonds of the substances break, and the atoms that compose them separate and rearrange themselves into new substances with new chemical bonds. When this process occurs, we call it a chemical reaction. A **chemical reaction** is the process in which one or more substances are changed into one or more new substances.

Reactants and Products

To describe a chemical reaction, we need to indicate what substances are present at the beginning and what substances are present at the end. The substances that are present at the beginning are called **reactants** and the substances present at the end are called **products**.

Sometimes when reactants are put into a reaction vessel, a reaction will take place to produce products. Reactants are the starting materials, that is, whatever we have as our initial ingredients. The products are just that—what is produced—or the result of what happens to the reactants when we put them together in the reaction vessel. If we think about baking chocolate chip cookies, our reactants would be flour, butter, sugar, vanilla, baking soda, salt, egg, and chocolate chips. What would be the products? Cookies! The reaction vessel would be our mixing bowl.

$$\underbrace{\text{Flour}+\text{Butter}+\text{Sugar}+\text{Vanilla}+\text{Baking Soda}+\text{Eggs}+\text{Chocolate Chips}}_{\text{Ingredients = Reactants}} \rightarrow \underbrace{\text{Cookies}}_{\text{Product}}$$

Writing Chemical Equations

When sulfur dioxide is added to oxygen, sulfur trioxide is produced. Sulfur dioxide and oxygen, $SO_2 + O_2$, are reactants and sulfur trioxide, SO_3, is the product.

$$\underbrace{2\,SO_2\,(g)+O_2\,(g)}_{\text{Reactants}} \rightarrow \underbrace{2\,SO_3\,(g)}_{\text{Products}}$$

In chemical reactions, the reactants are found before the symbol "$\rightarrow$" and the products are found after the symbol "$\rightarrow$". The general equation for a reaction is:

$$\text{Reactants} \rightarrow \text{Products}$$

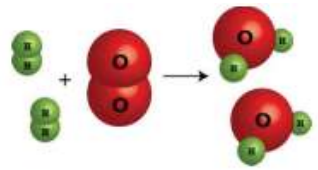
There are a few special symbols that we need to know in order to "talk" in chemical shorthand. In the table below is the summary of the major symbols used in chemical equations. Table **5.2.1** shows a listing of symbols used in chemical equations.

Table **5.2.1**: Symbols Used in Chemical Equations

Symbol	Description	Symbol	Description
$+$	used to separate multiple reactants or products	(s)	reactant or product in the solid state
$\rightarrow$	yield sign; separates reactants from products	(l)	reactant or product in the liquid state
$\rightleftharpoons$	replaces the yield sign for reversible reactions that reach equilibrium	(g)	reactant or product in the gas state
$\xrightarrow{\text{Pt}}$	formula written above the arrow is used as a catalyst in the reaction	(aq)	reactant or product in an aqueous solution (dissolved in water)
$\xrightarrow{\Delta}$	triangle indicates that the reaction is being heated		

Chemists have a choice of methods for describing a chemical reaction.

1. They could draw a picture of the chemical reaction.



2. They could write a word equation for the chemical reaction:
"Two molecules of hydrogen gas react with one molecule of oxygen gas to produce two molecules of water vapor."

3. They could write the equation in chemical shorthand.

$$\mathrm{2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(g)}$$

In the symbolic equation, chemical formulas are used instead of chemical names for reactants and products, while symbols are used to indicate the phase of each substance. It should be apparent that the chemical shorthand method is the quickest and clearest method for writing chemical equations.

We could write that an aqueous solution of calcium nitrate is added to an aqueous solution of sodium hydroxide to produce solid calcium hydroxide and an aqueous solution of sodium nitrate. Or in shorthand we could write:

$$\mathrm{Ca(NO_3)_2\,(aq) + 2NaOH\,(aq) \rightarrow Ca(OH)_2\,(s) + 2NaNO_3\,(aq)}$$

How much easier is that to read? Let's try it in reverse. Look at the following reaction in shorthand and write the word equation for the reaction:

$$\mathrm{Cu\,(s) + AgNO_3\,(aq) \rightarrow Cu(NO_3)_2\,(aq) + Ag\,(s)}$$

The word equation for this reaction might read something like "solid copper reacts with an aqueous solution of silver nitrate to produce a solution of copper (II) nitrate with solid silver."

To turn word equations into symbolic equations, we need to follow the given steps:

1. Identify the reactants and products. This will help you know which symbols go on each side of the arrow and where the $+$ signs go.
2. Write the correct formulas for all compounds. You will need to use the rules you learned in Chapter 5 (including making all ionic compounds charge balanced).

3. Write the correct formulas for all elements. Usually this is given straight off of the periodic table. However, there are seven elements that are considered diatomic, meaning that they are always found in pairs in nature. They include those elements listed in the table.

Table **5.2.1**: *Diatomic Elements*

Element Name	Hydrogen	Nitrogen	Oxygen	Fluorine	Chlorine	Bromine	Iodine
Formula	H_2	N_2	O_2	F_2	Cl_2	Br_2	I_2

Example 5.2.1

Transfer the following symbolic equations into word equations or word equations into symbolic equations.

a. $\mathrm{HCl}\,(aq) + \mathrm{NaOH}\,(aq) \rightarrow \mathrm{NaCl}\,(aq) + \mathrm{H_2O}\,(l)$

b. Gaseous propane, $\mathrm{C_3H_8}$, burns in oxygen gas to produce gaseous carbon dioxide and liquid water.

c. Hydrogen fluoride gas reacts with an aqueous solution of potassium carbonate to produce an aqueous solution of potassium fluoride, liquid water, and gaseous carbon dioxide.

Solution

a. An aqueous solution of hydrochloric acid reacts with an aqueous solution of sodium hydroxide to produce an aqueous solution of sodium chloride and liquid water.

b. Reactants: propane ($\mathrm{C_3H_8}$) and oxygen ($\mathrm{O_2}$)

Product: carbon dioxide ($\mathrm{CO_2}$) and water ($\mathrm{H_2O}$)

$$\mathrm{C_3H_8}\,(g) + \mathrm{O_2}\,(g) \rightarrow \mathrm{CO_2}\,(g) + \mathrm{H_2O}\,(l)$$

c. Reactants: hydrogen fluoride and potassium carbonate

Products: potassium fluoride, water, and carbon dioxide

$$\mathrm{HF}\,(g) + \mathrm{K_2CO_3}\,(aq) \rightarrow \mathrm{KF}\,(aq) + \mathrm{H_2O}\,(l) + \mathrm{CO_2}\,(g)$$

Exercise 5.2.1

Transfer the following symbolic equations into word equations or word equations into symbolic equations.

a. Hydrogen gas reacts with nitrogen gas to produce gaseous ammonia.

b. $\mathrm{HCl}\,(aq) + \mathrm{LiOH}\,(aq) \rightarrow \mathrm{LiCl}\,(aq) + \mathrm{H_2O}\,(l)$

c. Copper metal is heated with oxygen gas to produce solid copper(II) oxide.

Answer a

$H_2(g) + N_2(g) \rightarrow NH_3(g)$

Answer b

An aqueous solution of hydrochloric acid reacts with an aqueous solution of lithium hydroxide to produce an aqueous solution of lithium chloride and liquid water.

Answer c

$Cu(s) + O_2(g) \rightarrow CuO(s)$

Summary

- A chemical reaction is the process by which one or more substances are changed into one or more new substances.
- Chemical reactions are represented by chemical equations.
- Chemical equations have reactants on the left, an arrow that is read as "yields", and the products on the right.

5.2: Chemical Equations is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **7.3: The Chemical Equation** by Henry Agnew, Marisa Alviar-Agnew is licensed CK-12. Original source: https://www.ck12.org/c/chemistry/.

5.3: How to Write Balanced Chemical Equations

Learning Objectives

- Explain the roles of subscripts and coefficients in chemical equations.
- Balance a chemical equation when given the unbalanced equation.
- Explain the role of the Law of Conservation of Mass in a chemical reaction.

Even though chemical compounds are broken up and new compounds are formed during a chemical reaction, atoms in the reactants do not disappear, nor do new atoms appear to form the products. In chemical reactions, atoms are never created or destroyed. The same atoms that were present in the reactants are present in the products—they are merely reorganized into different arrangements. In a complete chemical equation, the two sides of the equation must be present on the reactant and the product sides of the equation.

Coefficients and Subscripts

There are two types of numbers that appear in chemical equations. There are subscripts, which are part of the chemical formulas of the reactants and products; and there are coefficients that are placed in front of the formulas to indicate how many molecules of that substance is used or produced.

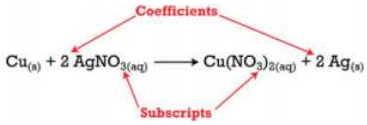
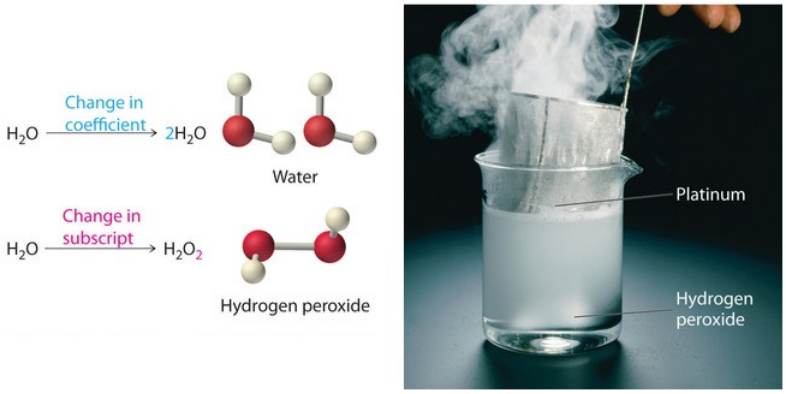


Figure **5.3.1**: Balancing Equations. You cannot change subscripts in a chemical formula to balance a chemical equation; you can change only the coefficients. Changing subscripts changes the ratios of atoms in the molecule and the resulting chemical properties. For example, water (H_2O) and hydrogen peroxide (H_2O_2) are chemically distinct substances. H_2O_2 decomposes to H_2O and O_2 gas when it comes in contact with the metal platinum, whereas no such reaction occurs between water and platinum.

The **subscripts** are part of the formulas and once the formulas for the reactants and products are determined, the subscripts may not be changed. The **coefficients** indicate the number of each substance involved in the reaction and may be changed in order to balance the equation. The equation above indicates that one mole of solid copper is reacting with two moles of aqueous silver nitrate to produce one mole of aqueous copper (II) nitrate and two atoms of solid silver.

Balancing a Chemical Equation

Because the identities of the reactants and products are fixed, the equation cannot be balanced by changing the subscripts of the reactants or the products. To do so would change the chemical identity of the species being described, as illustrated in Figure **5.3.1**.



Original molecule $\mathbf{H_2O}$: if the coefficient 2 is added in front, that makes 2 water molecules; but if the subscript 2 is added to make $\mathbf{H_2O_2}$, that's hydrogen peroxide.

The simplest and most generally useful method for balancing chemical equations is “inspection,” better known as trial and error. The following is an efficient approach to balancing a chemical equation using this method.

Steps in Balancing a Chemical Equation

1. Identify the most complex substance.
2. Beginning with that substance, choose an element(s) that appears in only one reactant and one product, if possible. Adjust the coefficients to obtain the same number of atoms of this element(s) on both sides.
3. Balance polyatomic ions (if present on both sides of the chemical equation) as a unit.
4. Balance the remaining atoms, usually ending with the least complex substance and using fractional coefficients if necessary. If a fractional coefficient has been used, multiply both sides of the equation by the denominator to obtain whole numbers for the coefficients.
5. Count the numbers of atoms of each kind on both sides of the equation to be sure that the chemical equation is balanced.

Example 5.3.1: Combustion of Heptane

Balance the chemical equation for the combustion of Heptane (C_7H_{16}).

$$C_7H_{16}(l) + O_2(g) \longrightarrow CO_2(g) + H_2O(g)$$

Solution

Solutions to Example 5.3.1

Steps	Example
1. **Identify the most complex substance.**	The most complex substance is the one with the largest number of different atoms, which is C_7H_{16}. We will assume initially that the final balanced chemical equation contains 1 molecule or formula unit of this substance.
2. **Adjust the coefficients.**	a. Because one molecule of n-heptane contains 7 carbon atoms, we need 7 CO_2 molecules, each of which contains 1 carbon atom, on the right side: $$C_7H_{16}(l) + O_2(g) \longrightarrow \underline{7}CO_2(g) + H_2O(g)$$ • 7 carbon atoms on both reactant and product sides b. Because one molecule of n-heptane contains 16 hydrogen atoms, we need 8 H_2O molecules, each of which contains 2 hydrogen atoms, on the right side: $$C_7H_{16}(l) + O_2(g) \longrightarrow 7\,CO_2(g) + \underline{8}H_2O(g)$$ • 16 hydrogen atoms on both reactant and product sides
3. **Balance polyatomic ions as a unit.**	There are no polyatomic ions to be considered in this reaction.
4. **Balance the remaining atoms.**	The carbon and hydrogen atoms are now balanced, but we have 22 oxygen atoms on the right side and only 2 oxygen atoms on the left. We can balance the oxygen atoms by adjusting the coefficient in front of the least complex substance, O_2, on the reactant side: $$C_7H_{16}(l) + \underline{11}O_2(g) \longrightarrow 7\,CO_2(g) + 8\,H_2O(g)$$ • 22 oxygen atoms on both reactant and product sides
5. **Check your work.**	The equation is now balanced, and there are no fractional coefficients: there are 7 carbon atoms, 16 hydrogen atoms, and 22 oxygen atoms on each side. Always check to be sure that a chemical equation is balanced.

Example 5.3.2: Combustion of Isooctane

Combustion of Isooctane (C_8H_{18})

$$C_8H_{18}\,(l) + O_2\,(g) \longrightarrow CO_2\,(g) + H_2O\,(g)$$

Solution

The assumption that the final balanced chemical equation contains only one molecule or formula unit of the most complex substance is not always valid, but it is a good place to start. The combustion of any hydrocarbon with oxygen produces carbon dioxide and water.

Solutions to Example 7.4.2

Steps	Example
1. **Identify the most complex substance.**	The most complex substance is the one with the largest number of different atoms, which is C_8H_{18}. We will assume initially that the final balanced chemical equation contains 1 molecule or formula unit of this substance.
2. **Adjust the coefficients.**	a. The first element that appears only once in the reactants is carbon: 8 carbon atoms in isooctane means that there must be 8 CO_2 molecules in the products: $$C_8H_{18}(l) + O_2(g) \longrightarrow \underline{8}CO_2(g) + H_2O(g)$$ • 8 carbon atoms on both reactant and product sides b. 18 hydrogen atoms in isooctane means that there must be 9 H_2O molecules in the products: $$C_8H_{18}(l) + O_2(g) \longrightarrow 8\,CO_2(g) + \underline{9}H_2O(g)$$ • 18 hydrogen atoms on both reactant and product sides
3. **Balance polyatomic ions as a unit.**	There are no polyatomic ions to be considered in this reaction.
4. **Balance the remaining atoms.**	The carbon and hydrogen atoms are now balanced, but we have 25 oxygen atoms on the right side and only 2 oxygen atoms on the left. We can balance the least complex substance, O_2, but because there are 2 oxygen atoms per O_2 molecule, we must use a fractional coefficient ($\frac{25}{2}$) to balance the oxygen atoms: $$C_8H_{18}(l) + \underline{\frac{25}{2}}O_2\ (g) \longrightarrow 8\,CO_2(g) + 9\,H_2O(g)$$ • 25 oxygen atoms on both reactant and product sides The equation is now balanced, but we usually write equations with whole number coefficients. We can eliminate the fractional coefficient by multiplying all coefficients on both sides of the chemical equation by **2**: $$\underline{2}C_8H_{18}(l) + \underline{25}O_2(g) \longrightarrow \underline{16}CO_2(g) + \underline{18}H_2O(g)$$
5. **Check your work.**	The balanced chemical equation has 16 carbon atoms, 36 hydrogen atoms, and 50 oxygen atoms on each side. Balancing equations requires some practice on your part as well as some common sense. If you find yourself using very large coefficients or if you have spent several minutes without success, go back and make sure that you have written the formulas of the reactants and products correctly.

Example 5.3.3: Precipitation of Lead (II) Chloride

Aqueous solutions of lead (II) nitrate and sodium chloride are mixed. The products of the reaction are an aqueous solution of sodium nitrate and a solid precipitate of lead (II) chloride. Write the balanced chemical equation for this reaction.

Solution

Solutions to Example 7.4.3

Steps	Example
1. **Identify the most complex substance.**	The most complex substance is lead (II) chloride. $\mathrm{Pb(NO_3)_2\,(aq) + NaCl\,(aq) \longrightarrow NaNO_3\,(aq) + PbCl_2\,(s)}$
2. **Adjust the coefficients.**	There are twice as many chloride ions in the reactants as there are in the products. Place a 2 in front of the NaCl in order to balance the chloride ions. $\mathrm{Pb(NO_3)_2\,(aq) + \underline{2}\,NaCl\,(aq) \longrightarrow NaNO_3\,(aq) + PbCl_2\,(s)}$ • 1 Pb atom on both reactant and product sides • 2 Na atoms on reactant side, 1 Na atom on product side • 2 Cl atoms on both reactant and product sides
3. **Balance polyatomic ions as a unit.**	The nitrate ions are still unbalanced. Place a 2 in front of the $NaNO_3$. The result is: $\mathrm{Pb(NO_3)_2\,(aq) + 2\,NaCl\,(aq) \longrightarrow \underline{2}\,NaNO_3\,(aq) + PbCl_2\,(s)}$ • 1 Pb atom on both reactant and product sides • 2 Na atoms on both reactant and product sides • 2 Cl atoms on both reactant and product sides • 2 NO_3^- atoms on both reactant and product sides
4. **Balance the remaining atoms.**	There is no need to balance the remaining atoms because they are already balanced.
5. **Check your work.**	$\mathrm{Pb(NO_3)_2\,(aq) + 2\,NaCl\,(aq) \longrightarrow 2\,NaNO_3\,(aq) + PbCl_2\,(s)}$ • 1 Pb atom on both reactant and product sides • 2 Na atoms on both reactant and product sides • 2 Cl atoms on both reactant and product sides • 2 NO_3^- atoms on both reactant and product sides

? Exercise 5.3.1

Is each chemical equation balanced?

a. $\mathrm{2\,Hg(\ell)^+\ O_2\,(g)\ \rightarrow Hg_2O_2\,(s)}$
b. $\mathrm{C_2H_4\,(g) + 2\,O_2(g) \longrightarrow 2\,CO_2\,(g) + 2\,H_2O\,(g)}$
c. $\mathrm{Mg(NO_3)_2\,(s) + 2\,Li\,(s)\ \rightarrow Mg(s)^+\ 2\,LiNO_3\,(s)}$

Answer a

yes

Answer b

no

Answer c

yes

? Exercise 5.3.2

Balance the following chemical equations.

a. $\mathbf{N_2\,(g) + O_2\,(g) \longrightarrow NO_2\,(g)}$
b. $\mathbf{Pb(NO_3)_2\,(aq) + FeCl_3\,(aq) \longrightarrow Fe(NO_3)_3\,(aq) + PbCl_2\,(s)}$
c. $\mathbf{C_6H_{14}\,(l) + O_2(g) \longrightarrow CO_2\,(g) + H_2O\,(g)}$

Answer a

$N_2\,(g) + 2O_2\,(g) \rightarrow 2NO_2\,(g)$

Answer b

$3Pb(NO_3)_2(aq) + 2FeCl_3(aq) \rightarrow 2Fe(NO_3)_3(aq) + 3PbCl_2(s)$

Answer c

$2C_6H_{14}(l) + 19O_2(g) \rightarrow 12CO_2(g) + 14H_2O(g)$

Summary

- To be useful, chemical equations must always be balanced. Balanced chemical equations have the same number and type of each atom on both sides of the equation.
- The coefficients in a balanced equation must be the simplest whole number ratio. Mass is always conserved in chemical reactions.

Vocabulary

- **Chemical reaction** - The process in which one or more substances are changed into one or more new substances.
- **Reactants** - The starting materials in a reaction.
- **Products** - Materials present at the end of a reaction.
- **Balanced chemical equation** - A chemical equation in which the number of each type of atom is equal on the two sides of the equation.
- **Subscripts** - Part of the chemical formulas of the reactants and products that indicate the number of atoms of the preceding element.
- **Coefficient** - A small whole number that appears in front of a formula in a balanced chemical equation.

5.3: How to Write Balanced Chemical Equations is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **7.4: How to Write Balanced Chemical Equations** by Henry Agnew, Marisa Alviar-Agnew is licensed CC BY-NC-SA 3.0.

5.4: Aqueous Solutions and Solubility - Compounds Dissolved in Water

Learning Objectives

- Define and give examples of electrolytes.

When some substances are dissolved in water, they undergo either a physical or a chemical change that yields ions in solution. These substances constitute an important class of compounds called electrolytes. Substances that do not yield ions when dissolved are called nonelectrolytes. If the physical or chemical process that generates the ions is essentially 100% efficient (all of the dissolved compound yields ions), then the substance is known as a strong electrolyte. If only a relatively small fraction of the dissolved substance undergoes the ion-producing process, it is called a weak electrolyte.

Substances may be identified as strong, weak, or nonelectrolytes by measuring the electrical conductance of an aqueous solution containing the substance. To conduct electricity, a substance must contain freely mobile, charged species. Most familiar is the conduction of electricity through metallic wires, in which case the mobile, charged entities are electrons. Solutions may also conduct electricity if they contain dissolved ions, with conductivity increasing as ion concentration increases. Applying a voltage to electrodes immersed in a solution permits assessment of the relative concentration of dissolved ions, either quantitatively, by measuring the electrical current flow, or qualitatively, by observing the brightness of a light bulb included in the circuit (Figure 5.4.1).

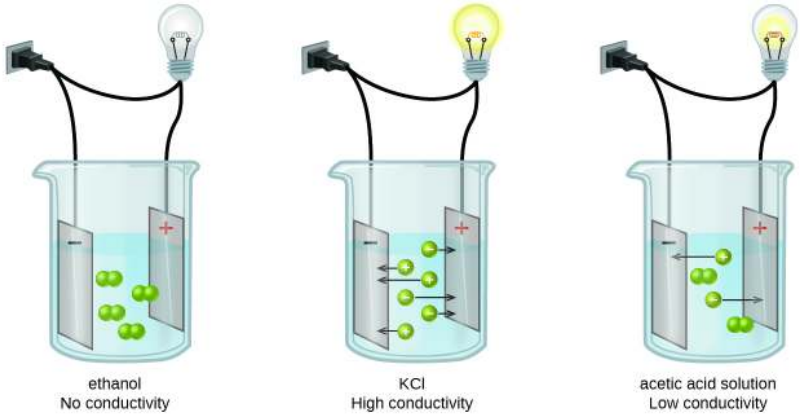


Figure 5.4.1: Solutions of nonelectrolytes, such as ethanol, do not contain dissolved ions and cannot conduct electricity. Solutions of electrolytes contain ions that permit the passage of electricity. The conductivity of an electrolyte solution is related to the strength of the electrolyte. This diagram shows three separate beakers. Each has a wire plugged into a wall outlet. In each case, the wire leads from the wall to the beaker and is split resulting in two ends. One end leads to a light bulb and continues on to a rectangle labeled with a plus sign. The other end leads to a rectangle labeled with a minus sign. The rectangles are in a solution. In the first beaker, labeled “Ethanol No Conductivity,” four pairs of linked small green spheres suspended in the solution between the rectangles. In the second beaker, labeled “K C l Strong Conductivity,” six individual green spheres, three labeled plus and three labeled minus are suspended in the solution. Each of the six spheres has an arrow extending from it pointing to the rectangle labeled with the opposite sign. In the third beaker, labeled “Acetic acid solution Weak conductivity,” two pairs of joined green spheres and two individual spheres, one labeled plus and one labeled minus are shown suspended between the two rectangles. The plus labeled sphere has an arrow pointing to the rectangle labeled minus and the minus labeled sphere has an arrow pointing to the rectangle labeled plus.

Ionic Electrolytes

Water and other polar molecules are attracted to ions, as shown in Figure 5.4.2. The electrostatic attraction between an ion and a molecule with a dipole is called an ion-dipole attraction. These attractions play an important role in the dissolution of ionic compounds in water.

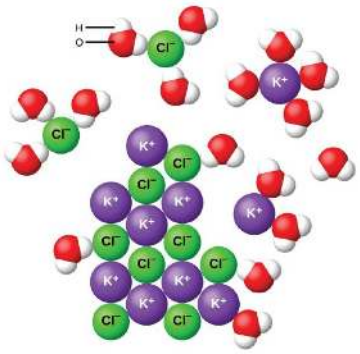


Figure 5.4.2: As potassium chloride (KCl) dissolves in water, the ions are hydrated. The polar water molecules are attracted by the charges on the K^+ and Cl^- ions. Water molecules in front of and behind the ions are not shown. The diagram shows eight purple spheres labeled K superscript plus and eight green spheres labeled C l superscript minus mixed and touching near the center of the diagram. Outside of this cluster of spheres are seventeen clusters of three spheres, which include one red and two white spheres. A red sphere in one of these clusters is labeled O. A white sphere is labeled H. Two of the green C l superscript minus spheres are surrounded by three of the red and white clusters, with the red spheres closer to the green spheres than the white spheres. One of the K superscript plus purple spheres is surrounded by four of the red and white clusters. The white spheres of these clusters are closest to the purple spheres.

When ionic compounds dissolve in water, the ions in the solid separate and disperse uniformly throughout the solution because water molecules surround and solvate the ions, reducing the strong electrostatic forces between them. This process represents a physical change known as dissociation. Under most conditions, ionic compounds will dissociate nearly completely when dissolved, and so they are classified as strong electrolytes.

Let us consider what happens at the microscopic level when we add solid KCl to water. Ion-dipole forces attract the positive (hydrogen) end of the polar water molecules to the negative chloride ions at the surface of the solid, and they attract the negative (oxygen) ends to the positive potassium ions. The water molecules penetrate between individual K^+ and Cl^- ions and surround them, reducing the strong interionic forces that bind the ions together and letting them move off into solution as solvated ions, as Figure 5.4.2 shows. The reduction of the electrostatic attraction permits the independent motion of each hydrated ion in a dilute solution, resulting in an increase in the disorder of the system, as the ions change from their fixed and ordered positions in the crystal to mobile and much more disordered states in solution. This increased disorder is responsible for the dissolution of many ionic compounds, including KCl, which dissolve with absorption of heat.

In other cases, the electrostatic attractions between the ions in a crystal are so large, or the ion-dipole attractive forces between the ions and water molecules are so weak, that the increase in disorder cannot compensate for the energy required to separate the ions, and the crystal is insoluble. Such is the case for compounds such as calcium carbonate (limestone), calcium phosphate (the inorganic component of bone), and iron oxide (rust).

Solubility Rules

Some combinations of aqueous reactants result in the formation of a solid precipitate as a product. However, some combinations will not produce such a product. If solutions of sodium nitrate and ammonium chloride are mixed, no reaction occurs. One could write a molecular equation showing a double-replacement reaction, but both products, sodium chloride and ammonium nitrate, are soluble and would remain in the solution as ions. Every ion is a spectator ion and there is no net ionic equation at all. It is useful to be able to predict when a precipitate will occur in a reaction. To do so, you can use a set of guidelines called the **solubility rules** (Tables 5.4.1 and 5.4.2).

Table 5.4.1: Solubility Rules for Soluble Substances

Soluble in Water	Important Exceptions (Insoluble)
All Group IA and NH_4^+ salts	none
All nitrates, chlorates, perchlorates and acetates	none
All sulfates	$CaSO_4$, $BaSO_4$, $SrSO_4$, $PbSO_4$
All chlorides, bromides, and iodides	AgX, Hg_2X_2, PbX_2 (X= Cl, Br, or I)

Table 5.4.2: Solubility Rules for Sparingly Soluble Substances

Sparingly Soluble in Water	Important Exceptions (Soluble)
All carbonates and phosphates	Group IA and NH_4^+ salts
All hydroxides	Group IA and NH_4^+ salts; Ba^{2+}, Sr^{2+}, Ca^{2+} sparingly soluble
All sulfides	Group IA, IIA and NH_4^+ salts; MgS, CaS, BaS sparingly soluble
All oxalates	Group IA and NH_4^+ salts
Special note: The following electrolytes are of only moderate solubility in water: CH_3COOAg, Ag_2SO_4, $KClO_4$. They will precipitate only if rather concentrated solutions are used.	

As an example on how to use the solubility rules, predict if a precipitate will form when solutions of cesium bromide and lead (II) nitrate are mixed.

$$Cs^+(aq) + Br^-(aq) + Pb^{2+}(aq) + 2NO_3^-(aq) \rightarrow ?$$

The potential precipitates from a double-replacement reaction are cesium nitrate and lead (II) bromide. According to the solubility rules table, cesium nitrate is soluble because all compounds containing the nitrate ion, as well as all compounds containing the alkali metal ions, are soluble. Most compounds containing the bromide ion are soluble, but lead (II) is an exception. Therefore, the cesium and nitrate ions are spectator ions and the lead (II) bromide is a precipitate. The balanced net ionic reaction is:

$$Pb^{2+}(aq) + 2Br^-(aq) \rightarrow PbBr_2(s)$$

✔ Example 5.4.1: Solubility

Classify each compound as soluble or insoluble

a. $Zn(NO_3)_2$
b. $PbBr_2$
c. $Sr_3(PO_4)_2$

Solution

a. All nitrates are soluble in water, so $Zn(NO_3)_2$ is soluble.
b. All bromides are soluble in water, except those combined with Pb^{2+}, so $PbBr_2$ is insoluble.
c. All phosphates are insoluble, so $Sr_3(PO_4)_2$ is insoluble.

? Exercise 5.4.1: Solubility

Classify each compound as soluble or insoluble.

a. $Mg(OH)_2$
b. KBr
c. $Pb(NO_3)_2$

Answer a

insoluble

Answer b

soluble

Answer c

soluble

Summary

Substances that dissolve in water to yield ions are called electrolytes. Nonelectrolytes are substances that do not produce ions when dissolved in water. Solubility rules allow prediction of what products will be insoluble in water.

Contributions & 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).
-

5.4: Aqueous Solutions and Solubility - Compounds Dissolved in Water is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **7.5: Aqueous Solutions and Solubility - Compounds Dissolved in Water** by Henry Agnew, Marisa Alviar-Agnew is licensed CK-12. Original source: https://www.ck12.org/c/chemistry/.

5.5: Precipitation Reactions

Learning Objectives

- To identify a precipitation reaction and predict solubility.

A precipitation reaction is a reaction that yields an insoluble product—a precipitate—when two solutions are mixed. When a colorless solution of silver nitrate is mixed with a yellow-orange solution of potassium dichromate, a reddish precipitate of silver dichromate is produced.

$$\mathrm{AgNO_3\,(aq) + K_2Cr_2O_7\,(aq) \rightarrow Ag_2Cr_2O_7\,(s) + KNO_3\,(aq)} \tag{5.5.1}$$

This unbalanced equation has the general form of an exchange reaction:

$$\mathrm{AC + BD \rightarrow \underset{insoluble}{AD} + BC} \tag{5.5.2}$$

Thus precipitation reactions are a subclass of exchange reactions that occur between ionic compounds when one of the products is insoluble. Because both components of each compound change partners, such reactions are sometimes called **double-displacement reactions**. Precipitation reactions are used to isolate metals that have been extracted from their ores, and to recover precious metals for recycling.



Video: Mixing potassium dichromate and silver nitrate together to initiate a precipitation reaction (Equation 5.5.1).

Just as important as predicting the product of a reaction is knowing when a chemical reaction will *not* occur. Simply mixing solutions of two different chemical substances does *not* guarantee that a reaction will take place. For example, if 500 mL of aqueous *NaCl* solution is mixed with 500 mL of aqueous *KBr* solution, the final solution has a volume of 1.00 L and contains $\mathrm{Na^+\,(aq)}$, $\mathrm{Cl^-\,(aq)}$, $\mathrm{K^+\,(aq)}$, and $\mathrm{Br^-\,(aq)}$. As you will see in (Figure 5.5.1), none of these species reacts with any of the others. When these solutions are mixed, the only effect is to dilute each solution with the other.

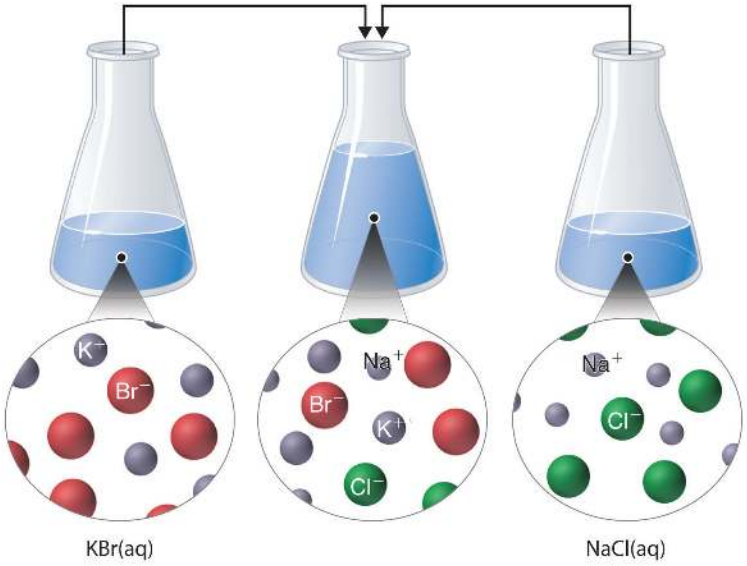


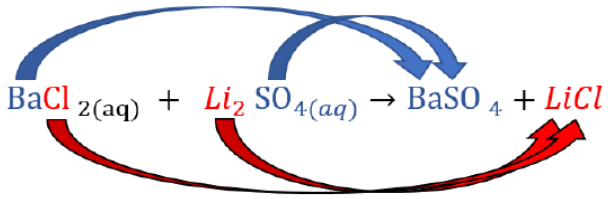
Figure 5.5.1: The Effect of Mixing Aqueous **KBr** and **NaCl** Solutions. Because no net reaction occurs, the only effect is to dilute each solution with the other. (Water molecules are omitted from molecular views of the solutions for clarity.)

Predicting Precipitation Reactions

A precipitation reaction occurs when a solid precipitate forms after mixing two strong electrolyte solutions. As stated previously, if none of the species in the solution reacts then no net reaction occurred.

Predict what will happen when aqueous solutions of barium chloride and lithium sulfate are mixed.

Change the partners of the anions and cations on the reactant side to form new compounds (products):



Chemical equation of the reactants barium chloride and lithium sulfate forming the products barium sulfate and lithium chloride.

Because barium chloride and lithium sulfate are strong electrolytes, each dissociates completely in water to give a solution that contains the constituent anions and cations. Mixing the two solutions *initially* gives an aqueous solution that contains Ba^{2+}, Cl^-, Li^+, and SO_4^{2-} ions. The only possible exchange reaction is to form **LiCl** and **$BaSO_4$**.

Correct the formulas of the products based on the charges of the ions.

No need to correct the formula as both compounds already have their charges balanced.

$$BaCl_2\,(aq) + Li_2SO_4\,(aq) \rightarrow BaSO_4 + LiCl$$

Refer to the solubility rules table to determine insoluble products which will therefore form a precipitate.

$$BaCl_2\,(aq) + Li_2SO_4\,(aq) \rightarrow BaSO_4\,(s) + LiCl\,(aq)$$

Table 7.5.1 from the previous section shows that **LiCl** is soluble in water, but **$BaSO_4$** is not soluble in water.

Balance the equation:

$$BaCl_2\,(aq) + Li_2SO_4\,(aq) \rightarrow BaSO_4\,(s) + 2\,LiCl\,(aq)$$

Although soluble barium salts are toxic, **$BaSO_4$** is so insoluble that it can be used to diagnose stomach and intestinal problems without being absorbed into tissues. An outline of the digestive organs appears on x-rays of patients who have been given a "barium milkshake" or a "barium enema"—a suspension of very fine **$BaSO_4$** particles in water.



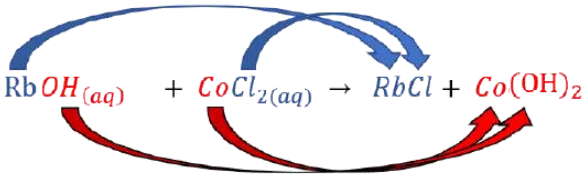
Figure 5.5.2: An x-ray of the digestive organs of a patient who has swallowed a “barium milkshake.” A barium milkshake is a suspension of very fine $BaSO_4$ particles in water; the high atomic mass of barium makes it opaque to x-rays. (Public Domain; Glitzy queen00 via Wikipedia).

Example 5.5.1

Predict what will happen if aqueous solutions of rubidium hydroxide and cobalt(II) chloride are mixed.

Solution

Solutions to Example 7.6.1

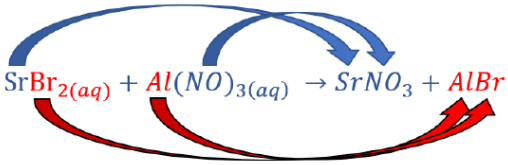
Steps	Example
Change the partners of the anions and cations on the reactant side to form new compounds (products).	 Chemical equation of the reactants rubidium hydroxide and cobalt(II) chloride forming the products rubidium chloride and cobalt hydroxide.
Correct the formulas of the products based on the charges of the ions.	$\mathrm{RbOH(aq) + CoCl_2(aq) \rightarrow RbCl + Co(OH)_2}$
Refer to the solubility rules table to determine insoluble products which will therefore form a precipitate.	$\mathrm{RbOH(aq) + CoCl_2(aq) \rightarrow RbCl(aq) + Co(OH)_2(s)}$
Balance the equation.	Coefficients already balanced. $\mathrm{RbOH(aq) + CoCl_2(aq) \rightarrow RbCl(aq) + Co(OH)_2(s)}$

Example 5.5.2

Predict what will happen if aqueous solutions of strontium bromide and aluminum nitrate are mixed.

Solution

Solutions for Example 7.6.2

Steps	Example
Change the partners of the anions and cations on the reactant side to form new compounds (products).	 Chemical equation of the reactants strontium bromide and aluminum nitrate forming the products strontium nitrate and aluminum bromide.
Correct the formulas of the products based on the charges of the ions.	$\mathbf{SrBr_2\,(aq) + Al(NO_3)_3\,(aq) \rightarrow Sr(NO_3)_2 + AlBr_3}$
Refer to the solubility rules table to determine insoluble products which will therefore form a precipitate.	$\mathbf{SrBr_2\,(aq) + Al(NO_3)_3\,(aq) \rightarrow Sr(NO_3)_2\,(aq) + AlBr_3\,(aq)}$ According to Table 7.5.1 from the previous section, both $\mathbf{AlBr_3}$ (rule 4) and $\mathbf{Sr(NO_3)_2}$ (rule 2) are soluble.
If all possible products are soluble, then no net reaction will occur.	$\mathbf{SrBr_2\,(aq) + Al(NO_3)_3\,(aq) \rightarrow}$ **NO REACTION**

Exercise 5.5.2

Using the information in Table 7.5.1 from the previous section, predict what will happen in each case involving strong electrolytes.

a. An aqueous solution of strontium hydroxide is added to an aqueous solution of iron(II) chloride.
b. Solid potassium phosphate is added to an aqueous solution of mercury(II) perchlorate.
c. Solid sodium fluoride is added to an aqueous solution of ammonium formate.
d. Aqueous solutions of calcium bromide and cesium carbonate are mixed.

Answer a

$Fe(OH)_2$ precipitate is formed.

Answer b

$Hg_3(PO_4)_2$ precipitate is formed.

Answer c

No Reaction.

Answer d

$CaCO_3$ is precipitate formed.

Summary

In a **precipitation reaction**, a subclass of exchange reactions, an insoluble material (a **precipitate**) forms when two electrolyte solutions are mixed. To predict the product of a precipitation reaction, all species initially present in the solutions are identified, as are any combinations likely to produce an insoluble salt.

Contributions & Attributions

- Modified by Joshua Halpern (Howard University)

5.5: Precipitation Reactions is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **7.6: Precipitation Reactions** by Henry Agnew, Marisa Alviar-Agnew is licensed CK-12. Original source: https://www.ck12.org/c/chemistry/.

5.6: Writing Chemical Equations for Reactions in Solution- Molecular, Complete Ionic, and Net Ionic Equations

A typical precipitation reaction occurs when an aqueous solution of barium chloride is mixed with one containing sodium sulfate. The **complete chemical equation** can be written to describe what happens, and such an equation is useful in making chemical calculations.

$$\underbrace{\mathrm{BaCl_2\,(aq) + Na_2SO_4\,(aq) \longrightarrow BaSO_4\,(s) + 2\,NaCl\,(aq)}}_{\text{Complete Chemical Equation}} \tag{5.6.1}$$

However, Equation 5.6.1 does not really represent the microscopic particles (that is, the ions) present in the solution. Below is the complete ionic equation:

$$\underbrace{\mathrm{Ba^{2+}\,(aq) + \overbrace{2Cl^-\,(aq)}^{\text{spectator}} + \overbrace{2Na^+\,(aq)}^{\text{spectator}} + SO_4{}^{2-}\,(aq) \longrightarrow BaSO_4\,(s) + \overbrace{2Na^+\,(aq)}^{\text{spectator}} + \overbrace{Cl^-\,(aq)}^{\text{spectator}}}}_{\text{Complete Ionic Equation}} \tag{5.6.2}$$

Equation 5.6.2 is rather cumbersome and includes so many different ions that it may be confusing. In any case, we are often interested in the independent behavior of ions, not the specific compound from which they came. A precipitate of $\mathrm{BaSO_4\,(s)}$ will form when *any* solution containing $\mathrm{Ba^{2+}\,(aq)}$ is mixed with *any* solution containing $\mathrm{SO_4{}^{2-}\,(aq)}$ (provided concentrations are not extremely small). This happens independently of the $\mathrm{Cl^-\,(aq)}$ and $\mathrm{Na^+\,(aq)}$ ions in Equation 5.6.2. These ions are called **spectator ions** because they do not participate in the reaction. When we want to emphasize the independent behavior of ions, a **net ionic equation** is written, omitting the spectator ions. For precipitation of $\mathrm{BaSO_4}$ the net ionic equation is

$$\underbrace{\mathrm{Ba^{2+}\,(aq) + SO_4{}^{2-}\,(aq) \longrightarrow BaSO_4\,(s)}}_{\text{Net Ionic Equation}} \tag{5.6.3}$$

Example 5.6.1

a. When a solution of $\mathrm{AgNO_3}$ is added to a solution of $\mathrm{CaCl_2}$, insoluble AgCl precipitates. Write three equations (complete chemical equation, complete ionic equation, and net ionic equation) that describe this process.

b. Write the balanced net ionic equation to describe any reaction that occurs when the solutions of $\mathrm{Na_2SO_4}$ and $\mathrm{NH_4I}$ are mixed.

Solution

Solutions to Example 7.7.1

Equation Type	Example 5.6.1*a*	Example 5.6.1*b*
Complete Chemical Equation	$\mathrm{2\,AgNO_3\,(aq) + CaCl_2\,(aq) \longrightarrow 2\,AgCl\,(s) + Ca(NO_3)_2\,(aq)}$ The proper states and formulas of all products are written and the chemical equation is balanced.	$\mathrm{Na_2SO_4\,(aq) + 2\,NH_4I\,(aq) \longrightarrow 2\,NaI\,(aq) + (NH_4)_2SO_4\,(aq)}$ Both products are aqueous so there is no net ionic equation that can be written.
Complete Ionic Equation	$\mathrm{2\,Ag^+\,(aq) + 2\,NO_3{}^-\,(aq) + Ca^{2+}\,(aq) + 2\,Cl^-\,(aq) \longrightarrow 2\,AgCl\,(s) + Ca^{2+}\,(aq) + 2\,NO_3{}^-\,(aq)}$ AgCl is a solid so it does not break up into ions in solution.	
Net Ionic Equation	$\mathrm{Ag^+\,(aq) + Cl^-\,(aq) \longrightarrow AgCl\,(s)}$ All spectator ions are removed. The chemical equation is written using the lowest common coefficients.	NaI and $\mathrm{(NH_4)_2SO_4}$ are both soluble. No net ionic equation. There is no reaction.

The occurrence or nonoccurrence of precipitates can be used to detect the presence or absence of various species in solution. A $BaCl_2$ solution, for instance, is often used as a test for the presence of $SO_4^{2-}(aq)$ ions. There are several insoluble salts of Ba, but they all dissolve in dilute acid except for $BaSO_4$. Thus, if $BaCl_2$ solution is added to an unknown solution which has previously been acidified, the occurrence of a white precipitate is proof of the presence of the SO_4^{2-} ion.



Figure 5.6.1: The three common silver halide precipitates: AgI, AgBr and AgCl (left to right). The silver halides precipitate out of solution, but often form suspensions before settling. (CC BY-SA 3.0; Cychr).

$AgNO_3$ solutions are often used in a similar way to test for halide ions. If $AgNO_3$ solution is added to an acidified unknown solution, a white precipitate indicates the presence of Cl^- ions, a cream-colored precipitate indicates the presence of Br^- ions, and a yellow precipitate indicates the presence of I^- ions (Figure 5.6.1). Further tests can then be made to see whether perhaps a mixture of these ions is present. When $AgNO_3$ is added to tap water, a white precipitate is almost always formed. The Cl^- ions in tap water usually come from the Cl_2 which is added to municipal water supplies to kill microorganisms.

? Exercise 5.6.1

Write balanced net ionic equations to describe any reaction that occurs when the following solutions are mixed.

a. $K_2CO_3 + SrCl_2$
b. $FeSO_4 + Ba(NO_3)_2$

Answer a

$$Sr^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow SrCO_3(s)$$

Answer b

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow Ba(SO_4)(s)$$

Precipitates are also used for quantitative analysis of solutions, that is, to determine the amount of solute or the mass of solute in a given solution. For this purpose it is often convenient to use the first of the three types of equations described above. Then the rules of stoichiometry may be applied.

Contributions & Attributions

- Ed Vitz (Kutztown University), John W. Moore (UW-Madison), Justin Shorb (Hope College), Xavier Prat-Resina (University of Minnesota Rochester), Tim Wendorff, and Adam Hahn.

5.6: Writing Chemical Equations for Reactions in Solution- Molecular, Complete Ionic, and Net Ionic Equations is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **7.7: Writing Chemical Equations for Reactions in Solution- Molecular, Complete Ionic, and Net Ionic Equations** by Henry Agnew, Marisa Alviar-Agnew is licensed CK-12. Original source: https://www.ck12.org/c/chemistry/.

5.7: Acid–Base and Gas Evolution Reactions

Learning Objectives

- Identify when a reaction will evolve a gas.

Neutralization Reactions

Acids and bases react chemically with each other to form *salts*. A salt is a general chemical term for any ionic compound formed from an acid and a base. In reactions where the acid is a hydrogen-ion-containing compound and the base is a hydroxide-ion-containing compound, water is also a product. The general reaction is as follows:

$$\textbf{acid} + \textbf{base} \rightarrow \textbf{water} + \textbf{salt}$$

The reaction of acid and base to make water and a salt is called **neutralization**. Like any chemical equation, a neutralization chemical equation must be properly balanced. For example, the neutralization reaction between sodium hydroxide and hydrochloric acid is as follows:

$$\mathbf{NaOH\,(aq) + HCl\,(aq) \rightarrow NaCl\,(aq) + H_2O\,(\ell)} \tag{5.7.1}$$

with coefficients all understood to be one. The neutralization reaction between sodium hydroxide and sulfuric acid is as follows:

$$\mathbf{2\,NaOH\,(aq) + H_2SO_4\,(aq) \rightarrow Na_2SO_4\,(aq) + 2\,H_2O\,(\ell)} \tag{5.7.2}$$

Example 5.7.1: Neutralizing Nitric Acid

Nitric acid (HNO_3(aq)) can be neutralized by calcium hydroxide ($Ca(OH)_2$(aq)). Write a balanced chemical equation for the reaction between these two compounds and identify the salt that it produces.

Solution

Solutions to Example 7.8.1

Steps	Explanation	Equation
Write the unbalanced equation.	This is a double displacement reaction, so the cations and anions swap to create new products.	$Ca(OH)_2(aq) + HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + H_2O(\ell)$
Balance the equation.	Because there are two OH^- ions in the formula for $Ca(OH)_2$, we need two moles of HNO_3 to provide H^+ ions	$Ca(OH)_2(aq) + \underline{2}HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + \underline{2}H_2O(\ell)$
Additional step: identify the salt.		The salt formed is calcium nitrate.

Exercise 5.7.1

Hydrocyanic acid ($\mathbf{HCN\,(aq)}$) can be neutralized by potassium hydroxide ($\mathbf{KOH\,(aq)}$). Write a balanced chemical equation for the reaction between these two compounds and identify the salt that it produces.

Answer

\[\ce{KOH (aq) + HCN(aq) → KCN (aq) + H2O(ℓ)} \nonumber \]

Gas Evolving Reactions

A gas evolution reaction is a chemical process that produces a gas, such as oxygen or carbon dioxide. In the following examples, an acid reacts with a carbonate, producing salt, carbon dioxide, and water, respectively. For example, nitric acid reacts with sodium carbonate to form sodium nitrate, carbon dioxide, and water (Table 5.7.1):

$$\mathbf{2\,HNO_3(aq) + Na_2CO_3(aq) \longrightarrow 2\,NaNO_3(aq) + CO_2(g) + H_2O(l)}$$

Sulfuric acid reacts with calcium carbonate to form calcium sulfate, carbon dioxide, and water:

$$\mathbf{H_2SO_4\,(aq) + CaCO_3\,(aq) \longrightarrow CaSO_4\,(aq) + CO_2(g) + H_2O\,(l)}$$

Hydrochloric acid reacts with calcium carbonate to form calcium chloride, carbon dioxide, and water:

$$\mathbf{2\,HCl\,(aq) + CaCO_3\,(aq) \longrightarrow CaCl_2\,(aq) + CO_2\,(g) + H_2O\,(l)}$$

Figure 5.7.1 demonstrates this type of reaction:

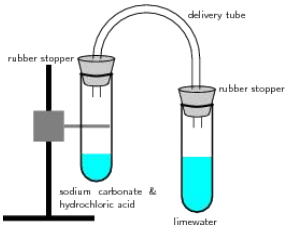


Figure 5.7.1: Reaction of acids with carbonates. In this reaction setup, lime water (water + calcium hydroxide) is poured into one of the test tubes and sealed with a stopper. A small amount of hydrochloric acid is carefully poured into the remaining test tube. A small amount of sodium carbonate is added to the acid, and the tube is sealed with a rubber stopper. The two tubes are connected. As a result of the acid-carbonate reaction, carbon dioxide is produced and the lime water turns milky.

In this reaction setup, lime water, a dilute calcium hydroxide ($Ca(OH)_2$) solution, is poured into one of the test tubes and sealed with a stopper. A small amount of hydrochloric acid is carefully poured into the remaining test tube. A small amount of sodium carbonate is added to the acid, and the tube is sealed with a rubber stopper. The two tubes are connected. As a result of the acid-carbonate reaction, carbon dioxide is produced and the lime water turns milky.

Table 5.7.1: Types of Compounds That Undergo Gas-Evolution Reactions

Reactant Type	Intermediate Product	Gas Evolved	Example
sulfide	none	H_2S	$2\,HCl\,(aq) + K_2S \rightarrow H_2S\,(g) + 2\,KCl\,(aq)$
carbonates and bicarbonates	H_2CO_3	CO_2	$2\,HCl\,(aq) + K_2CO_2 \rightarrow H_2O\,(l) + CO_2\,(g)$
sulfites and bisulfites	H_2SO_3	SO_2	$2\,HCl\,(aq) + K_2SO_2 \rightarrow H_2O\,(l) + SO_2\,(g)$
ammonia	NH_4OH	NH_3	\(\ce{NH4Cl(aq) + KOH \rightarrow H2O (l) + NH3(g) + 2KCl (aq)}\)

The gas-evolving experiment lime water is illustrated in the following video:



***Video* 5.7.1:** *Carbon Dioxide (CO_2) & Limewater (Chemical Reaction). As the reaction proceeds, the limewater on the turns from clear to milky; this is due to the $CO_2(g)$ reacting with the aqueous calcium hydroxide to form calcium carbonate, which is only slightly soluble in water.*

When this experiment is repeated with nitric or sulfuric acid instead of HCl, it yields the same results: the clear limewater turns milky, indicating the production of carbon dioxide. Another method to chemically generate gas is the oxidation of metals in acidic solutions. This reaction will yield a metal salt and hydrogen gas.

$$2\,HCl\,(aq) + Zn\,(s) \rightarrow ZnCl_2\,(aq) + H_2\,(g)$$

Here, hydrochloric acid oxidizes zinc to produce an aqueous metal salt and hydrogen gas bubbles. Recall that oxidation refers to a loss of electrons, and reduction refers to the gain of electrons. In the above redox reaction, neutral zinc is oxidized to Zn^{2+}, and the acid, H^+, is reduced to $H_2(g)$. The oxidation of metals by strong acids is another common example of a gas evolution reaction.

Contributors & Affiliations

- Boundless (www.boundless.com)
- Wikipedia (CC-BY-SA-3.0)
- 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).

5.7: Acid–Base and Gas Evolution Reactions is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **7.8: Acid–Base and Gas Evolution Reactions** by Henry Agnew, Marisa Alviar-Agnew is licensed CK-12. Original source: https://www.ck12.org/c/chemistry/.

5.8: Oxidation–Reduction Reactions

Learning Objectives

- Define *oxidation* and *reduction*.
- Assign oxidation numbers to atoms in simple compounds.
- Recognize a reaction as an oxidation-reduction reaction.

In the course of a chemical reaction between a metal and a nonmetal, electrons are transferred from the metal atoms to the nonmetal atoms. For example, when zinc metal is mixed with sulfur and heated, the compound zinc sulfide is produced. Two valence electrons from each zinc atom are transferred to each sulfur atom.

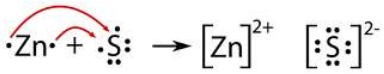


Figure 5.8.1: Reaction between zinc and sulfur.

Since the zinc is losing electrons in the reaction, it is being oxidized. The sulfur is gaining electrons and is thus being reduced. An **oxidation-reduction reaction** is a reaction that involves the full or partial transfer of electrons from one reactant to another. **Oxidation** is the full or partial loss of electrons or the gain of oxygen. **Reduction** is the full or partial gain of electrons or the loss of oxygen. A **redox reaction** is another term for an oxidation-reduction reaction.

Each of these processes can be shown in a separate equation called a half-reaction. A **half-reaction** is an equation that shows either the oxidation or the reduction reaction that occurs during a redox reaction.

$$\underbrace{Zn \longrightarrow Zn_2^{2+} + e^-}_{\text{Oxidation}} \tag{5.8.1}$$

$$\underbrace{S^+ \; 2\,e^- \longrightarrow S^{2-}}_{\text{Reduction}} \tag{5.8.2}$$

It is important to remember that the two half-reactions occur simultaneously. The resulting ions that are formed are then attracted to one another in an ionic bond.

Another example of an oxidation-reduction reaction involving electron transfer is the well-known combination of metallic sodium and chlorine gas to form sodium chloride:

$$2\,Na^+Cl_2 \longrightarrow 2\,NaCl \tag{5.8.3}$$

The half reactions are as follows:

$$\underbrace{2\,Na \longrightarrow 2\,Na^+ + 2\,e^-}_{\text{Oxidation}} \tag{5.8.4}$$

$$\underbrace{Cl_2 + 2\,e^- \longrightarrow 2\,Cl^-}_{\text{Reduction}} \tag{5.8.5}$$

We will concern ourselves with the balancing of these equations at another time.

Oxidation Numbers

Redox reactions require that we keep track of the electrons assigned to each atom in a chemical reaction. How do we do that? We use **oxidation numbers** to keep track of electrons in atoms. Oxidation numbers are assigned to atoms based on four rules. Oxidation numbers are not necessarily equal to the charge on the atom (although sometimes they can be); we must keep the concepts of charge and oxidation numbers separate.

Assigning Oxidation Numbers

The rules for assigning oxidation numbers to atoms are as follows:

1. Atoms in their elemental state are assigned an oxidation number of 0.

In H_2, both H atoms have an oxidation number of 0.

2. Atoms in monatomic (i.e., one-atom) ions are assigned an oxidation number equal to their charge. Oxidation numbers are usually written with the sign first, then the magnitude, to differentiate them from charges.

In $MgCl_2$, magnesium has an oxidation number of +2, while chlorine has an oxidation number of −1.

3. In compounds, fluorine is assigned a −1 oxidation number; oxygen is usually assigned a −2 oxidation number (except in peroxide compounds [where it is −1] and in binary compounds with fluorine [where it is positive]); and hydrogen is usually assigned a +1 oxidation number [except when it exists as the hydride ion (H^-), in which case rule 2 prevails].

In H_2O, the H atoms each have an oxidation number of +1, while the O atom has an oxidation number of −2, even though hydrogen and oxygen do not exist as ions in this compound (rule 3). By contrast, by rule 3, each H atom in hydrogen peroxide (H_2O_2) has an oxidation number of +1, while each O atom has an oxidation number of −1.

4. In compounds, all other atoms are assigned an oxidation number so that the sum of the oxidation numbers on all the atoms in the species equals the charge on the species (which is zero if the species is neutral).

In SO_2, each O atom has an oxidation number of −2; for the sum of the oxidation numbers to equal the charge on the species (which is zero), the S atom is assigned an oxidation number of +4. Does this mean that the sulfur atom has a 4+ charge on it? No, it means only that the S atom is assigned a +4 oxidation number by our rules of apportioning electrons among the atoms in a compound.

Example 5.8.1: Assigning Oxidation States

Assign oxidation numbers to the atoms in each substance.

a. Cl_2
b. GeO_2
c. $Ca(NO_3)_2$

Solution

a. Cl_2 is the elemental form of chlorine. Rule 1 states that each atom has an oxidation number of 0.
b. By rule 3, oxygen is normally assigned an oxidation number of −2. For the sum of the oxidation numbers to equal the charge on the species (zero), the Ge atom is assigned an oxidation number of +4.
c. $Ca(NO_3)_2$ can be separated into two parts: the Ca^{2+} ion and the NO_3^- ion. Considering these separately, the Ca^{2+} ion has an oxidation number of +2 by rule 2. Now consider the NO_3^- ion. Oxygen is assigned an oxidation number of −2, and there are three of them. According to rule 4, the sum of the oxidation numbers on all atoms must equal the charge on the species, so we have the simple algebraic equation

$$x + 3(-2) = -1$$

where x is the oxidation number of the N atom and the −1 represents the charge on the species. Evaluating for x,

$$x + (-6) = -1 \quad x = +5$$

Thus the oxidation number on the N atom in the NO_3^- ion is +5.

Exercise 5.8.1: Assigning Oxidation States

Assign oxidation numbers to the atoms in the following:

a. H_3PO_4
b. MgO

Answer a

https://chem.libretexts.org/@go/page/216900

H: +1; O: −2; P: +5

Answer b

Mg: +2, O: −2

All redox reactions occur with a simultaneous change in the oxidation numbers of some atoms. At least two elements must change their oxidation numbers. When an oxidation number of an atom is increased in the course of a redox reaction, that atom is being *oxidized*. When an oxidation number of an atom is decreased in the course of a redox reaction, that atom is being *reduced*. Thus oxidation and reduction can also be defined in terms of increasing or decreasing oxidation numbers, respectively.

Example 5.8.2: Formation of Sodium Bromide

Identify what is being oxidized and reduced in the following redox reaction.

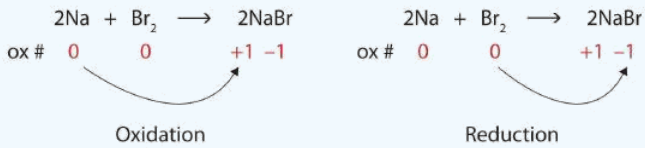
$$2\,Na + Br_2 \longrightarrow 2\,NaBr$$

Solution

Both reactants are the elemental forms of their atoms, so the Na and Br atoms have oxidation numbers of 0. In the ionic product, the Na^+ ions have an oxidation number of +1, while the Br^- ions have an oxidation number of −1.

$$\overset{0}{2Na} + \overset{0}{Br_2} \rightarrow \overset{+1-1}{2NaBr}$$

Sodium is increasing its oxidation number from 0 to +1, so it is being oxidized; bromine is decreasing its oxidation number from 0 to −1, so it is being reduced:



Equation of sodium and bromine reacting, labeled with sodium's oxidation number change from 0 to +1 and bromine's oxidation number change from 0 to -1

Because oxidation numbers are changing, this is a redox reaction. The total number of electrons being lost by sodium (two, one lost from each Na atom) is gained by bromine (two, one gained for each Br atom).

Exercise 5.8.2: Oxidation of Carbon

Identify what is being oxidized and reduced in this redox reaction.

$$C + O_2 \rightarrow CO_2$$

Answer

C is being oxidized from 0 to +4; O is being reduced from 0 to −2

Oxidation reactions can become quite complex, as attested by the following redox reaction:

$$6H^+(aq) + 2\overset{+7}{MnO_4^-}(aq) + 5\overset{-1}{H_2O_2}(l) \rightarrow 2\overset{+2}{Mn^{2+}}(aq) + 5\overset{0}{O_2}(g) + 8H_2O(l)$$

To demonstrate that this is a redox reaction, the oxidation numbers of the species being oxidized and reduced are listed; can you determine what is being oxidized and what is being reduced? This is also an example of a net ionic reaction; spectator ions that do not change oxidation numbers are not displayed in the equation. Eventually, we will need to learn techniques for writing correct (i.e., balanced) redox reactions.

Combustion Reactions

A **combustion reaction** is a reaction in which a substance reacts with oxygen gas, releasing energy in the form of light and heat. Combustion reactions must involve $\mathbf{O_2}$ as one reactant. The combustion of hydrogen gas produces water vapor.

$$\mathbf{2H_2}\,(g) + \mathbf{O_2}\,(g) \rightarrow \mathbf{2H_2O}\,(g) \tag{5.8.6}$$

Notice that this reaction also qualifies as a combination reaction.

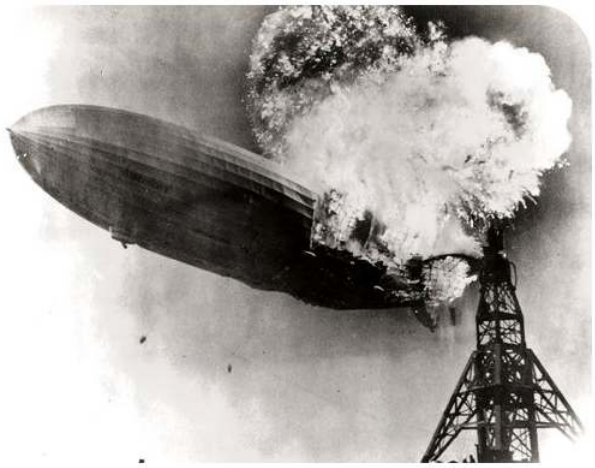


Figure 5.8.2: Explosion of the Hindenberg.

The *Hindenberg* was a hydrogen-filled airship that suffered an accident upon its attempted landing in New Jersey in 1937. The hydrogen immediately combusted in a huge fireball, destroying the airship and killing 36 people. The chemical reaction was a simple one: hydrogen combining with oxygen to produce water (Equation 5.8.6).

Many combustion reactions occur with a hydrocarbon, a compound made up solely of carbon and hydrogen. The products of the combustion of hydrocarbons are carbon dioxide and water. Many hydrocarbons are used as fuel because their combustion releases very large amounts of heat energy. Propane ($\mathbf{C_3H_8}$) is a gaseous hydrocarbon that is commonly used as the fuel source in gas grills.

$$\mathbf{C_3H_8}\,(g) + 5\mathbf{O_2}\,(g) \rightarrow 3\mathbf{CO_2}\,(g) + 4\mathbf{H_2O}\,(g)$$

Example 5.8.3: Combustion of Ethanol

Ethanol can be used as a fuel source in an alcohol lamp. The formula for ethanol is $\mathbf{C_2H_5OH}$. Write the balanced equation for the combustion of ethanol.

Solution

Solutions to Example 7.9.3

Steps	Example Solution
Write the unbalanced reaction.	$\mathbf{C_2H_5OH}\,(l) + \mathbf{O_2}\,(g) \rightarrow \mathbf{CO_2}\,(g) + \mathbf{H_2O}\,(g)$ Ethanol and atmospheric oxygen are the reactants. As with a hydrocarbon, the products of the combustion of an alcohol are carbon dioxide and water.
Balance the equation.	$\mathbf{C_2H_5OH}\,(l) + 3\mathbf{O_2}\,(g) \rightarrow 2\mathbf{CO_2}\,(g) + 3\mathbf{H_2O}\,(g)$
Think about your result.	Combustion reactions must have oxygen as a reactant. Note that the water produced is in the gas state, rather than the liquid state, because of the high temperatures that accompany a combustion reaction.

Exercise 5.8.3: Combustion of Hexane

Write the balanced equation for the combustion of hexane, C_6H_{14}

Answer

$$2\,C_6H_{14}\,(\ell) + 19\,O_2\,(g) \longrightarrow 12\,CO_2\,(g) + 14\,H_2O(\ell)$$

Contributors & Affiliations

5.8: Oxidation–Reduction Reactions is shared under a CC BY-NC license and was authored, remixed, and/or curated by LibreTexts.

- **7.9: Oxidation–Reduction Reactions** by Henry Agnew, Marisa Alviar-Agnew is licensed CK-12. Original source: https://www.ck12.org/c/chemistry/.

5.9: Classifying Chemical Reactions

Learning Objectives

- Classify a chemical reaction as a synthesis, decomposition, single replacement, double replacement, or a combustion reaction.
- Predict the products of simple reactions.

The chemical reactions we have described are only a tiny sampling of the infinite number of chemical reactions possible. How do chemists cope with this overwhelming diversity? How do they predict which compounds will react with one another and what products will be formed? The key to success is to find useful ways to categorize reactions. Familiarity with a few basic types of reactions will help you to predict the products that form when certain kinds of compounds or elements come in contact.

Most chemical reactions can be classified into one or more of five basic types: acid–base reactions, exchange reactions, condensation reactions (and the reverse, cleavage reactions), and oxidation–reduction reactions. The general forms of these five kinds of reactions are summarized in Table **5.9.1**, along with examples of each. It is important to note, however, that many reactions can be assigned to more than one classification, as you will see in our discussion.

Table **5.9.1:** *Basic Types of Chemical Reactions*

Name of Reaction	General Form	Examples
Oxidation–Reduction (redox)	oxidant + reductant → reduced oxidant + oxidized reductant	$C_7H_{16}(l) + 11O_2(g) \rightarrow 7CO_2(g) + 8H_2O(g)$
Acid–Base	acid + base → salt	$NaOH(aq) + HNO_3(aq) \rightarrow NaNO_3(aq) + H_2O(l)$
Exchange: Single Replacement	AB + C → AC + B	$ZnCl_2(aq) + Mg(s) \rightarrow MgCl_2(aq) + Zn(s)$
Exchange: Double Replacement	AB + CD → AD + CB	$BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaCl(aq)$
Combination (Synthesis)	A + B → AB	$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$ $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$
Decomposition	AB → A + B	$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

The classification scheme is only for convenience; the same reaction can be classified in different ways, depending on which of its characteristics is most important. Oxidation–reduction reactions, in which there is a net transfer of electrons from one atom to another, and condensation reactions are discussed in this section. Acid–base reactions are one kind of exchange reaction—the formation of an insoluble salt, such as barium sulfate, when solutions of two soluble salts are mixed together.

Combination Reactions

A **combination reaction** is a reaction in which two or more substances combine to form a single new substance. Combination reactions can also be called synthesis reactions. The general form of a combination reaction is:

$$\mathbf{A + B \rightarrow AB}$$

One combination reaction is two elements combining to form a compound. Solid sodium metal reacts with chlorine gas to produce solid sodium chloride.

$$\mathbf{2Na\,(\mathit{s}) + Cl_2\,(\mathit{g}) \rightarrow 2NaCl\,(\mathit{s})}$$

Notice that in order to write and balance the equation correctly, it is important to remember the seven elements that exist in nature as diatomic molecules ($\mathbf{H_2}$, $\mathbf{N_2}$, $\mathbf{O_2}$, $\mathbf{F_2}$, $\mathbf{Cl_2}$, $\mathbf{Br_2}$, and $\mathbf{I_2}$).

One type of combination reaction that occurs frequently is the reaction of an element with oxygen to form an oxide. Metals and nonmetals both react readily with oxygen under most conditions. Magnesium reacts rapidly and dramatically when ignited, combining with oxygen from the air to produce a fine powder of magnesium oxide:

$$2\text{Mg}\,(s) + \text{O}_2\,(g) \rightarrow 2\text{MgO}\,(s)$$

Sulfur reacts with oxygen to form sulfur dioxide:

$$\text{S}\,(s) + \text{O}_2\,(g) \rightarrow \text{SO}_2\,(g)$$

When nonmetals react with one another, the product is a molecular compound. Often, the nonmetal reactants can combine in different ratios and produce different products. Sulfur can also combine with oxygen to form sulfur trioxide:

$$2\text{S}\,(s) + 3\text{O}_2\,(g) \rightarrow 2\text{SO}_3\,(g)$$

Transition metals are capable of adopting multiple positive charges within their ionic compounds. Therefore, most transition metals are capable of forming different products in a combination reaction. Iron reacts with oxygen to form both iron (II) oxide and iron (III) oxide:

$$2\text{Fe}\,(s) + \text{O}_2\,(g) \rightarrow 2\text{FeO}\,(s)$$

$$4\text{Fe}\,(s) + 3\text{O}_2\,(g) \rightarrow 2\text{Fe}_2\text{O}_3\,(s)$$

Example 5.9.1: Combustion of Solid Potassium

Potassium is a very reactive alkali metal that must be stored under oil in order to prevent it from reacting with air. Write the balanced chemical equation for the combination reaction of potassium with oxygen.

Solution

Solutions to Example 7.10.1

Steps	Example Solution
Plan the problem.	Make sure formulas of all reactants and products are correct before balancing the equation. Oxygen gas is a diatomic molecule. Potassium oxide is an ionic compound and so its formula is constructed by the crisscross method. Potassium as an ion becomes K^+, while the oxide ion is O^{2-}.
Solve.	The skeleton (unbalanced) equation: $\text{K}\,(s) + \text{O}_2\,(g) \rightarrow \text{K}_2\text{O}\,(s)$ The equation is then easily balanced with coefficients. $4\text{K}\,(s) + \text{O}_2\,(g) \rightarrow 2\text{K}_2\text{O}\,(s)$
Think about your result.	Formulas are correct and the resulting combination reaction is balanced.

Combination reactions can also take place when an element reacts with a compound to form a new compound composed of a larger number of atoms. Carbon monoxide reacts with oxygen to form carbon dioxide according to the equation:

$$2\text{CO}\,(g) + \text{O}_2\,(g) \rightarrow 2\text{CO}_2\,(g)$$

Two compounds may also react to form a more complex compound. A very common example is the reactions of oxides with water. Calcium oxide reacts readily with water to produce an aqueous solution of calcium hydroxide:

$$\text{CaO}\,(s) + \text{H}_2\text{O}\,(l) \rightarrow \text{Ca(OH)}_2\,(aq)$$

Sulfur trioxide gas reacts with water to form sulfuric acid. This is an unfortunately common reaction that occurs in the atmosphere in some places where oxides of sulfur are present as pollutants. The acid formed in the reaction falls to the ground as acid rain.

$$SO_3\,(g) + H_2O\,(l) \rightarrow H_2SO_4\,(aq)$$



Figure 5.9.1: Acid rain has severe consequences on both natural and manmade objects. Acid rain degrades marble statues like the one on the left (A). The trees in the forest on the right (B) have been killed by acid rain.

? Exercise 5.9.1

a. Write the chemical equation for the synthesis of silver bromide, $AgBr$.
b. Predict the products for the following reaction: $CO_2\,(g) + H_2O\,(l)$

Answer a:

$$2Ag + Br_2 \rightarrow 2AgBr$$

Answer b:

$$CO_2\,(g) + H_2O\,(l) \rightarrow H_2CO_3$$

Decomposition Reactions

A **decomposition reaction** is a reaction in which a compound breaks down into two or more simpler substances. The general form of a decomposition reaction is:

$$AB \rightarrow A + B$$

Most decomposition reactions require an input of energy in the form of heat, light, or electricity.

Binary compounds are compounds composed of just two elements. The simplest kind of decomposition reaction is when a binary compound decomposes into its elements. Mercury (II) oxide, a red solid, decomposes when heated to produce mercury and oxygen gas:

$$2HgO\,(s) \rightarrow 2Hg\,(l) + O_2\,(g)$$



***Video* 5.9.2:** *Mercury (II) oxide is a red solid. When it is heated, it decomposes into mercury metal and oxygen gas.*

A reaction is also considered to be a decomposition reaction even when one or more of the products are still compounds. A metal carbonate decomposes into a metal oxide and carbon dioxide gas. For example, calcium carbonate decomposes into calcium oxide and carbon dioxide:

$$CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)$$

Metal hydroxides decompose on heating to yield metal oxides and water. Sodium hydroxide decomposes to produce sodium oxide and water:

$$2NaOH\,(s) \rightarrow Na_2O\,(s) + H_2O\,(g)$$

Some unstable acids decompose to produce nonmetal oxides and water. Carbonic acid decomposes easily at room temperature into carbon dioxide and water:

$$H_2CO_3\,(aq) \rightarrow CO_2\,(g) + H_2O\,(l)$$

Example 5.9.2: Electrolysis of Water

When an electric current is passed through pure water, it decomposes into its elements. Write a balanced equation for the decomposition of water.

Solution

Solutions to Example 7.10.2

Steps	Example Solution
Plan the problem.	Water is a binary compound composed of hydrogen and oxygen. The hydrogen and oxygen gases produced in the reaction are both diatomic molecules.
Solve.	The skeleton (unbalanced) equation: $$H_2O\,(l) \xrightarrow{elec} H_2\,(g) + O_2\,(g)$$ Note the abbreviation "**elec**" above the arrow to indicate the passage of an electric current to initiate the reaction. Balance the equation. $$2H_2O\,(l) \xrightarrow{elec} 2H_2\,(g) + O_2\,(g)$$
Think about your result.	The products are elements and the equation is balanced.

Exercise 5.9.2

Write the chemical equation for the decomposition of:

a. Al_2O_3
b. Ag_2S

Answer a

$$2Al_2O_3 \rightarrow 4Al + 3O_2$$

Answer b

$$Ag_2S \rightarrow 2Ag + S$$

Single Replacement Reactions

A third type of reaction is the single replacement reaction, in which one element replaces a similar element in a compound. The general form of a single-replacement (also called single-displacement) reaction is:

$$A + BC \rightarrow AC + B$$

In this general reaction, element **A** is a metal and replaces element **B**, also a metal, in the compound. When the element that is doing the replacing is a nonmetal, it must replace another nonmetal in a compound, and the general equation becomes:

$$\mathbf{Y + XZ \rightarrow XY + Z}$$

where **Y** is a nonmetal and replaces the nonmetal **Z** in the compound with **X**.

Metal Replacement

Magnesium is a more reactive metal than copper. When a strip of magnesium metal is placed in an aqueous solution of copper (II) nitrate, it replaces the copper. The products of the reaction are aqueous magnesium nitrate and solid copper metal.

$$\mathbf{Mg\,(\mathit{s}) + Cu(NO_3)_2\,(\mathit{aq}) \rightarrow Mg(NO_3)_2\,(\mathit{aq}) + Cu\,(\mathit{s})}$$

This subcategory of single-replacement reactions is called a metal replacement reaction because it is a metal that is being replaced (copper).

Hydrogen Replacement

Many metals react easily with acids and when they do so, one of the products of the reaction is hydrogen gas. Zinc reacts with hydrochloric acid to produce aqueous zinc chloride and hydrogen (figure below).

$$\mathbf{Zn\,(\mathit{s}) + 2HCl\,(\mathit{aq}) \rightarrow ZnCl_2\,(\mathit{aq}) + H_2\,(\mathit{g})}$$

In a hydrogen replacement reaction, the hydrogen in the acid is replaced by an active metal. Some metals are so reactive that they are capable of replacing the hydrogen in water. The products of such a reaction are the metal hydroxide and hydrogen gas. All Group 1 metals undergo this type of reaction. Sodium reacts vigorously with water to produce aqueous sodium hydroxide and hydrogen (see figure below).

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



Figure **5.9.2**: (First image) Zinc metal reacts with hydrochloric acid to give off hydrogen gas in a single-displacement reaction. (Second image) Sodium metal reacts vigorously with water, giving off hydrogen gas. A large piece of sodium will often generate so much heat that the hydrogen will ignite.

Halogen Replacement

The element chlorine reacts with an aqueous solution of sodium bromide to produce aqueous sodium chloride and elemental bromine:

$$\mathbf{Cl_2\,(\mathit{g}) + 2NaBr\,(\mathit{aq}) \rightarrow 2NaCl\,(\mathit{aq}) + Br_2\,(\mathit{l})}$$

The reactivity of the halogen group (group 17) decreases from top to bottom within the group. Fluorine is the most reactive halogen, while iodine is the least. Since chlorine is above bromine, it is more reactive than bromine and can replace it in a halogen replacement reaction.

Example 5.9.3

What are the products of the reaction between solid aluminum (**Al**) and iron (III) oxide ($\mathbf{Fe_2O_3}$)?

Solution

Solutions to Example 7.10.3

Steps	Example Solution
Plan the problem.	To predict the products, we need to know that aluminum will replace iron and form aluminum oxide (the metal will replace the metal ion in the compound). Aluminum has a charge of $+3$ and oxygen has a charge of -2. The compound formed between aluminum and oxygen, therefore, will be Al_2O_3. Since iron is replaced in the compound by aluminum, the iron will now be the single element in the products.
Solve.	The unbalanced equation will be: $$Al + Fe_2O_3 \rightarrow Al_2O_3 + Fe$$ and the balanced equation will be: $$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$$
Think about your result.	This is a single replacement reaction, and when balanced the coefficients accurately reflect that the iron and aluminum have the same charge in this reaction.

? Exercise 5.9.3

a. Write the chemical equation for the single replacement reaction between zinc solid and lead (II) nitrate solution to produce zinc nitrate solution and solid lead. (Note that zinc forms ions with a $+2$ charge.)

b. Predict the products for the following reaction: $Fe + CuSO_4$. (In this reaction, assume iron forms ions with a $+2$ charge.)

Answer a

$$Zn + Pb(NO_3)_2 \rightarrow Pb + Zn(NO_3)_2$$

Answer b

$$Fe + CuSO_4 \rightarrow Cu + FeSO_4$$

Double Replacement Reactions

A **double-replacement reaction** is a reaction in which the positive and negative ions of two ionic compounds exchange places to form two new compounds. The general form of a double-replacement (also called double-displacement) reaction is:

$$AB + CD \rightarrow AD + BC$$

In this reaction, A and C are positively-charged cations, while B and D are negatively-charged anions. Double-replacement reactions generally occur between substances in aqueous solution. In order for a reaction to occur, one of the products is usually a solid precipitate, a gas, or a molecular compound such as water.

Formation of a Precipitate

A precipitate forms in a double-replacement reaction when the cations from one of the reactants combine with the anions from the other reactant to form an insoluble ionic compound. When aqueous solutions of potassium iodide and lead (II) nitrate are mixed, the following reaction occurs:

$$2KI\,(aq) + Pb(NO_3)_2\,(aq) \rightarrow 2KNO_3\,(aq) + PbI_2\,(s) \qquad (5.9.1)$$

There are very strong attractive forces that occur between Pb^{2+} and I^- ions and the result is a brilliant yellow precipitate (Figure 5.9.3). The other product of the reaction, potassium nitrate, remains soluble.



Figure 5.9.3: Lead (II) iodide precipitates when potassium iodide is mixed with lead (II) nitrate (Equation 5.9.1). (CC BY-SA 3.0; PRHaney).

Formation of a Gas

Some double-replacement reactions produce a gaseous product which then bubbles out of the solution and escapes into the air. When solutions of sodium sulfide and hydrochloric acid are mixed, the products of the reaction are aqueous sodium chloride and hydrogen sulfide gas:

$$\mathrm{Na_2S}\,(aq) + 2\mathrm{HCl}\,(aq) \rightarrow 2\mathrm{NaCl}\,(aq) + \mathrm{H_2S}\,(g)$$

Formation of a Molecular Compound

Another kind of double-replacement reaction is one that produces a molecular compound as one of its products. Many examples in this category are reactions that produce water. When aqueous hydrochloric acid is reacted with aqueous sodium hydroxide, the products are aqueous sodium chloride and water:

$$\mathrm{HCl}\,(aq) + \mathrm{NaOH}\,(aq) \rightarrow \mathrm{NaCl}\,(aq) + \mathrm{H_2O}\,(l)$$

Example 5.9.4

Write a complete and balanced chemical equation for the double-replacement reaction $\mathrm{NaCN}\,(aq) + \mathrm{HBr}\,(aq) \rightarrow$ (hydrogen cyanide gas is formed).

Solution

Solutions to Example 7.10.4

Steps	Example Solution
Plan the problem.	The production of a gas drives the reaction.
Solve.	The cations of both reactants are $+1$ charged ions, while the anions are -1 charged ions. After exchanging partners, the balanced equation is: $\mathrm{NaCN}\,(aq) + \mathrm{HBr}\,(aq) \rightarrow \mathrm{NaBr}\,(aq) + \mathrm{HCN}\,(g)$
Think about your result.	This is a double replacement reaction. All formulas are correct and the equation is balanced.

Exercise 5.9.4

Write a complete and balanced chemical equation for the double-replacement reaction $(\mathrm{NH_4})_2\mathrm{SO_4}\,(aq) + \mathrm{Ba(NO_3)_2}\,(aq) \rightarrow$ (a precipitate of barium sulfate forms).

Answer a:

$$(\mathrm{NH_4})_2\mathrm{SO_4}\,(aq) + \mathrm{Ba(NO_3)_2}\,(aq) \rightarrow 2\mathrm{NH_4NO_3}\,(aq) + \mathrm{BaSO_4}\,(s)$$

Occasionally, a reaction will produce both a gas and a molecular compound. The reaction of a sodium carbonate solution with hydrochloric acid produces aqueous sodium chloride, carbon dioxide gas, and water:

$$\mathrm{Na_2CO_3}\,(aq) + \mathrm{2HCl}\,(aq) \rightarrow 2\ \mathrm{NaCl}\,(aq) + \mathrm{CO_2}\,(g) + \mathrm{H_2O}\,(l)$$

5.9: Classifying Chemical Reactions is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **7.10: Classifying Chemical Reactions** by Henry Agnew, Marisa Alviar-Agnew is licensed CK-12. Original source: https://www.ck12.org/c/chemistry/.

CHAPTER OVERVIEW

6: Stoichiometry of Chemical Reactions

A general chemistry Libretexts Textmap organized around the textbook
General Chemistry -Atoms First
By OpenStax

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*.

6.1: Reaction Stoichiometry
6.2: Reaction Yields
6.3: Quantitative Chemical Analysis
6.E: Stoichiometry of Chemical Reactions (Exercises)

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

6.1: 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

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

$$\mathrm{1\ cup\ mix} + \frac{3}{4}\ \mathrm{cup\ milk} + \mathrm{1\ egg} \rightarrow \mathrm{8\ pancakes} \tag{6.1.1}$$

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

$$24\ \cancel{\mathrm{pancakes}} \times \frac{1\ \mathrm{egg}}{8\ \cancel{\mathrm{pancakes}}} = 3\ \mathrm{eggs} \tag{6.1.2}$$

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:

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightarrow 2\,\mathrm{NH_3}(g) \tag{6.1.3}$$

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:

$$\frac{2\,NH3\ molecules}{3H2\ molecules} \text{ or } \frac{2\ doz\ NH3\ molecules}{3\ doz\ H2\ molecules} \text{ or } \frac{2\ mol\ NH3\ molecules}{3\ mol\ H2\ molecules} \tag{6.1.4}$$

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 6.1.1: 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 **6.1.2**)?

$$2\,\mathrm{Al} + 3\,\mathrm{I_2} \rightarrow 2\,\mathrm{AlI_3} \tag{6.1.5}$$

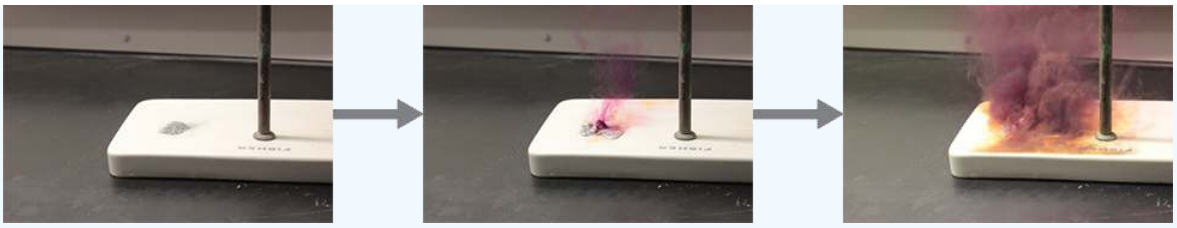
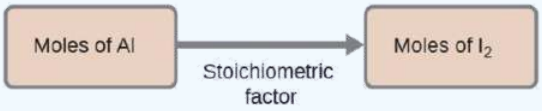


Figure **6.1.1**: Aluminum and iodine react to produce aluminum iodide. The heat of the reaction vaporizes some of the solid iodine as a purple vapor. (credit: modification of work by Mark Ott)

Three pictures showing the progression of the reaction between iodine and aluminum. The first diagram shows only a pile of silver powder while the second diagram shows small amount of vapor forming. The final picture shows a large release of purple vapor.

Solution

Referring to the balanced chemical equation, the stoichiometric factor relating the two substances of interest is $\frac{3\ mol\ I2}{2\ mol\ Al}$. The molar amount of iodine is derived by multiplying the provided molar amount of aluminum by this factor:



$$\text{mol I}_2 = 0.429\ \cancel{\text{mol Al}} \times \frac{3\ \text{mol I}_2}{2\ \cancel{\text{mol Al}}}$$

$$= 0.644\ \text{mol I}_2$$

Exercise 6.1.1

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 $3\,Ca(OH)_2 + 2\,H_3PO_4 \rightarrow Ca_3(PO_4)_2 + 6\,H_2O$?

Answer

2.04 mol

Example 6.1.2: Number of Product Molecules Generated by a Reaction

How many carbon dioxide molecules are produced when 0.75 mol of propane is combusted according to this equation?

$$C_3H_8 + 5\,O_2 \rightarrow 3\,CO_2 + 4\,H_2O \tag{6.1.6}$$

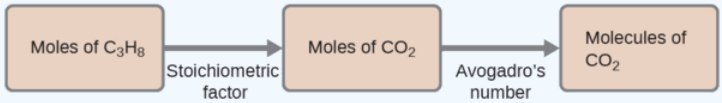
Solution

The approach here is the same as for Example **6.1.1**, though the absolute number of molecules is requested, not the number of moles of molecules. This will simply require use of the moles-to-numbers conversion factor, Avogadro's number.

The balanced equation shows that carbon dioxide is produced from propane in a 3:1 ratio:

\[\ce{\dfrac{3\: mol\: CO2}{1\: mol\: C3H8}} \label{4.4.7} \]

Using this stoichiometric factor, the provided molar amount of propane, and Avogadro's number,



$$0.75\ \cancel{\text{mol C}_3\text{H}_8} \times \frac{3\ \cancel{\text{mol CO}_2}}{1\ \cancel{\text{mol C}_3\text{H}_8}} \times \frac{6.022 \times 10^{23}\ \text{CO}_2\ \text{molecules}}{\cancel{\text{mol CO}_2}} \tag{6.1.7}$$

$$= 1.4 \times 10^{24}\ \text{CO}_2\ \text{molecules}$$

? Exercise 6.1.1

How many NH_3 molecules are produced by the reaction of 4.0 mol of $Ca(OH)_2$ according to the following equation:

$$(NH_4)_2SO_4 + Ca(OH)_2 \rightarrow 2\,NH_3 + CaSO_4 + 2\,H_2O \tag{6.1.8}$$

Answer

4.8×10^{24} NH_3 molecules

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.

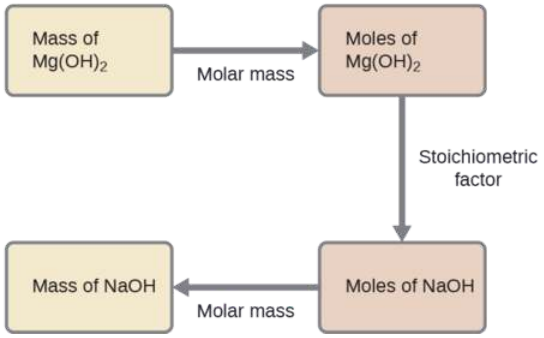
✓ Example 6.1.3: Relating Masses of Reactants and Products

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?

$$MgCl_2(aq) + 2\,NaOH(aq) \rightarrow Mg(OH)_2(s) + 2\,NaCl(aq)$$

Solution

The approach used previously in Examples **6.1.1** and **6.1.2** 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:



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

? Exercise 6.1.3

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

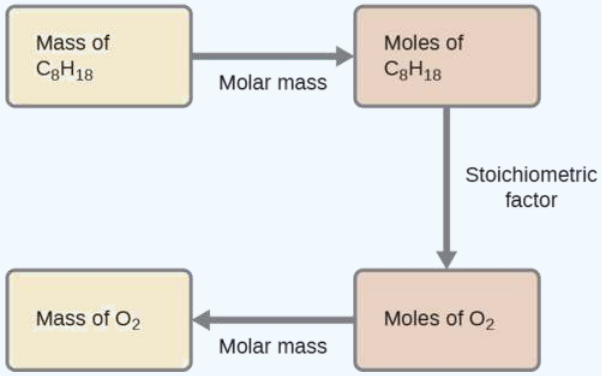
✓ Example 6.1.4: Relating Masses of Reactants

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 **6.1.3**, differing only in that the provided and requested masses are both for reactant species.



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

? Exercise 6.1.4

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

Answer

13.22 g

These examples illustrate just a few instances of reaction stoichiometry calculations. Numerous variations on the beginning and ending computational steps are possible depending upon what particular quantities are provided and sought (volumes, solution concentrations, and so forth). Regardless of the details, all these calculations share a common essential component: the use of stoichiometric factors derived from balanced chemical equations. Figure **6.1.2** provides a general outline of the various computational steps associated with many reaction stoichiometry calculations.

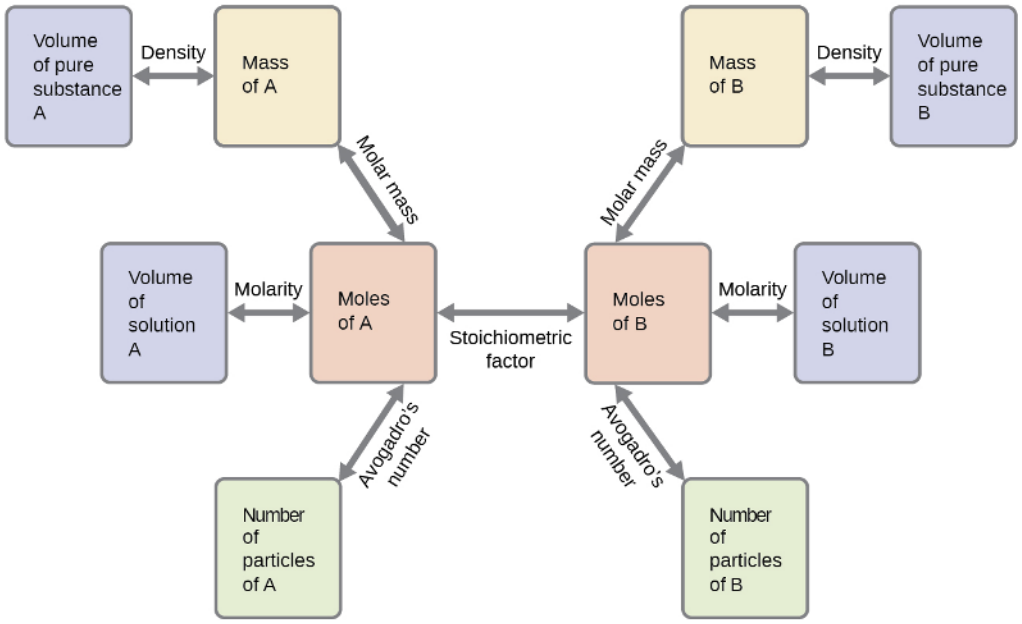


Figure **6.1.2**: The flowchart depicts the various computational steps involved in most reaction stoichiometry calculations.

Schematic flowchart showing how density is used for converting volume of pure substance to mass, molar mass for mass and moles, molarity for moles and volume of solution, Avogadro's number for moles and number of particles, and stoichiometric factor for relating moles of one substance to another.

Airbags

Airbags (Figure **6.1.3**) are a safety feature provided in most automobiles since the 1990s. The effective operation of an airbag requires that it be rapidly inflated with an appropriate amount (volume) of gas when the vehicle is involved in a collision. This requirement is satisfied in many automotive airbag systems through use of explosive chemical reactions, one common choice being the decomposition of sodium azide, NaN_3. When sensors in the vehicle detect a collision, an electrical current is passed through a carefully measured amount of NaN_3 to initiate its decomposition:

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

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

Summary

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.

Glossary

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

---

This page titled 6.1: Reaction Stoichiometry is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

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

6.2: Reaction Yields

Learning Objectives

- Explain the concepts of theoretical yield and limiting reactants/reagents.
- Derive the theoretical yield for a reaction under specified conditions.
- Calculate the percent yield 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.

Limiting Reactant

Consider another food analogy, making grilled cheese sandwiches (Figure **6.2.1**):

$$\textbf{1 slice of cheese} + \textbf{2 slices of bread} \rightarrow \textbf{1 sandwich} \tag{6.2.1}$$

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*.

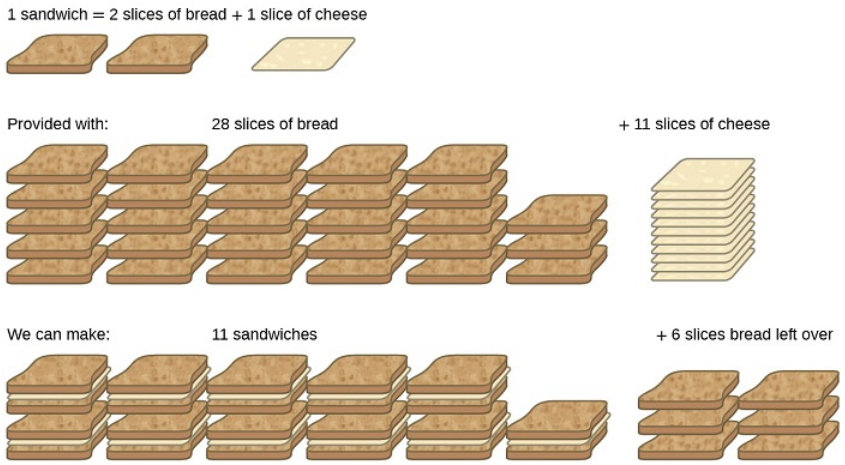


Figure **6.2.1**: Sandwich making can illustrate the concepts of limiting and excess reactants.

This figure has three rows showing the ingredients needed to make a sandwich. The first row reads, “1 sandwich = 2 slices of bread + 1 slice of cheese.” Two slices of bread and one slice of cheese are shown. The second row reads, “Provided with: 28 slices of bread + 11 slices of cheese.” There are 28 slices of bread and 11 slices of cheese shown. The third row reads, “We can make: 11 sandwiches + 6 slices of bread left over.” 11 sandwiches are shown with six extra slices of bread.

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 will nearly always be entirely consumed, thus limiting the amount of product that may be generated. This substance is the limiting reactant, and the other substance is 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

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

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 **6.2.2**). 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

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

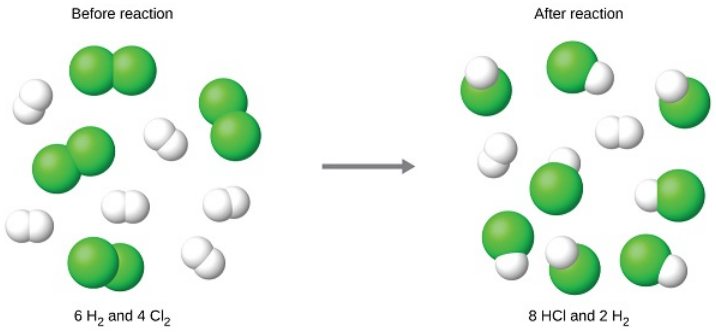


Figure **6.2.2**: When H_2 and Cl_2 are combined in nonstoichiometric amounts, one of these reactants will limit the amount of HCl that can be produced. This illustration shows a reaction in which hydrogen is present in excess and chlorine is the limiting reactant.

The figure shows a space-filling molecular models reacting. There is a reaction arrow pointing to the right in the middle. To the left of the reaction arrow there are three molecules each consisting of two green spheres bonded together. There are also five molecules each consisting of two smaller, white spheres bonded together. Above these molecules is the label, "Before reaction," and below these molecules is the label, "6 H subscript 2 and 4 C l subscript 2." To the right of the reaction arrow, there are eight molecules each consisting of one green sphere bonded to a smaller white sphere. There are also two molecules each consisting of two white spheres bonded together. Above these molecules is the label, "After reaction," and below these molecules is the label, "8 H C l and 2 H subscript 2."

✔ Example 6.2.1: 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.

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

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

The provided Si:N_2 molar ratio is:

$$\frac{0.0712 \text{ mol Si}}{0.0535 \text{ mol } N_2} = \frac{1.33 \text{ mol Si}}{1 \text{ mol } N_2}$$

The stoichiometric Si:N_2 ratio is:

$$\frac{3 \text{ mol Si}}{2 \text{ mol } N_2} = \frac{1.5 \text{ mol Si}}{1 \text{ mol } N_2}$$

Comparing these ratios shows that Si is provided in a less-than-stoichiometric amount, and so is the limiting reactant.

Alternatively, 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.

? Exercise 6.2.1

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

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. In practice, the amount of product obtained is called the actual yield, and it is often less than the theoretical yield for a number of reasons. Some reactions are inherently inefficient, being accompanied by *side reactions* that generate other products. Others are, by nature, incomplete (consider the partial reactions of weak acids and bases discussed earlier in this text). Some products are difficult to collect without some loss, and so less than perfect recovery will reduce 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 6.2.2: 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:

Double subscripts: use braces to clarify

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

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

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

Exercise 6.2.2

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?

$$\mathrm{CCl_4} + 2\,\mathrm{HF} \rightarrow \mathrm{CF_2Cl_2} + 2\,\mathrm{HCl}$$

Answer

48.3%

Green Chemistry and 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 final 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 **6.2.3**). 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.

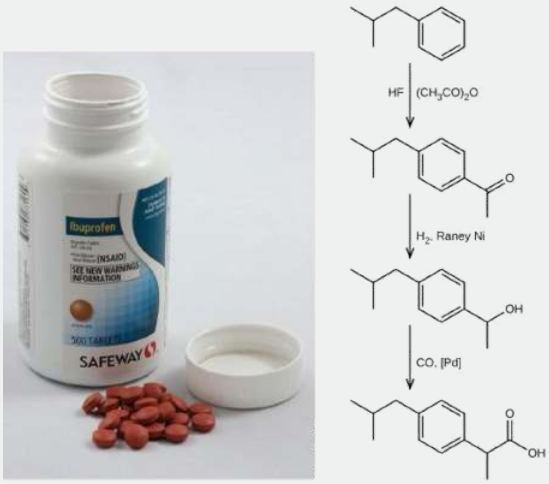


Figure **6.2.3**: (a) Ibuprofen is a popular nonprescription pain medication commonly sold as 200 mg tablets. (b) The BHC process for synthesizing ibuprofen requires only three steps and exhibits an impressive atom economy. (credit a: modification of work by Derrick Coetzee)

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.

Key Equations

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

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

theoretical yield
amount of product that may be produced from a given amount of reactant(s) according to the reaction stoichiometry

This page titled 6.2: Reaction Yields is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

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

6.3: Quantitative Chemical Analysis

Learning Objectives

- Describe the fundamental aspects of titrations and gravimetric analysis.
- Perform stoichiometric calculations using typical titration and gravimetric data.

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:

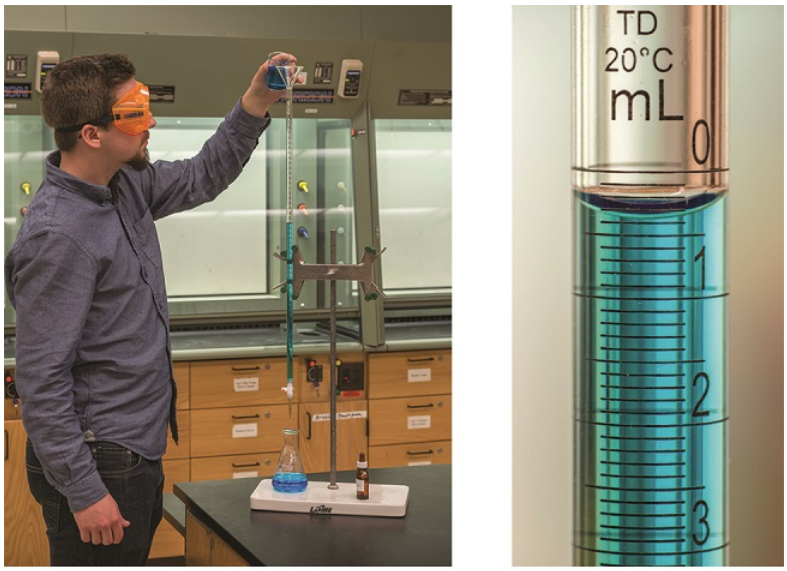
$$2\,CH_3CO_2H(aq) + K_2CO_3(s) \rightarrow 2KCH_3CO_3(aq) + CO_2(g) + H_2O(l)$$

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.

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 **6.3.1**) 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, the three described in this chapter (precipitation, acid-base, and redox) are most common. Additional details regarding titration analysis are provided in the chapter on acid-base equilibria.



(a) (b)

Figure 6.3.1: (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)

Two pictures are shown. In a, a person is shown pouring a liquid from a small beaker into a buret. The person is wearing goggles and gloves as she transfers the solution into the buret. In b, a close up view of the markings on the side of the buret is shown. The markings for 10, 15, and 20 are clearly shown with horizontal rings printed on the buret. Between each of these whole number markings, half markings are also clearly shown with horizontal line segment markings.

Example 6.3.1: 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:

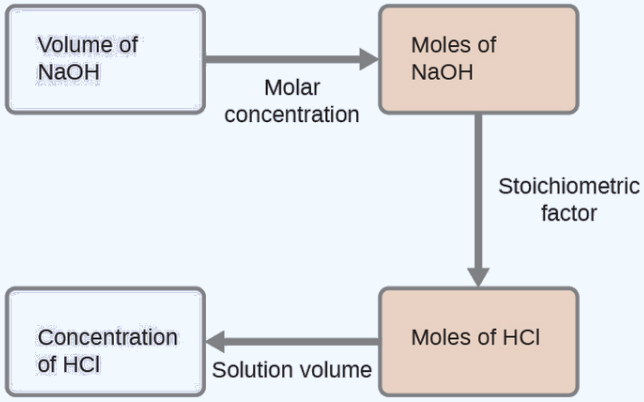
$$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \rightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l)$$

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:



This figure shows four rectangles. The first is shaded lavender and is labeled, “Volume of N a O H.” This rectangle is followed by an arrow pointing right which is labeled, “Molar concentration,” to a second rectangle. This second rectangle is shaded pink and is labeled, “Moles of N a O H.” This rectangle is followed by an arrow pointing right which is labeled, “Stoichiometric factor,” to a third rectangle which is shaded pink and is labeled, “Moles of H C l.” This rectangle is followed by an arrow labeled, “Solution volume,” which points right to a fourth rectangle. This fourth rectangle is shaded lavender and is labeled, “Concentration of H C l.”

The molar amount of HCl is calculated to be:

$$35.23\ \cancel{\text{mL NaOH}} \times \frac{1\ \cancel{L}}{1000\ \cancel{\text{mL}}} \times \frac{0.250\ \cancel{\text{mol NaOH}}}{1\ \cancel{L}} \times \frac{1\ \text{mol HCl}}{1\ \cancel{\text{mol NaOH}}} = 8.81 \times 10^{-3}\ \text{mol HCl}$$

Using the provided volume of HCl solution and the definition of molarity, the HCl concentration is:

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

$$M = \frac{8.81 \times 10^{-3}\ \text{mol HCl}}{50.00\ \text{mL} \times \dfrac{1\ \text{L}}{1000\ \text{mL}}}$$

$$M = 0.176\ M$$

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:

$$M = \frac{\text{mol solute}}{\text{L solution}} \times \frac{\dfrac{10^3\ \text{mmol}}{\text{mol}}}{\dfrac{10^3\ \text{mL}}{\text{L}}} = \frac{\text{mmol solute}}{\text{mL solution}}$$

Using this version of the molarity unit will shorten the calculation by eliminating two conversion factors:

$$\frac{35.23\ \text{mL NaOH} \times \dfrac{0.250\ \text{mmol NaOH}}{\text{mL NaOH}} \times \dfrac{1\ \text{mmol HCl}}{1\ \text{mmol NaOH}}}{50.00\ \text{mL solution}} = 0.176\ M\ \text{HCl}$$

? Exercise 6.3.1

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*

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 **6.3.2**). The mass of the precipitate may then be used, along with relevant stoichiometric relationships, to calculate analyte concentration.



Figure **6.3.2**: Precipitate may be removed from a reaction mixture by filtration.

"A photo is shown of a flask and funnel used for filtration. The flask contains a slightly opaque liquid filtrate with a slight yellow tint. A funnel, which contains a bright yellow and orange material, sits atop the flask. The flask is held in place by a clamp and is connected to a vacuum line. The connection between the funnel and flask is sealed with a rubber bung or gasket."

Example **6.3.2**: Gravimetric Analysis

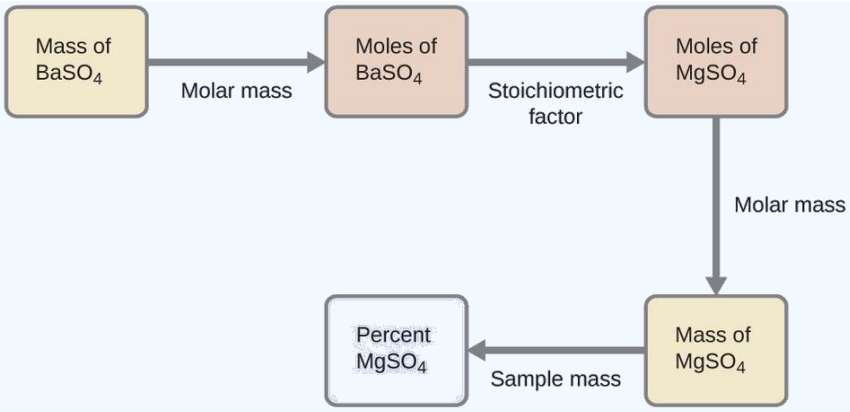
A 0.4550-g solid mixture containing $MgSO_4$ is dissolved in water and treated with an excess of $Ba(NO_3)_2$, resulting in the precipitation of 0.6168 g of $BaSO_4$.

$$MgSO_4(aq) + Ba(NO_3)_2(aq) \rightarrow BaSO_4(s) + Mg(NO_3)_2(aq)$$

What is the concentration (percent) of $MgSO_4$ in the 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.



"This figure shows five rectangles. The first is shaded yellow and is labeled “Mass of B a S O subscript 4.” This rectangle is followed by an arrow pointing right to a second rectangle. The arrow is labeled, “Molar mass.” The second rectangle is shaded pink and is labeled, “Moles of B a S O subscript 4.” This rectangle is followed by an arrow pointing right to a third rectangle. The arrow is labeled, “Stoichiometric factor.” This third rectangle is shaded pink and is labeled, “Moles of M g S O subscript 4.” This rectangle is followed by an arrow labeled, “Molar mass,” which points downward to a fourth rectangle. This fourth rectangle is shaded yellow and is labeled, “Mass of M g S O subscript 4.” This rectangle is followed by an arrow labeled, “Sample mass,” which points left to a fifth rectangle. This fifth rectangle is shaded lavender and is labeled, “Percent M g S O subscript 4."

The mass of $MgSO_4$ that would yield the provided precipitate mass is

$$0.6168 \cancel{\text{ g BaSO}_4} \times \frac{1 \cancel{\text{ mol BaSO}_4}}{233.43 \cancel{\text{ g BaSO}_4}} \times \frac{1 \cancel{\text{ mol MgSO}_4}}{1 \cancel{\text{ mol BaSO}_4}} \times \frac{120.37 \text{ g MgSO}_4}{1 \cancel{\text{ mol MgSO}_4}} = 0.3181 \text{ g MgSO}_4$$

The concentration of $MgSO_4$ in the sample mixture is then calculated to be

$$\text{percent } \text{MgSO}_4 = \frac{mass\ MgSO4}{mass\ sample} \times 100\%$$

$$\frac{0.3181 \text{ g}}{0.4550 \text{ g}} \times 100\% = 69.91\%$$

? Exercise 6.3.2

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^+?

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

Answer

23.76%

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 **6.3.3**). 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.

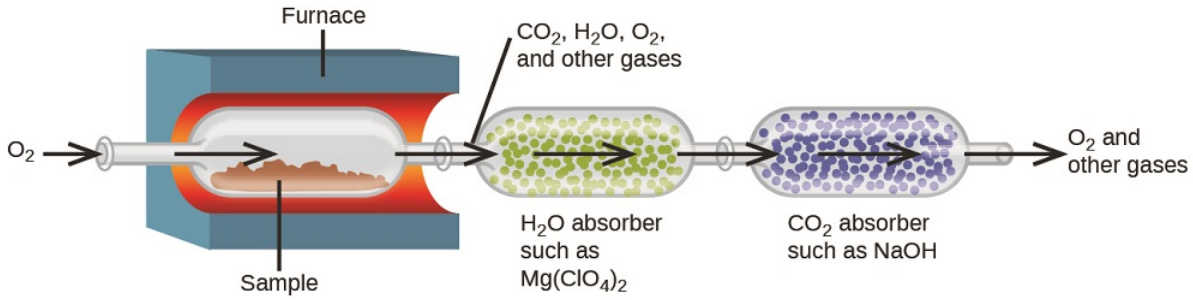


Figure **6.3.3**: This schematic diagram illustrates the basic components of a combustion analysis device for determining the carbon and hydrogen content of a sample.

This diagram shows an arrow pointing from O subscript 2 into a tube that leads into a vessel containing a red material, labeled “Sample.” This vessel is inside a blue container with a red inner lining which is labeled “Furnace.” An arrow points from the tube to the right into the vessel above the red sample material. An arrow leads out of this vessel through a tube into a second vessel outside the furnace. An line points from this tube to a label above the diagram that reads “C O subscript 2, H subscript 2 O, O subscript 2, and other gases.” Many small green spheres are visible in the second vessel which is labeled below, “H subscript 2 O absorber such as M g (C l O subscript 4) subscript 2.” An arrow points to the right through the vessel, and another arrow points right heading out of the vessel through a tube into a third vessel. The third vessel contains many small blue spheres. It is labeled “C O subscript 2 absorber such as N a O H.” An arrow points right through this vessel, and a final arrow points out of a tube at the right end of the vessel. Outside the end of this tube at the end of the arrow is the label, “O subscript 2 and other gases.”

Example **6.3.3**: 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?

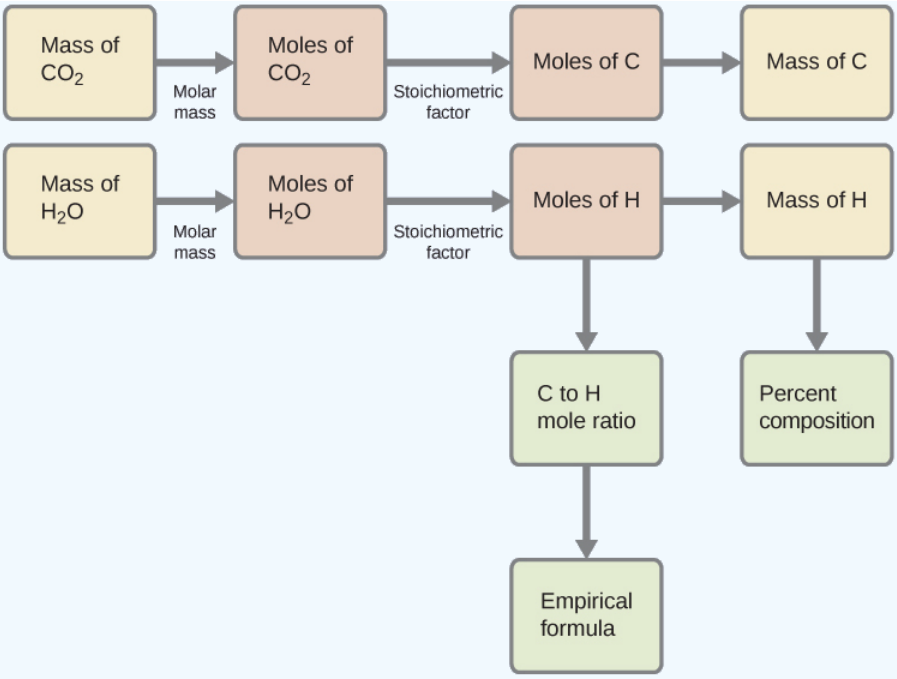
Solution

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:

Double subscripts: use braces to clarify

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:



This figure shows two flowcharts. The first row is a single flow chart. In this row, a rectangle at the left is shaded yellow and is labeled, “Mass of C O subscript 2.” This rectangle is followed by an arrow pointing right to a second rectangle. The arrow is labeled, “Molar mass.” The second rectangle is shaded pink and is labeled, “Moles of C O subscript 2.” This rectangle is followed by an arrow pointing right to a third rectangle. The arrow is labeled, “Stoichiometric factor.” The third rectangle is shaded pink and is labeled, “Moles of C.” This rectangle is followed by an arrow labeled “Molar mass” which points right to a fourth rectangle. The fourth rectangle is shaded yellow and is labeled “Mass of C.” Below, is a second flowchart. It begins with a yellow shaded rectangle on the left which is labeled, “Mass of H subscript 2 O.” This rectangle is followed by an arrow labeled, “Molar mass,” which points right to a second rectangle. The second rectangle is shaded pink and is labeled, “Moles of H subscript 2 O.” This rectangle is followed by an arrow pointing right to a third rectangle. The arrow is labeled, “Stoichiometric factor.” The third rectangle is shaded pink and is labeled “Moles of H.” This rectangle is followed to the right by an arrow labeled, “Molar mass,” which points to a fourth rectangle. The fourth rectangle is shaded yellow and is labeled “Mass of H.” An arrow labeled, “Sample mass” points down beneath this rectangle to a green shaded rectangle. This rectangle is labeled, “Percent composition.” An arrow extends beneath the pink rectangle labeled, “Moles of H,” to a green shaded rectangle labeled, “C to H mole ratio.” Beneath this rectangle, an arrow extends to a second green shaded rectangle which is labeled, “Empirical formula.”

$$\text{mol C} = 0.00394\ \text{g CO}_2 \times \frac{1\ \text{mol CO}_2}{44.01\ \text{g/mol}} \times \frac{1\ \text{mol C}}{1\ \text{mol CO}_2} = 8.95 \times 10^{-5}\ \text{mol C}$$

$$\text{mol H} = 0.00161\ \text{g H}_2\text{O} \times \frac{1\ \text{mol H}_2\text{O}}{18.02\ \text{g/mol}} \times \frac{2\ \text{mol H}}{1\ \text{mol H}_2\text{O}} = 1.79 \times 10^{-4}\ \text{mol H}$$

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 6.3.3

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

Summary

The stoichiometry of chemical reactions may serve as the basis for quantitative chemical analysis methods. Titrations involve measuring the volume of a titrant solution required to completely react with a sample solution. This volume is then used to calculate the concentration of analyte in the sample using the stoichiometry of the titration reaction. Gravimetric analysis involves separating the analyte from the sample by a physical or chemical process, determining its mass, and then calculating its concentration in the sample based on the stoichiometry of the relevant process. Combustion analysis is a gravimetric method used to determine the elemental composition of a compound by collecting and weighing the gaseous products of its combustion.

Glossary

analyte
chemical species of interest

buret
device used for the precise delivery of variable liquid volumes, such as in a titration analysis

combustion analysis
gravimetric technique used to determine the elemental composition of a compound via the collection and weighing of its gaseous combustion products

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

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

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

This page titled 6.3: Quantitative Chemical Analysis is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

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

6.E: Stoichiometry of Chemical Reactions (Exercises)

4.1: Writing and Balancing Chemical Equations

Q4.1.1

What does it mean to say an equation is balanced? Why is it important for an equation to be balanced?

S4.1.1

An equation is balanced when the same number of each element is represented on the reactant and product sides. Equations must be balanced to accurately reflect the law of conservation of matter.

Q4.1.2

Consider molecular, complete ionic, and net ionic equations.

a. What is the difference between these types of equations?
b. In what circumstance would the complete and net ionic equations for a reaction be identical?

Q4.1.3

Balance the following equations:

a. $\mathrm{PCl_5}(s) + \mathrm{H_2O}(l) \rightarrow \mathrm{POCl_3}(l) + \mathrm{HCl}(aq)$
b. $\mathrm{Cu}(s) + \mathrm{HNO_3}(aq) \rightarrow \mathrm{Cu(NO_3)_2}(aq) + \mathrm{H_2O}(l) + \mathrm{NO}(g)$
c. $\mathrm{H_2}(g) + \mathrm{I_2}(s) \rightarrow \mathrm{HI}(s)$
d. $\mathrm{Fe}(s) + \mathrm{O_2}(g) \rightarrow \mathrm{Fe_2O_3}(s)$
e. $\mathrm{Na}(s) + \mathrm{H_2O}(l) \rightarrow \mathrm{NaOH}(aq) + \mathrm{H_2}(g)$
f. $\mathrm{(NH_4)_2Cr_2O_7}(s) \rightarrow \mathrm{Cr_2O_3}(s) + \mathrm{N_2}(g) + \mathrm{H_2O}(g)$
g. $\mathrm{P_4}(s) + \mathrm{Cl_2}(g) \rightarrow \mathrm{PCl_3}(l)$
h. $\mathrm{PtCl_4}(s) \rightarrow \mathrm{Pt}(s) + \mathrm{Cl_2}(g)$

S4.1.3

a. $\mathrm{PCl_5}(s) + \mathrm{H_2O}(l) \rightarrow \mathrm{POCl_3}(l) + 2\,\mathrm{HCl}(aq)$;
b. $3\,\mathrm{Cu}(s) + 8\,\mathrm{HNO_3}(aq) \rightarrow 3\,\mathrm{Cu(NO_3)_2}(aq) + 4\,\mathrm{H_2O}(l) + 2\,\mathrm{NO}(g)$;
c. $\mathrm{H_2}(g) + \mathrm{I_2}(s) \rightarrow 2\,\mathrm{HI}(s)$;
d. $4\,\mathrm{Fe}(s) + 3\,\mathrm{O_2}(g) \rightarrow 2\,\mathrm{Fe_2O_3}(s)$;
e. $2\,\mathrm{Na}(s) + 2\,\mathrm{H_2O}(l) \rightarrow 2\,\mathrm{NaOH}(aq) + \mathrm{H_2}(g)$;
f. $\mathrm{(NH_4)_2Cr_{52}O_7}(s) \rightarrow \mathrm{Cr_2O_3}(s) + \mathrm{N_2}(g) + 4\,\mathrm{H_2O}(g)$;
g. $\mathrm{P_4}(s) + 6\,\mathrm{Cl_2}(g) \rightarrow 4\,\mathrm{PCl_3}(l)$;
h. $\mathrm{PtCl_4}(s) \rightarrow \mathrm{Pt}(s) + 2\,\mathrm{Cl_2}(g)$

Q4.1.4

Balance the following equations:

a. $\mathrm{Ag}(s) + \mathrm{H_2S}(g) + \mathrm{O_2}(g) \rightarrow \mathrm{Ag_2S}(s) + \mathrm{H_2O}(l)$
b. $\mathrm{P_4}(s) + \mathrm{O_2}(g) \rightarrow \mathrm{P_4O_{10}}(s)$
c. $\mathrm{Pb}(s) + \mathrm{H_2O}(l) + \mathrm{O_2}(g) \rightarrow \mathrm{Pb(OH)_2}(s)$
d. $\mathrm{Fe}(s) + \mathrm{H_2O}(l) \rightarrow \mathrm{Fe_3O_4}(s) + \mathrm{H_2}(g)$
e. $\mathrm{Sc_2O_3}(s) + \mathrm{SO_3}(l) \rightarrow \mathrm{Sc_2(SO_4)_3}(s)$
f. $\mathrm{Ca_3(PO_4)_2}(aq) + \mathrm{H_3PO_4}(aq) \rightarrow \mathrm{Ca(H_2PO_4)_2}(aq)$
g. $\mathrm{Al}(s) + \mathrm{H_2SO_4}(aq) \rightarrow \mathrm{Al_2(SO_4)_3}(s) + \mathrm{H_2}(g)$
h. $\mathrm{TiCl_4}(s) + \mathrm{H_2O}(g) \rightarrow \mathrm{TiO_2}(s) + \mathrm{HCl}(g)$

S4.1.4

a. $4\,Ag(s) + 2\,H_2S(g) + O_2(g) \rightarrow 2\,Ag_2S(s) + 2\,H_2O(l)$
b. $P_4(s) + 5\,O_2(g) \rightarrow P_4O_{10}(s)$
c. $2\,Pb(s) + 2\,H_2O(l) + O_2(g) \rightarrow 2\,Pb(OH)_2(s)$
d. $3\,Fe(s) + 4\,H_2O(l) \rightarrow Fe_3O_4(s) + 4\,H_2(g)$
e. $Sc_2O_3(s) + 3\,SO_3(l) \rightarrow Sc_2(SO_4)_3(s)$
f. $Ca_3(PO_4)_2(aq) + 4\,H_3PO_4(aq) \rightarrow 3\,Ca(H_2PO_4)_2(aq)$
g. $2\,Al(s) + 3\,H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(s) + 3\,H_2(g)$
h. $TiCl_4(s) + 2\,H_2O(g) \rightarrow TiO_2(s) + 4\,HCl(g)$

Q4.1.5

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.
c. Aqueous solutions of magnesium chloride and sodium hydroxide react to produce solid magnesium hydroxide and aqueous sodium chloride.
d. Water vapor reacts with sodium metal to produce solid sodium hydroxide and hydrogen gas.

S4.1.5

a. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$;
b. $2\,C_4H_{10}(g) + 13\,O_2(g) \rightarrow 8\,CO_2(g) + 10\,H_2O(g)$;
c. $MgCl_2(aq) + 2\,NaOH(aq) \rightarrow Mg(OH)_2(s) + 2\,NaCl(aq)$;
d. $2\,H_2O(g) + 2\,Na(s) \rightarrow 2\,NaOH(s) + H_2(g)$

Q4.1.6

Write a balanced equation describing each of the following chemical reactions.

a. Solid potassium chlorate, $KClO_3$, decomposes to form solid potassium chloride and diatomic oxygen gas.
b. Solid aluminum metal reacts with solid diatomic iodine to form solid Al_2I_6.
c. When solid sodium chloride is added to aqueous sulfuric acid, hydrogen chloride gas and aqueous sodium sulfate are produced.
d. Aqueous solutions of phosphoric acid and potassium hydroxide react to produce aqueous potassium dihydrogen phosphate and liquid water.

Q4.1.7

Colorful fireworks often involve the decomposition of barium nitrate and potassium chlorate and the reaction of the metals magnesium, aluminum, and iron with oxygen.

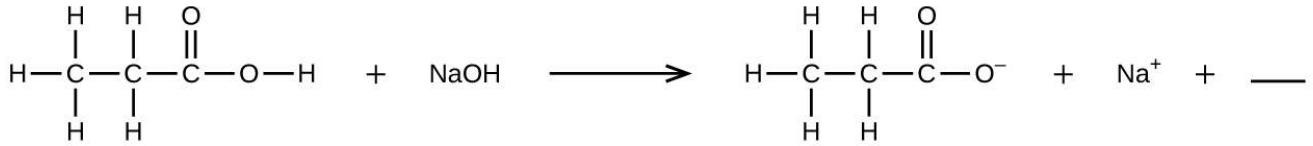
a. Write the formulas of barium nitrate and potassium chlorate.
b. The decomposition of solid potassium chlorate leads to the formation of solid potassium chloride and diatomic oxygen gas. Write an equation for the reaction.
c. The decomposition of solid barium nitrate leads to the formation of solid barium oxide, diatomic nitrogen gas, and diatomic oxygen gas. Write an equation for the reaction.
d. Write separate equations for the reactions of the solid metals magnesium, aluminum, and iron with diatomic oxygen gas to yield the corresponding metal oxides. (Assume the iron oxide contains Fe^{3+} ions.)

Q4.1.7

a. $Ba(NO_3)_2$, $KClO_3$;
b. $2\,KClO_3(s) \rightarrow 2\,KCl(s) + 3\,O_2(g)$;
c. $2\,Ba(NO_3)_2(s) \rightarrow 2\,BaO(s) + 2\,N_2(g) + 5\,O_2(g)$;
d. $2\,Mg(s) + O_2(g) \rightarrow 2\,MgO(s)$; $4\,Al(s) + 3\,O_2(g) \rightarrow 2\,Al_2O_3(g)$; $4\,Fe(s) + 3\,O_2(g) \rightarrow 2\,Fe_2O_3(s)$

Q4.1.8

Fill in the blank with a single chemical formula for a covalent compound that will balance the equation:



Q4.1.9

Aqueous hydrogen fluoride (hydrofluoric acid) is used to etch glass and to analyze minerals for their silicon content. Hydrogen fluoride will also react with sand (silicon dioxide).

a. Write an equation for the reaction of solid silicon dioxide with hydrofluoric acid to yield gaseous silicon tetrafluoride and liquid water.
b. The mineral fluorite (calcium fluoride) occurs extensively in Illinois. Solid calcium fluoride can also be prepared by the reaction of aqueous solutions of calcium chloride and sodium fluoride, yielding aqueous sodium chloride as the other product. Write complete and net ionic equations for this reaction.

S4.1.9

a. $4\,HF(aq) + SiO_2(s) \rightarrow SiF_4(g) + 2\,H_2O(l)$;
b. complete ionic equation: $2\,Na^+(aq) + 2\,F^-(aq) + Ca^{2+}(aq) + 2\,Cl^-(aq) \rightarrow CaF_2(s) + 2\,Na^+(aq) + 2\,Cl^-(aq)$, net ionic equation: $2\,F^-(aq) + Ca^{2+}(aq) \rightarrow CaF_2(s)$

Q4.1.10

A novel process for obtaining magnesium from sea water involves several reactions. Write a balanced chemical equation for each step of the process.

a. The first step is the decomposition of solid calcium carbonate from seashells to form solid calcium oxide and gaseous carbon dioxide.
b. The second step is the formation of solid calcium hydroxide as the only product from the reaction of the solid calcium oxide with liquid water.
c. Solid calcium hydroxide is then added to the seawater, reacting with dissolved magnesium chloride to yield solid magnesium hydroxide and aqueous calcium chloride.
d. The solid magnesium hydroxide is added to a hydrochloric acid solution, producing dissolved magnesium chloride and liquid water.
e. Finally, the magnesium chloride is melted and electrolyzed to yield liquid magnesium metal and diatomic chlorine gas.

Q4.1.11

From the balanced molecular equations, write the complete ionic and net ionic equations for the following:

a. $K_2C_2O_4(aq) + Ba(OH)_2(aq) \rightarrow 2\,KOH(aq) + BaC_2O_2(s)$
b. $Pb(NO_3)_2(aq) + H_2SO_4(aq) \rightarrow PbSO_4(s) + 2\,HNO_3(aq)$
c. $CaCO_3(s) + H_2SO_4(aq) \rightarrow CaSO_4(s) + CO_2(g) + H_2O(l)$

S4.1.11

a.

$$2\,K^+(aq) + {C_2O_4}^{2-}(aq) + Ba^{2+}(aq) + 2\,OH^-(aq) \rightarrow 2\,K^+(aq) + 2\,OH^-(aq) + BaC_2O_4(s) \quad \text{(complete)} \tag{6.E.1}$$

$$Ba^{2+}(aq) + {C_2O_4}^{2-}(aq) \rightarrow BaC_2O_4(s) \quad \text{(net)} \tag{6.E.2}$$

b.

$$Pb^{2+}(aq) + 2\,{NO_3}^-(aq) + 2\,H^+(aq) + {SO_4}^{2-}(aq) \rightarrow PbSO_4(s) + 2\,H^+(aq) + 2\,{NO_3}^-(aq) \quad \text{(complete)} \tag{6.E.3}$$

$$Pb^{2+}(aq) + {SO_4}^{2-}(aq) \rightarrow PbSO_4(s) \quad \text{(net)} \tag{6.E.4}$$

c. $$\mathrm{CaCO_3}(s) + 2\,\mathrm{H^+}(aq) + \mathrm{SO_4^{2-}}(aq) \rightarrow \mathrm{CaSO_4}(s) + \mathrm{CO_2}(g) + \mathrm{H_2O}(l) \quad \text{(complete)} \tag{6.E.5}$$

$$\mathrm{CaCO_3}(s) + 2\,\mathrm{H^+}(aq) + \mathrm{SO_4^{2-}}(aq) \rightarrow \mathrm{CaSO_4}(s) + \mathrm{CO_2}(g) + \mathrm{H_2O}(l) \quad \text{(net)} \tag{6.E.6}$$

4.2: Classifying Chemical Reactions

Q4.2.1

Use the following equations to answer the next five questions:

i. $\mathrm{H_2O}(s) \rightarrow \mathrm{H_2O}(l)$
ii. $\mathrm{Na^+}(aq) + \mathrm{Cl^-}(aq)\mathrm{Ag^+}(aq) + \mathrm{NO_3^-}(aq) \rightarrow \mathrm{AgCl}(s) + \mathrm{Na^+}(aq) + \mathrm{NO_3^-}(aq)$
iii. $\mathrm{CH_3OH}(g) + \mathrm{O_2}(g) \rightarrow \mathrm{CO_2}(g) + \mathrm{H_2O}(g)$
iv. $2\,\mathrm{H_2O}(l) \rightarrow 2\,\mathrm{H_2}(g) + \mathrm{O_2}(g)$
v. $\mathrm{H^+}(aq) + \mathrm{OH^-}(aq) \rightarrow \mathrm{H_2O}(l)$

a. Which equation describes a physical change?
b. Which equation identifies the reactants and products of a combustion reaction?
c. Which equation is not balanced?
d. Which is a net ionic equation?

S4.2.1

a.) **i.** $H_2O(solid) \rightarrow H_2O(liquid)$

b.) **iii.**

c.) **iii.** $2\,\mathrm{CH_3OH}(g) + 3\,\mathrm{O_2}(g) \rightarrow 2\,\mathrm{CO_2}(g) + 4\,\mathrm{H_2O}(g)$

d.) **v.**

Q4.2.2

Indicate what type, or types, of reaction each of the following represents:

a. $\mathrm{Ca}(s) + \mathrm{Br_2}(l) \rightarrow \mathrm{CaBr_2}(s)$
b. $\mathrm{Ca(OH)_2}(aq) + 2\,\mathrm{HBr}(aq) \rightarrow \mathrm{CaBr_2}(aq) + 2\,\mathrm{H_2O}(l)$
c. $\mathrm{C_6H_{12}}(l) + 9\,\mathrm{O_2}(g) \rightarrow 6\,\mathrm{CO_2}(g) + 6\,\mathrm{H_2O}(g)$

S4.2.2

oxidation-reduction (addition); acid-base (neutralization); oxidation-reduction (combustion)

<

Q4.2.3

Indicate what type, or types, of reaction each of the following represents:

a. $\mathrm{H_2O}(g) + \mathrm{C}(s) \rightarrow \mathrm{CO}(g) + \mathrm{H_2}(g)$
b. $2\,\mathrm{KClO_3}(s) \rightarrow 2\,\mathrm{KCl}(s) + 3\,\mathrm{O_2}(g)$
c. $\mathrm{Al(OH)_3}(aq) + 3\,\mathrm{HCl}(aq) \rightarrow \mathrm{AlBr_3}(aq) + 3\,\mathrm{H_2O}(l)$
d. $\mathrm{Pb(NO_3)_2}(aq) + \mathrm{H_2SO_4}(aq) \rightarrow \mathrm{PbSO_4}(s) + 2\,\mathrm{HNO_3}(aq)$

Q4.2.4

Silver can be separated from gold because silver dissolves in nitric acid while gold does not. Is the dissolution of silver in nitric acid an acid-base reaction or an oxidation-reduction reaction? Explain your answer.

S4.2.4

It is an oxidation-reduction reaction because the oxidation state of the silver changes during the reaction.

Q4.2.5

Determine the oxidation states of the elements in the following compounds:

a. NaI
b. $GdCl_3$
c. $LiNO_3$
d. H_2Se
e. Mg_2Si
f. RbO_2, rubidium superoxide
g. HF

Q4.2.6

Determine the oxidation states of the elements in the compounds listed. None of the oxygen-containing compounds are peroxides or superoxides.

a. H_3PO_4
b. $Al(OH)_3$
c. SeO_2
d. KNO_2
e. In_2S_3
f. P_4O_6

S4.2.6

H +1, P +5, O −2; Al +3, H +1, O −2; Se +4, O −2; K +1, N +3, O −2; In +3, S −2; P +3, O −2

Q4.2.7

Determine the oxidation states of the elements in the compounds listed. None of the oxygen-containing compounds are peroxides or superoxides.

a. H_2SO_4
b. $Ca(OH)_2$
c. BrOH
d. $ClNO_2$
e. $TiCl_4$
f. NaH

S4.2.7

a. H^{1+}, O^{2-}, S^{6+}
b. H^{1+}, O^{2-}, Ca^{+2}
c. H^{1+}, O^{2-}, Br^{1+}
d. O^{2-}, Cl^{1-}, N^{5+}
e. Cl^{1-}, Ti^{4+}
f. H^{1+}, Na^{1-}

Q4.2.8

Classify the following as acid-base reactions or oxidation-reduction reactions:

a. $\mathbf{Na_2S}(aq) + \mathbf{2\,HCl}(aq) \rightarrow \mathbf{2\,NaCl}(aq) + \mathbf{H_2S}(g)$
b. $\mathbf{2\,Na}(s) + \mathbf{2\,HCl}(aq) \rightarrow \mathbf{2\,NaCl}(aq) + \mathbf{H_2}(g)$
c. $\mathbf{Mg}(s) + \mathbf{Cl_2}(g) \rightarrow \mathbf{MgCl_2}(s)$
d. $\mathbf{MgO}(s) + \mathbf{2\,HCl}(aq) \rightarrow \mathbf{MgCl_2}(aq) + \mathbf{H_2O}(l)$
e. $\mathbf{K_3P}(s) + \mathbf{2\,O_2}(g) \rightarrow \mathbf{K_3PO_4}(s)$
f. $\mathbf{3\,KOH}(aq) + \mathbf{H_3PO_4}(aq) \rightarrow \mathbf{K_3PO_4}(aq) + \mathbf{3\,H_2O}(l)$

S4.2.9

acid-base; oxidation-reduction: Na is oxidized, H^+ is reduced; oxidation-reduction: Mg is oxidized, Cl_2 is reduced; acid-base; oxidation-reduction: P^{3-} is oxidized, O_2 is reduced; acid-base

Q4.2.10

Identify the atoms that are oxidized and reduced, the change in oxidation state for each, and the oxidizing and reducing agents in each of the following equations:

a. $\mathrm{Mg}(s) + \mathrm{NiCl_2}(aq) \rightarrow \mathrm{MgCl_2}(aq) + \mathrm{Ni}(s)$
b. $\mathrm{PCl_3}(l) + \mathrm{Cl_2}(g) \rightarrow \mathrm{PCl_5}(s)$
c. $\mathrm{C_2H_4}(g) + 3\,\mathrm{O_2}(g) \rightarrow 2\,\mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(g)$
d. $\mathrm{Zn}(s) + \mathrm{H_2SO_4}(aq) \rightarrow \mathrm{ZnSO_4}(aq) + \mathrm{H_2}(g)$
e. $2\,\mathrm{K_2S_2O_3}(s) + \mathrm{I_2}(s) \rightarrow \mathrm{K_2S_4O_6}(s) + 2\,\mathrm{KI}(s)$
f. $3\,\mathrm{Cu}(s) + 8\,\mathrm{HNO_3}(aq) \rightarrow 3\,\mathrm{Cu(NO_3)_2}(aq) + 2\,\mathrm{NO}(g) + 4\,\mathrm{H_2O}(l)$

Q4.2.11

Complete and balance the following acid-base equations:

a. HCl gas reacts with solid $Ca(OH)_2(s)$.
b. A solution of $Sr(OH)_2$ is added to a solution of HNO_3.

S4.2.11

a. $2\,\mathrm{HCl}(g) + \mathrm{Ca(OH)_2}(s) \rightarrow \mathrm{CaCl_2}(s) + 2\,\mathrm{H_2O}(l)$;
b. $\mathrm{Sr(OH)_2}(aq) + 2\,\mathrm{HNO_3}(aq) \rightarrow \mathrm{Sr(NO_3)_2}(aq) + 2\,\mathrm{H_2O}(l)$

Q4.2.12

Complete and balance the following acid-base equations:

a. A solution of $HClO_4$ is added to a solution of LiOH.
b. Aqueous H_2SO_4 reacts with NaOH.
c. $Ba(OH)_2$ reacts with HF gas.

Q4.2.13

Complete and balance the following oxidation-reduction reactions, which give the highest possible oxidation state for the oxidized atoms.

a. $\mathrm{Al}(s) + \mathrm{F_2}(g) \rightarrow$
b. $\mathrm{Al}(s) + \mathrm{CuBr_2}(aq) \rightarrow$ (single displacement)
c. $\mathrm{P_4}(s) + \mathrm{O_2}(g) \rightarrow$
d. $\mathrm{Ca}(s) + \mathrm{H_2O}(l) \rightarrow$ (products are a strong base and a diatomic gas)

S4.2.13

a. $2\,\mathrm{Al}(s) + 3\,\mathrm{F_2}(g) \rightarrow 2\,\mathrm{AlF_3}(s)$;
b. $2\,\mathrm{Al}(s) + 3\,\mathrm{CuBr_2}(aq) \rightarrow 3\,\mathrm{Cu}(s) + 2\,\mathrm{AlBr_3}(aq)$;
c. $\mathrm{P_4}(s) + 5\,\mathrm{O_2}(g) \rightarrow \mathrm{P_4O_{10}}(s)$; $\mathrm{Ca}(s) + 2\,\mathrm{H_2O}(l) \rightarrow \mathrm{Ca(OH)_2}(aq) + \mathrm{H_2}(g)$

Q4.2.14

Complete and balance the following oxidation-reduction reactions, which give the highest possible oxidation state for the oxidized atoms.

a. $\mathrm{K}(s) + \mathrm{H_2O}(l) \rightarrow$
b. $\mathrm{Ba}(s) + \mathrm{HBr}(aq) \rightarrow$
c. $\mathrm{Sn}(s) + \mathrm{I_2}(s) \rightarrow$

Q4.2.15

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.

a. $\mathrm{Mg(OH)_2}(s) + \mathrm{HClO_4}(aq) \rightarrow$
b. $\mathrm{SO_3}(g) + \mathrm{H_2O}(l) \rightarrow$ (assume an excess of water and that the product dissolves)
c. $\mathrm{SrO}(s) + \mathrm{H_2SO_4}(l) \rightarrow$

S4.2.15

a. $\mathrm{Mg(OH)_2}(s) + 2\,\mathrm{HClO_4}(aq) \rightarrow \mathrm{Mg^{2+}}(aq) + 2\,\mathrm{ClO_4^-}(aq) + 2\,\mathrm{H_2O}(l)$;
b. $\mathrm{SO_3}(g) + 2\,\mathrm{H_2O}(l) \rightarrow \mathrm{H_3O^+}(aq) + \mathrm{HSO_4^-}(aq)$, (a solution of H_2SO_4);
c. $\mathrm{SrO}(s) + \mathrm{H_2SO_4}(l) \rightarrow \mathrm{SrSO_4}(s) + \mathrm{H_2O}$

Q4.2.16

When heated to 700–800 °C, diamonds, which are pure carbon, are oxidized by atmospheric oxygen. (They burn!) Write the balanced equation for this reaction.

Q4.2.17

The military has experimented with lasers that produce very intense light when fluorine combines explosively with hydrogen. What is the balanced equation for this reaction?

S4.2.17

$\mathrm{H_2}(g) + \mathrm{F_2}(g) \rightarrow 2\,\mathrm{HF}(g)$

Q4.2.18

Write the molecular, total ionic, and net ionic equations for the following reactions:

a. $\mathrm{Ca(OH)_2}(aq) + \mathrm{HC_2H_3O_2}(aq) \rightarrow$
b. $\mathrm{H_3PO_4}(aq) + \mathrm{CaCl_2}(aq) \rightarrow$

Q4.2.19

Great Lakes Chemical Company produces bromine, Br_2, from bromide salts such as NaBr, in Arkansas brine by treating the brine with chlorine gas. Write a balanced equation for the reaction of NaBr with Cl_2.

S4.2.19

$2\,\mathrm{NaBr}(aq) + \mathrm{Cl_2}(g) \rightarrow 2\,\mathrm{NaCl}(aq) + \mathrm{Br_2}(l)$

Q4.2.20

In a common experiment in the general chemistry laboratory, magnesium metal is heated in air to produce MgO. MgO is a white solid, but in these experiments it often looks gray, due to small amounts of Mg_3N_2, a compound formed as some of the magnesium reacts with nitrogen. Write a balanced equation for each reaction.

Q4.2.21

Lithium hydroxide may be used to absorb carbon dioxide in enclosed environments, such as manned spacecraft and submarines. Write an equation for the reaction that involves 2 mol of LiOH per 1 mol of CO_2. (Hint: Water is one of the products.)

S4.2.21

$2\,\mathrm{LiOH}(aq) + \mathrm{CO_2}(g) \rightarrow \mathrm{Li_2CO_3}(aq) + \mathrm{H_2O}(l)$

Q4.2.22

Calcium propionate is sometimes added to bread to retard spoilage. This compound can be prepared by the reaction of calcium carbonate, $CaCO_3$, with propionic acid, $C_2H_5CO_2H$, which has properties similar to those of acetic acid. Write the balanced

equation for the formation of calcium propionate.

Q4.2.23

Complete and balance the equations of the following reactions, each of which could be used to remove hydrogen sulfide from natural gas:

a. $\mathrm{Ca(OH)_2}(s) + \mathrm{H_2S}(g) \rightarrow$
b. $\mathrm{Na_2CO_3}(aq) + \mathrm{H_2S}(g) \rightarrow$

S4.2.23

a. $\mathrm{Ca(OH)_2}(s) + \mathrm{H_2S}(g) \rightarrow \mathrm{CaS}(s) + 2\,\mathrm{H_2O}(l)$;
b. $\mathrm{Na_2CO_3}(aq) + \mathrm{H_2S}(g) \rightarrow \mathrm{Na_2S}(aq) + \mathrm{CO_2}(g) + \mathrm{H_2O}(l)$

Q4.2.24

Copper(II) sulfide is oxidized by molecular oxygen to produce gaseous sulfur trioxide and solid copper(II) oxide. The gaseous product then reacts with liquid water to produce liquid hydrogen sulfate as the only product. Write the two equations which represent these reactions.

Q4.2.25

Write balanced chemical equations for the reactions used to prepare each of the following compounds from the given starting material(s). In some cases, additional reactants may be required.

a. solid ammonium nitrate from gaseous molecular nitrogen via a two-step process (first reduce the nitrogen to ammonia, then neutralize the ammonia with an appropriate acid)
b. gaseous hydrogen bromide from liquid molecular bromine via a one-step redox reaction
c. gaseous H_2S from solid Zn and S via a two-step process (first a redox reaction between the starting materials, then reaction of the product with a strong acid)

S4.2.25

a. step 1: $\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightarrow 2\,\mathrm{NH_3}(g)$, step 2: $\mathrm{NH_3}(g) + \mathrm{HNO_3}(aq) \rightarrow \mathrm{NH_4NO_3}(aq) \rightarrow \mathrm{NH_4NO_3}(s)(\text{after drying})$;
b. $\mathrm{H_2}(g) + \mathrm{Br_2}(l) \rightarrow 2\,\mathrm{HBr}(g)$;
c. $\mathrm{Zn}(s) + \mathrm{S}(s) \rightarrow \mathrm{ZnS}(s)$ and $\mathrm{ZnS}(s) + 2\,\mathrm{HCl}(aq) \rightarrow \mathrm{ZnCl_2}(aq) + \mathrm{H_2S}(g)$

Q4.2.26

Calcium cyclamate $Ca(C_6H_{11}NHSO_3)_2$ is an artificial sweetener used in many countries around the world but is banned in the United States. It can be purified industrially by converting it to the barium salt through reaction of the acid $C_6H_{11}NHSO_3H$ with barium carbonate, treatment with sulfuric acid (barium sulfate is very insoluble), and then neutralization with calcium hydroxide. Write the balanced equations for these reactions.

Q4.2.27

Complete and balance each of the following half-reactions (steps 2–5 in half-reaction method):

a. $\mathrm{Sn^{4+}}(aq) \rightarrow \mathrm{Sn^{2+}}(aq)$
b. $\mathrm{[Ag(NH_3)_2]^+}(aq) \rightarrow \mathrm{Ag}(s) + \mathrm{NH_3}(aq)$
c. $\mathrm{Hg_2Cl_2}(s) \rightarrow \mathrm{Hg}(l) + \mathrm{Cl^-}(aq)$
d. $\mathrm{H_2O}(l) \rightarrow \mathrm{O_2}(g)\ (\text{in acidic solution})$
e. $\mathrm{IO_3^-}(aq) \rightarrow \mathrm{I_2}(s)$
f. $\mathrm{SO_3^{2-}}(aq) \rightarrow \mathrm{SO_4^{2-}}(aq)\ (\text{in acidic solution})$
g. $\mathrm{MnO_4^-}(aq) \rightarrow \mathrm{Mn^{2+}}(aq)\ (\text{in acidic solution})$
h. $\mathrm{Cl^-}(aq) \rightarrow \mathrm{ClO_3^-}(aq)\ (\text{in basic solution})$

S4.2.27

a. $\mathrm{Sn^{4+}}(aq) + 2\,\mathrm{e^-} \rightarrow \mathrm{Sn^{2+}}(aq)$,
b. $\mathrm{[Ag(NH_3)_2]^+}(aq) + \mathrm{e^-} \rightarrow \mathrm{Ag}(s) + 2\,\mathrm{NH_3}(aq)$;

c. $Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-(aq)$;
d. $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$;
e. $6H_2O(l) + 2IO_3^-(aq) + 10e^- \rightarrow I_2(s) + 12OH^-(aq)$;
f. $H_2O(l) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e^-$;
g. (g) $8H^+(aq) + MnO_4^-(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$;
h. (h) $Cl^-(aq) + 6OH^-(aq) \rightarrow ClO_3^-(aq) + 3H_2O(l) + 6e^-$

Q4.2.28

Complete and balance each of the following half-reactions (steps 2–5 in half-reaction method):

a. $Cr^{2+}(aq) \rightarrow Cr^{3+}(aq)$
b. $Hg(l) + Br^-(aq) \rightarrow HgBr_4^{2-}(aq)$
c. $ZnS(s) \rightarrow Zn(s) + S^{2-}(aq)$
d. $H_2(g) \rightarrow H_2O(l)$ (in basic solution)
e. $H_2(g) \rightarrow H_3O^+(aq)$ (in acidic solution)
f. $NO_3^-(aq) \rightarrow HNO_2(aq)$ (in acidic solution)
g. $MnO_2(s) \rightarrow MnO_4^-(aq)$ (in basic solution)
h. $Cl^-(aq) \rightarrow ClO_3^-(aq)$ (in acidic solution)

Q4.2.29

Balance each of the following equations according to the half-reaction method:

a. $Sn^{2+}(aq) + Cu^{2+}(aq) \rightarrow Sn^{4+}(aq) + Cu^+(aq)$
b. $H_2S(g) + Hg_2^{2+}(aq) \rightarrow Hg(l) + S(s)$ (in acid)
c. $CN^-(aq) + ClO_2(aq) \rightarrow CNO^-(aq) + Cl^-(aq)$ (in acid)
d. $Fe^{2+}(aq) + Ce^{4+}(aq) \rightarrow Fe^{3+}(aq) + Ce^{3+}(aq)$
e. $HBrO(aq) \rightarrow Br^-(aq) + O_2(g)$ (in acid)

S4.2.29

a. $Sn^{2+}(aq) + 2Cu^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2Cu^+(aq)$;
b. $H_2S(g) + Hg_2^{2+}(aq) + 2H_2O(l) \rightarrow 2Hg(l) + S(s) + 2H_3O^+(aq)$;
c. $5CN^-(aq) + 2ClO_2(aq) + 3H_2O(l) \rightarrow 5CNO^-(aq) + 2Cl^-(aq) + 2H_3O^+(aq)$;
d. $Fe^{2+}(aq) + Ce^{4+}(aq) \rightarrow Fe^{3+}(aq) + Ce^{3+}(aq)$;
e. $2HBrO(aq) + 2H_2O(l) \rightarrow 2H_3O^+(aq) + 2Br^-(aq) + O_2(g)$

Q4.2.30

Balance each of the following equations according to the half-reaction method:

a. $Zn(s) + NO_3^-(aq) \rightarrow Zn^{2+}(aq) + N_2(g)$ (in acid)
b. $Zn(s) + NO_3^-(aq) \rightarrow Zn^{2+}(aq) + NH_3(aq)$ (in base)
c. $CuS(s) + NO_3^-(aq) \rightarrow Cu^{2+}(aq) + S(s) + NO(g)$ (in acid)
d. $NH_3(aq) + O_2(g) \rightarrow NO_2(g)$ (gas phase)
e. $Cl_2(g) + OH^-(aq) \rightarrow Cl^-(aq) + ClO_3^-(aq)$ (in base)
f. $H_2O_2(aq) + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + O_2(g)$ (in acid)
g. $NO_2(g) \rightarrow NO_3^-(aq) + NO_2^-(aq)$ (in base)
h. $Fe^{3+}(aq) + I^-(aq) \rightarrow Fe^{2+}(aq) + I_2(aq)$

Q4.2.31

Balance each of the following equations according to the half-reaction method:

a. $MnO_4^-(aq) + NO_2^-(aq) \rightarrow MnO_2(s) + NO_3^-(aq)$ (in base)
b. $MnO_4^{2-}(aq) \rightarrow MnO_4^-(aq) + MnO_2(s)$ (in base)
c. $Br_2(l) + SO_2(g) \rightarrow Br^-(aq) + SO_4^{2-}(aq)$ (in acid)

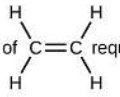
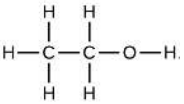
S4.2.31

a. $2\,MnO_4^-(aq) + 3\,NO_2^-(aq) + H_2O(l) \rightarrow 2\,MnO_2(s) + 3\,NO_3^-(aq) + 2\,OH^-(aq)$;
b. $3\,MnO_4^{2-}(aq) + 2\,H_2O(l) \rightarrow 2\,MnO_4^-(aq) + 4\,OH^-(aq) + MnO_2(s)$ (in base);
c. $Br_2(l) + SO_2(g) + 2\,H_2O(l) \rightarrow 4\,H^+(aq) + 2\,Br^-(aq) + SO_4^{2-}(aq)$

4.3: Reaction Stoichiometry

Q4.3.1

Write the balanced equation, then outline the steps necessary to determine the information requested in each of the following:

a. The number of moles and the mass of chlorine, Cl_2, required to react with 10.0 g of sodium metal, Na, to produce sodium chloride, NaCl.
b. The number of moles and the mass of oxygen formed by the decomposition of 1.252 g of mercury(II) oxide.
c. The number of moles and the mass of sodium nitrate, $NaNO_3$, required to produce 128 g of oxygen. ($NaNO_2$ is the other product.)
d. The number of moles and the mass of carbon dioxide formed by the combustion of 20.0 kg of carbon in an excess of oxygen.
e. The number of moles and the mass of copper(II) carbonate needed to produce 1.500 kg of copper(II) oxide. (CO_2 is the other product.)
f. The number of moles and the mass of  required to react with H_2O to produce 9.55 g of  .

Q4.3.2

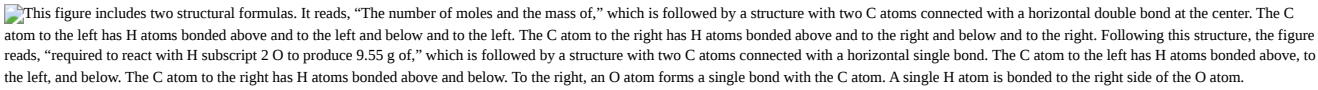
Determine the number of moles and the mass requested for each reaction in Exercise.

S4.3.2

0.435 mol Na, 0.217 mol Cl_2, 15.4 g Cl_2; 0.005780 mol HgO, 2.890×10^{-3} mol O_2, 9.248×10^{-2} g O_2; 8.00 mol $NaNO_3$, 6.8×10^2 g $NaNO_3$; 1665 mol CO_2, 73.3 kg CO_2; 18.86 mol CuO, 2.330 kg $CuCO_3$; 0.4580 mol $C_2H_4Br_2$, 86.05 g $C_2H_4Br_2$

Q4.3.3

Write the balanced equation, then outline the steps necessary to determine the information requested in each of the following:

a. The number of moles and the mass of Mg required to react with 5.00 g of HCl and produce $MgCl_2$ and H_2.
b. The number of moles and the mass of oxygen formed by the decomposition of 1.252 g of silver(I) oxide.
c. The number of moles and the mass of magnesium carbonate, $MgCO_3$, required to produce 283 g of carbon dioxide. (MgO is the other product.)
d. The number of moles and the mass of water formed by the combustion of 20.0 kg of acetylene, C_2H_2, in an excess of oxygen.
e. The number of moles and the mass of barium peroxide, BaO_2, needed to produce 2.500 kg of barium oxide, BaO (O_2 is the other product.)
f. 

Q4.3.4

Determine the number of moles and the mass requested for each reaction in Exercise.

S4.3.4

0.0686 mol Mg, 1.67 g Mg; 2.701×10^{-3} mol O_2, 0.08644 g O_2; 6.43 mol $MgCO_3$, 542 g $MgCO_3$ 713 mol H_2O, 12.8 kg H_2O; 16.31 mol BaO_2, 2762 g BaO_2; 0.207 mol C_2H_4, 5.81 g C_2H_4

Q4.3.5

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.
b. Perform the calculations outlined.

S4.3.5

a.)

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.)

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. $0.1560\ moles\ H_2 \times \dfrac{2.02g}{1\ mole} = 0.3151g\ H_2$

Q4.3.6

Gallium chloride is formed by the reaction of 2.6 L of a 1.44 M solution of HCl according to the following equation: $2\,Ga + 6\,HCl \rightarrow 2\,GaCl_3 + 3\,H_2$.

a. Outline the steps necessary to determine the number of moles and mass of gallium chloride.
b. Perform the calculations outlined.

S4.3.6

$\text{volume HCl solution} \rightarrow \text{mol HCl} \rightarrow \text{mol } GaCl_3$; 1.25 mol $GaCl_3$, 2.2×10^2 g $GaCl_3$

Q4.3.7

I_2 is produced by the reaction of 0.4235 mol of $CuCl_2$ according to the following equation: $2\,CuCl_2 + 4\,KI \rightarrow 2\,CuI + 4\,KCl + I_2$.

a. How many molecules of I_2 are produced?
b. What mass of I_2 is produced?

Q4.3.8

Silver is often extracted from ores as $K[Ag(CN)_2]$ and then recovered by the reaction

$$2\,K[Ag(CN)_2](aq) + Zn(s) \rightarrow 2\,Ag(s) + Zn(CN)_2(aq) + 2\,KCN(aq)$$

a. How many molecules of $Zn(CN)_2$ are produced by the reaction of 35.27 g of $K[Ag(CN)_2]$?
b. What mass of $Zn(CN)_2$ is produced?

S4.3.8

5.337×10^{22} molecules; 10.41 g $Zn(CN)_2$

Q4.3.9

What mass of silver oxide, Ag_2O, is required to produce 25.0 g of silver sulfadiazine, $AgC_{10}H_9N_4SO_2$, from the reaction of silver oxide and sulfadiazine?

$$2\,C_{10}H_{10}N_4SO_2 + Ag_2O \rightarrow 2\,AgC_{10}H_9N_4SO_2 + H_2O$$

Q4.3.10

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.

S4.3.10

$\mathbf{SiO_2 + 3\,C \rightarrow SiC + 2\,CO}$, 4.50 kg SiO_2

Q4.3.11

Automotive air bags inflate when a sample of sodium azide, NaN_3, is very rapidly decomposed.

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

What mass of sodium azide is required to produce 2.6 ft^3 (73.6 L) of nitrogen gas with a density of 1.25 g/L?

S4.3.11

142g NaN_3

Q4.3.12

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?

$$\mathbf{CO_2(\mathit{g}) + 2\,NH_3(\mathit{g}) \rightarrow CO(NH_2)_2(\mathit{s}) + H_2O(\mathit{l})} \tag{6.E.7}$$

S4.3.12

5.00×10^3 kg

Q4.3.13

In an accident, a solution containing 2.5 kg of nitric acid was spilled. Two kilograms of Na_2CO_3 was quickly spread on the area and CO_2 was released by the reaction. Was sufficient Na_2CO_3 used to neutralize all of the acid?

Q4.3.14

A compact car gets 37.5 miles per gallon on the highway. If gasoline contains 84.2% carbon by mass and has a density of 0.8205 g/mL, determine the mass of carbon dioxide produced during a 500-mile trip (3.785 liters per gallon).

S4.3.14

1.28×10^5 g CO_2

Q4.3.15

What volume of a 0.750 M solution of hydrochloric acid, a solution of HCl, can be prepared from the HCl produced by the reaction of 25.0 g of NaCl with an excess of sulfuric acid?

$$\mathbf{NaCl(\mathit{s}) + H_2SO_4(\mathit{l}) \rightarrow HCl(\mathit{g}) + NaHSO_4(\mathit{s})} \tag{6.E.8}$$

Q4.3.16

What volume of a 0.2089 *M* KI solution contains enough KI to react exactly with the $Cu(NO_3)_2$ in 43.88 mL of a 0.3842 *M* solution of $Cu(NO_3)_2$?

$$\mathbf{2\,Cu(NO_3)_2 + 4\,KI \rightarrow 2\,CuI + I_2 + 4\,KNO_3} \tag{6.E.9}$$

S4.3.16

161.40 mL KI solution

Q4.3.17

A mordant is a substance that combines with a dye to produce a stable fixed color in a dyed fabric. Calcium acetate is used as a mordant. It is prepared by the reaction of acetic acid with calcium hydroxide.

$$\mathbf{2\,CH_3CO_2H + Ca(OH)_2 \rightarrow Ca(CH_3CO_2)_2 + 2\,H_2O} \tag{6.E.10}$$

What mass of $Ca(OH)_2$ is required to react with the acetic acid in 25.0 mL of a solution having a density of 1.065 g/mL and containing 58.0% acetic acid by mass?

Q4.3.18

The toxic pigment called white lead, $Pb_3(OH)_2(CO_3)_2$, has been replaced in white paints by rutile, TiO_2. How much rutile (g) can be prepared from 379 g of an ore that contains 88.3% ilmenite ($FeTiO_3$) by mass?

$$2\,FeTiO_3 + 4\,HCl + Cl_2 \rightarrow 2\,FeCl_3 + 2\,TiO_2 + 2\,H_2O \tag{6.E.11}$$

S4.3.18

176 g TiO_2

4.4: Reaction Yields

Q4.4.1

The following quantities are placed in a container: 1.5×10^{24} atoms of hydrogen, 1.0 mol of sulfur, and 88.0 g of diatomic oxygen.

a. What is the total mass in grams for the collection of all three elements?
b. What is the total number of moles of atoms for the three elements?
c. If the mixture of the three elements formed a compound with molecules that contain two hydrogen atoms, one sulfur atom, and four oxygen atoms, which substance is consumed first?
d. How many atoms of each remaining element would remain unreacted in the change described in ?

Q4.4.2

What is the limiting reactant in a reaction that produces sodium chloride from 8 g of sodium and 8 g of diatomic chlorine?

S4.4.2

The limiting reactant is Cl_2.

Q4.4.3

Which of the postulates of Dalton's atomic theory explains why we can calculate a theoretical yield for a chemical reaction?

Q4.4.4

A student isolated 25 g of a compound following a procedure that would theoretically yield 81 g. What was his percent yield?

S4.4.4

$\textbf{Percent yield} = 31\%$

Q4.4.5

A sample of 0.53 g of carbon dioxide was obtained by heating 1.31 g of calcium carbonate. What is the percent yield for this reaction?

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(s) \tag{6.E.12}$$

Q4.4.6

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.

S4.4.6

$\textbf{g } CCl_4 \rightarrow \textbf{mol } CCl_4 \rightarrow \textbf{mol } CCl_2F_2 \rightarrow \textbf{g } CCl_2F_2, \textbf{ percent yield} = 48.3\%$

Q4.4.7

Citric acid, $C_6H_8O_7$, a component of jams, jellies, and fruity soft drinks, is prepared industrially via fermentation of sucrose by the mold *Aspergillus niger*. The equation representing this reaction is

$$\mathbf{C_{12}H_{22}O_{11} + H_2O + 3\,O_2 \rightarrow 2\,C_6H_8O_7 + 4\,H_2O} \tag{6.E.13}$$

What mass of citric acid is produced from exactly 1 metric ton (1.000×10^3 kg) of sucrose if the yield is 92.30%?

Q4.4.8

Toluene, $C_6H_5CH_3$, is oxidized by air under carefully controlled conditions to benzoic acid, $C_6H_5CO_2H$, which is used to prepare the food preservative sodium benzoate, $C_6H_5CO_2Na$. What is the percent yield of a reaction that converts 1.000 kg of toluene to 1.21 kg of benzoic acid?

$$\mathbf{2\,C_6H_5CH_3 + 3\,O_2 \rightarrow 2\,C_6H_5CO_2H + 2\,H_2O} \tag{6.E.14}$$

S4.4.8

$\mathbf{\text{percent yield} = 91.3\%}$

Q4.4.9

In a laboratory experiment, the reaction of 3.0 mol of H_2 with 2.0 mol of I_2 produced 1.0 mol of HI. Determine the theoretical yield in grams and the percent yield for this reaction.

Q4.4.10

Outline the steps needed to solve the following problem, then do the calculations. Ether, $(C_2H_5)_2O$, which was originally used as an anesthetic but has been replaced by safer and more effective medications, is prepared by the reaction of ethanol with sulfuric acid.

$$2C_2H_5OH + H_2SO_4 \longrightarrow (C_2H_5)_2 + H_2SO_4{\cdot}H_2O$$

Q4.4.11

What is the percent yield of ether if 1.17 L (d = 0.7134 g/mL) is isolated from the reaction of 1.500 L of C_2H_5OH (d = 0.7894 g/mL)?

S4.4.11

Convert mass of ethanol to moles of ethanol; relate the moles of ethanol to the moles of ether produced using the stoichiometry of the balanced equation. Convert moles of ether to grams; divide the actual grams of ether (determined through the density) by the theoretical mass to determine the percent yield; 87.6%

Q4.4.12

Outline the steps needed to determine the limiting reactant when 30.0 g of propane, C_3H_8, is burned with 75.0 g of oxygen.

$$\mathbf{\text{percent yield} = \frac{0.8347\ \cancel{g}}{0.9525\ \cancel{g}} \times 100\% = 87.6\%} \tag{6.E.15}$$

Determine the limiting reactant.

Q4.4.13

Outline the steps needed to determine the limiting reactant when 0.50 g of Cr and 0.75 g of H_3PO_4 react according to the following chemical equation?

$$\mathbf{2\,Cr + 2\,H_3PO_4 \rightarrow 2\,CrPO_4 + 3\,H_2} \tag{6.E.16}$$

Determine the limiting reactant.

S4.4.13

The conversion needed is $\mathbf{\text{mol Cr} \rightarrow \text{mol } H_2PO_4}$. Then compare the amount of Cr to the amount of acid present. Cr is the limiting reactant.

Q4.4.14

What is the limiting reactant when 1.50 g of lithium and 1.50 g of nitrogen combine to form lithium nitride, a component of advanced batteries, according to the following unbalanced equation?

$$\mathrm{Li} + \mathrm{N_2} \rightarrow \mathrm{Li_3N} \tag{6.E.17}$$

S4.4.14

$$6\,\mathrm{Li} + \mathrm{N_2} \rightarrow 2\,\mathrm{Li_3N} \tag{6.E.18}$$

$$1.50g\,\mathrm{Li} \times \frac{1\,mole\,\mathrm{Li}}{6.94g\,\mathrm{Li}} \times \frac{2\,mole\,\mathrm{Li_3N}}{6\,mole\,\mathrm{Li}} = 0.0720\,moles\,\mathrm{Li_3N} \tag{6.E.19}$$

$$1.50g\,\mathrm{N_2} \times \frac{1\,mole\,\mathrm{N_2}}{28.02g\,\mathrm{N_2}} \times \frac{2\,mole\,\mathrm{Li_3N}}{1\,mole\,\mathrm{N_2}} = 0.107\,moles\,\mathrm{Li_3N} \tag{6.E.20}$$

Li is the limiting reactant

Q4.4.15

Uranium can be isolated from its ores by dissolving it as $UO_2(NO_3)_2$, then separating it as solid $UO_2(C_2O_4)\cdot 3H_2O$. Addition of 0.4031 g of sodium oxalate, $Na_2C_2O_4$, to a solution containing 1.481 g of uranyl nitrate, $UO_2(NO_2)_2$, yields 1.073 g of solid $UO_2(C_2O_4)\cdot 3H_2O$.

$$\mathrm{Na_2C_2O_4} + \mathrm{UO_2(NO_3)_2} + 3\,\mathrm{H_2O} \longrightarrow \mathrm{UO_2(C_2O_4)\cdot 3\,H_2O} + 2\,\mathrm{NaNO_3} \tag{6.E.21}$$

Determine the limiting reactant and the percent yield of this reaction.

S4.4.15

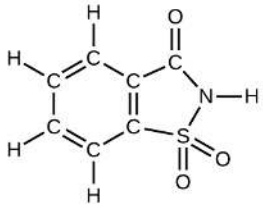
$Na_2C_2O_4$ is the limiting reactant. percent yield = 86.6%

Q4.4.16

How many molecules of $C_2H_4Cl_2$ can be prepared from 15 C_2H_4 molecules and 8 Cl_2 molecules?

Q4.4.17

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?



S4.4.17

Only four molecules can be made.

Q4.4.18

The phosphorus pentoxide used to produce phosphoric acid for cola soft drinks is prepared by burning phosphorus in oxygen.

a. What is the limiting reactant when 0.200 mol of P_4 and 0.200 mol of O_2 react according to

$$\mathrm{P_4} + 5\,\mathrm{O_2} \rightarrow \mathrm{P_4O_{10}} \tag{6.E.22}$$

b. Calculate the percent yield if 10.0 g of P_4O_{10} is isolated from the reaction.

Q4.4.19

Would you agree to buy 1 trillion (1,000,000,000,000) gold atoms for $5? Explain why or why not. Find the current price of gold at http://money.cnn.com/data/commodities/ $(1\ \text{troy ounce} = 31.1\ \text{g})$

S4.4.19

This amount cannot be weighted by ordinary balances and is worthless.

4.5: Quantitative Chemical Analysis

Q4.5.1

What volume of 0.0105-M HBr solution is be required to titrate 125 mL of a 0.0100-*M* $Ca(OH)_2$ solution?

$$\text{Ca(OH)}_2(aq) + 2\,\text{HBr}(aq) \rightarrow \text{CaBr}_2(aq) + 2\,\text{H}_2\text{O}(l) \tag{6.E.23}$$

Q4.5.2

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?

S4.5.2

3.4×10^{-3} *M* H_2SO_4

Q4.5.3

What is the concentration of NaCl in a solution if titration of 15.00 mL of the solution with 0.2503 *M* $AgNO_3$ requires 20.22 mL of the $AgNO_3$ solution to reach the end point?

$$\text{AgNO}_3(aq) + \text{NaCl}(aq) \rightarrow \text{AgCl}(s) + \text{NaNO}_3(aq) \tag{6.E.24}$$

Q4.5.4

In a common medical laboratory determination of the concentration of free chloride ion in blood serum, a serum sample is titrated with a $Hg(NO_3)_2$ solution.

$$2\,\text{Cl}^-(aq) + \text{Hg(NO}_3)_2(aq) \rightarrow 2\,\text{NO}_3{}^-(aq) + \text{HgCl}_2(s) \tag{6.E.25}$$

What is the Cl^- concentration in a 0.25-mL sample of normal serum that requires 1.46 mL of 5.25×10^{-4} *M* $Hg(NO_3)_2(aq)$ to reach the end point?

S4.5.4

9.6×10^{-3} *M* Cl^-

Q4.5.5

Potatoes can be peeled commercially by soaking them in a 3-M to 6-M solution of sodium hydroxide, then removing the loosened skins by spraying them with water. Does a sodium hydroxide solution have a suitable concentration if titration of 12.00 mL of the solution requires 30.6 mL of 1.65 M HCI to reach the end point?

Q4.5.6

A sample of gallium bromide, $GaBr_2$, weighing 0.165 g was dissolved in water and treated with silver nitrate, $AgNO_3$, resulting in the precipitation of 0.299 g AgBr. Use these data to compute the %Ga (by mass) $GaBr_2$.

S4.5.6

22.4%

Q4.5.7

The principal component of mothballs is naphthalene, a compound with a molecular mass of about 130 amu, containing only carbon and hydrogen. A 3.000-mg sample of naphthalene burns to give 10.3 mg of CO_2. Determine its empirical and molecular

formulas.

Q4.5.8

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.

S4.5.8

The empirical formula is BH_3. The molecular formula is B_2H_6.

Q4.5.9

Sodium bicarbonate (baking soda), $NaHCO_3$, can be purified by dissolving it in hot water (60 °C), filtering to remove insoluble impurities, cooling to 0 °C to precipitate solid $NaHCO_3$, and then filtering to remove the solid, leaving soluble impurities in solution. Any $NaHCO_3$ that remains in solution is not recovered. The solubility of $NaHCO_3$ in hot water of 60 °C is 164 g L. Its solubility in cold water of 0 °C is 69 g/L. What is the percent yield of $NaHCO_3$ when it is purified by this method?

Q4.5.10

What volume of 0.600 *M* HCl is required to react completely with 2.50 g of sodium hydrogen carbonate?

$$\mathrm{NaHCO_3}(aq) + \mathrm{HCl}(aq) \rightarrow \mathrm{NaCl}(aq) + \mathrm{CO_2}(g) + \mathrm{H_2O}(l) \tag{6.E.26}$$

S4.5.10

49.6 mL

Q4.5.11

What volume of 0.08892 *M* HNO_3 is required to react completely with 0.2352 g of potassium hydrogen phosphate?

$$2\,\mathrm{HNO_3}(aq) + \mathrm{K_2HPO_4}(aq) \rightarrow \mathrm{H_2PO_4}(aq) + 2\,\mathrm{KNO_3}(aq) \tag{6.E.27}$$

Q4.5.12

What volume of a 0.3300-*M* solution of sodium hydroxide would be required to titrate 15.00 mL of 0.1500 *M* oxalic acid?

$$\mathrm{C_2O_4H_2}(aq) + 2\,\mathrm{NaOH}(aq) \rightarrow \mathrm{Na_2C_2O_4}(aq) + 2\,\mathrm{H_2O}(l) \tag{6.E.28}$$

S4.5.12

13.64 mL

Q4.5.13

What volume of a 0.00945-*M* solution of potassium hydroxide would be required to titrate 50.00 mL of a sample of acid rain with a H_2SO_4 concentration of 1.23×10^{-4} *M*.

$$\mathrm{H_2SO_4}(aq) + 2\,\mathrm{KOH}(aq) \rightarrow \mathrm{K_2SO_4}(aq) + 2\,\mathrm{H_2O}(l) \tag{6.E.29}$$

S4.5.13

1.30 mL

Q4.5.14

A sample of solid calcium hydroxide, $Ca(OH)_2$, is allowed to stand in water until a saturated solution is formed. A titration of 75.00 mL of this solution with 5.00×10^{-2} *M* HCl requires 36.6 mL of the acid to reach the end point.

$$\mathrm{Ca(OH)_2}(aq) + 2\,\mathrm{HCl}(aq) \rightarrow \mathrm{CaCl_2}(aq) + 2\,\mathrm{H_2O}(l) \tag{6.E.30}$$

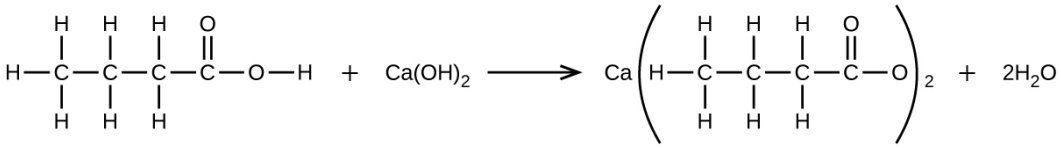
What is the molarity?

S4.5.14

1.22 *M*

Q4.5.15

What mass of $Ca(OH)_2$ will react with 25.0 g of propionic acid to form the preservative calcium propionate according to the equation?



Q4.5.16

How many milliliters of a 0.1500-*M* solution of KOH will be required to titrate 40.00 mL of a 0.0656-*M* solution of H_3PO_4?

$$\mathbf{H_3PO_4}(aq) + \mathbf{2\,KOH}(aq) \rightarrow \mathbf{K_2HPO_4}(aq) + \mathbf{2\,H_2O}(l) \tag{6.E.31}$$

S4.5.16

34.99 mL KOH

Q4.5.17

Potassium acid phthalate, $KHC_6H_4O_4$, or KHP, is used in many laboratories, including general chemistry laboratories, to standardize solutions of base. KHP is one of only a few stable solid acids that can be dried by warming and weighed. A 0.3420-g sample of $KHC_6H_4O_4$ reacts with 35.73 mL of a NaOH solution in a titration. What is the molar concentration of the NaOH?

$$\mathbf{KHC_6H_4O_4}(aq) + \mathbf{NaOH}(aq) \rightarrow \mathbf{KNaC_6H_4O_4}(aq) + \mathbf{H_2O}(aq) \tag{6.E.32}$$

Q4.5.18

The reaction of WCl_6 with Al at ~400 °C gives black crystals of a compound containing only tungsten and chlorine. A sample of this compound, when reduced with hydrogen, gives 0.2232 g of tungsten metal and hydrogen chloride, which is absorbed in water. Titration of the hydrochloric acid thus produced requires 46.2 mL of 0.1051 *M* NaOH to reach the end point. What is the empirical formula of the black tungsten chloride?

S4.5.19

The empirical formula is WCl_4.

This page titled 6.E: Stoichiometry of Chemical Reactions (Exercises) is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

CHAPTER OVERVIEW

7: Gases

A general chemistry Libretexts Textmap organized around the textbook
General Chemistry -Atoms First
By OpenStax

I II III IV V VI VII VIII IX X XI XII XIII XIV XV XVI XVII XVIII XIX XX XXI ● **Homework**

In this chapter, we examine the relationships between gas temperature, pressure, amount, and volume. We will study a simple theoretical model and use it to analyze the experimental behavior of gases. The results of these analyses will show us the limitations of the theory and how to improve on it.

7.1: Gas Pressure

7.2: Relating Pressure, Volume, Amount, and Temperature- The Ideal Gas Law

7.3: Stoichiometry of Gaseous Substances, Mixtures, and Reactions

7.4: The Kinetic-Molecular Theory

7.E: Gases (Exercises)

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: Gases is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

7.1: Gas Pressure

Learning Objectives

- Define the property of pressure
- Define and convert among the units of pressure measurements
- Describe the operation of common tools for measuring gas pressure
- Calculate pressure from manometer data

The earth's atmosphere exerts a pressure, as does any other gas. Although we do not normally notice atmospheric pressure, we are sensitive to pressure changes—for example, when your ears "pop" during take-off and landing while flying, or when you dive underwater. Gas pressure is caused by the force exerted by gas molecules colliding with the surfaces of objects (Figure **7.1.1**). Although the force of each collision is very small, any surface of appreciable area experiences a large number of collisions in a short time, which can result in a high pressure. In fact, normal air pressure is strong enough to crush a metal container when not balanced by equal pressure from inside the container.

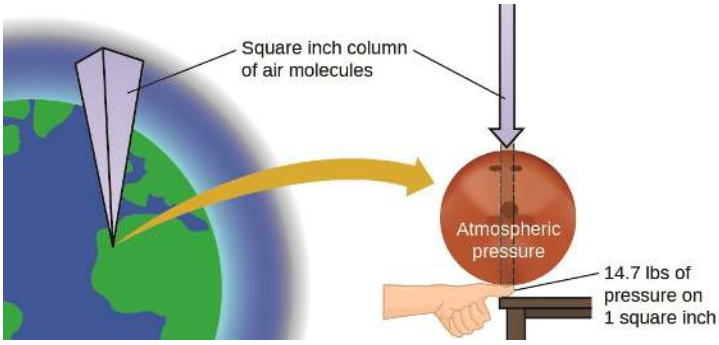


Figure **7.1.1**: The atmosphere above us exerts a large pressure on objects at the surface of the earth, roughly equal to the weight of a bowling ball pressing on an area the size of a human thumbnail.

Diagram of Earth with a square inch column of air molecules extending to the atmosphere. This column points to an arrow pointing down on a bowling ball resting on a human thumbnail placed on top of a table.

Atmospheric pressure is caused by the weight of the column of air molecules in the atmosphere above an object, such as the tanker car. At sea level, this pressure is roughly the same as that exerted by a full-grown African elephant standing on a doormat, or a typical bowling ball resting on your thumbnail. These may seem like huge amounts, and they are, but life on earth has evolved under such atmospheric pressure. If you actually perch a bowling ball on your thumbnail, the pressure experienced is twice the usual pressure, and the sensation is unpleasant.



A dramatic illustration of atmospheric pressure is provided in this brief video, which shows a railway tanker car imploding when its internal pressure is decreased.

Pressure is defined as the force exerted on a given area:

$$P = \frac{F}{A} \tag{7.1.1}$$

Since pressure is directly proportional to force and inversely proportional to area (Equation 7.1.1), pressure can be increased either by either **increasing** the amount of force or by **decreasing** the area over which it is applied. Correspondingly, pressure can be decreased by either **decreasing** the force or **increasing** the area.

Let's apply the definition of pressure (Equation 7.1.1) to determine which would be more likely to fall through thin ice in Figure 7.1.2.—the elephant or the figure skater?



Figure 7.1.2: Although (a) an elephant's weight is large, creating a very large force on the ground, (b) the figure skater exerts a much higher pressure on the ice due to the small surface area of her skates. (credit a: modification of work by Guido da Rozze; credit b: modification of work by Ryosuke Yagi).

Figure a is a photo of a large gray elephant on grassy, beige terrain. Figure b is a photo of a figure skater with her right skate on the ice, upper torso lowered, arms extended upward behind her chest, and left leg extended upward behind her.

A large African elephant can weigh 7 tons, supported on four feet, each with a diameter of about 1.5 ft (footprint area of 250 in^2), so the pressure exerted by each foot is about 14 lb/in^2:

$$\text{pressure per elephant foot} = 14,000\frac{\text{lb}}{\text{elephant}} \times \frac{1\text{ elephant}}{4\text{ feet}} \times \frac{1\text{ foot}}{250\text{ in}^2} = 14\text{ lb/in}^2 \tag{7.1.2}$$

The figure skater weighs about 120 lbs, supported on two skate blades, each with an area of about 2 in^2, so the pressure exerted by each blade is about 30 lb/in^2:

$$\text{pressure per skate blade} = 120\frac{\text{lb}}{\text{skater}} \times \frac{1\text{ skater}}{2\text{ blades}} \times \frac{1\text{ blade}}{2\text{ in}^2} = 30\text{ lb/in}^2 \tag{7.1.3}$$

Even though the elephant is more than one hundred times heavier than the skater, it exerts less than one-half of the pressure and would therefore be less likely to fall through thin ice. On the other hand, if the skater removes her skates and stands with bare feet (or regular footwear) on the ice, the larger area over which her weight is applied greatly reduces the pressure exerted:

$$\text{pressure per human foot} = 120\frac{\text{lb}}{\text{skater}} \times \frac{1\text{ skater}}{2\text{ feet}} \times \frac{1\text{ foot}}{30\text{ in}^2} = 2\text{ lb/in}^2 \tag{7.1.4}$$

The SI unit of pressure is the pascal (Pa), with 1 Pa = 1 N/m^2, where N is the newton, a unit of force defined as 1 kg m/s^2. One pascal is a small pressure; in many cases, it is more convenient to use units of kilopascal (1 kPa = 1000 Pa) or bar (1 bar = 100,000 Pa). In the United States, pressure is often measured in pounds of force on an area of one square inch—pounds per square inch (psi)—for example, in car tires. Pressure can also be measured using the unit atmosphere (atm), which originally represented the average sea level air pressure at the approximate latitude of Paris (45°). Table 7.1.1 provides some information on these and a few other common units for pressure measurements

Table 7.1.1: Pressure Units

Unit Name and Abbreviation	Definition or Relation to Other Unit	Comment
pascal (Pa)	1 Pa = 1 N/m^2	recommended IUPAC unit
kilopascal (kPa)	1 kPa = 1000 Pa	
pounds per square inch (psi)	air pressure at sea level is ~14.7 psi	
atmosphere (atm)	1 atm = 101,325 Pa	air pressure at sea level is ~1 atm
bar (bar, or b)	1 bar = 100,000 Pa (exactly)	commonly used in meteorology
millibar (mbar, or mb)	1000 mbar = 1 bar	
inches of mercury (in. Hg)	1 in. Hg = 3386 Pa	used by aviation industry, also some weather reports
torr	$1\ \text{torr} = \frac{1}{760}\ \text{atm}$	named after Evangelista Torricelli, inventor of the barometer
millimeters of mercury (mm Hg)	1 mm Hg ~1 torr	

Example 7.1.1: Conversion of Pressure Units

The United States National Weather Service reports pressure in both inches of Hg and millibars. Convert a pressure of 29.2 in. Hg into:

a. torr
b. atm
c. kPa
d. mbar

Solution

This is a unit conversion problem. The relationships between the various pressure units are given in Table 9.2.1.

a. $29.2\ \cancel{\text{in Hg}} \times \frac{25.4\ \cancel{\text{mm}}}{1\ \cancel{\text{in}}} \times \frac{1\ \text{torr}}{1\ \cancel{\text{mm Hg}}} = 742\ \text{torr}$

b. $742\ \cancel{\text{torr}} \times \frac{1\ \text{atm}}{760\ \cancel{\text{torr}}} = 0.976\ \text{atm}$

c. $742\ \cancel{\text{torr}} \times \frac{101.325\ \text{kPa}}{760\ \cancel{\text{torr}}} = 98.9\ \text{kPa}$

d. $98.9\ \cancel{\text{kPa}} \times \frac{1000\ \cancel{\text{Pa}}}{1\ \cancel{\text{kPa}}} \times \frac{1\ \cancel{\text{bar}}}{100,000\ \cancel{\text{Pa}}} \times \frac{1000\ \text{mbar}}{1\ \cancel{\text{bar}}} = 989\ \text{mbar}$

Exercise 7.1.1

A typical barometric pressure in Kansas City is 740 torr. What is this pressure in atmospheres, in millimeters of mercury, in kilopascals, and in bar?

Answer

0.974 atm; 740 mm Hg; 98.7 kPa; 0.987 bar

We can measure atmospheric pressure, the force exerted by the atmosphere on the earth's surface, with a barometer (Figure **7.1.3**). A barometer is a glass tube that is closed at one end, filled with a nonvolatile liquid such as mercury, and then inverted and immersed in a container of that liquid. The atmosphere exerts pressure on the liquid outside the tube, the column of liquid exerts

pressure inside the tube, and the pressure at the liquid surface is the same inside and outside the tube. The height of the liquid in the tube is therefore proportional to the pressure exerted by the atmosphere.

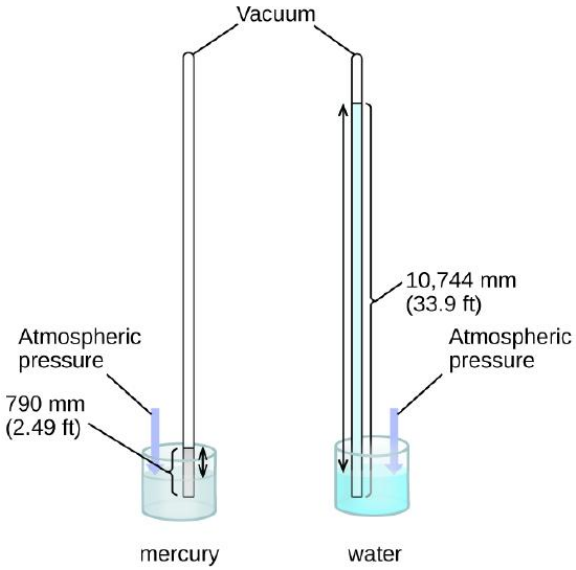


Figure 7.1.3: In a barometer, the height, h, of the column of liquid is used as a measurement of the air pressure. Using very dense liquid mercury (left) permits the construction of reasonably sized barometers, whereas using water (right) would require a barometer more than 30 feet tall.

Two barometers are in vacuum. One utilizes mercury while the other uses water in the capillary tube. Both barometers are exposed to atmospheric pressure. The barometer with mercury shows mercury levels of 2.49 feet. The barometer with water has a much greater level of 33.9 feet.

If the liquid is water, normal atmospheric pressure will support a column of water over 10 meters high, which is rather inconvenient for making (and reading) a barometer. Because mercury (Hg) is about 13.6-times denser than water, a mercury barometer only needs to be $\frac{1}{13.6}$ as tall as a water barometer—a more suitable size. Standard atmospheric pressure of 1 atm at sea level (101,325 Pa) corresponds to a column of mercury that is about 760 mm (29.92 in.) high. The torr was originally intended to be a unit equal to one millimeter of mercury, but it no longer corresponds exactly. The pressure exerted by a fluid due to gravity is known as hydrostatic pressure, p:

$$p = h\rho g \tag{7.1.5}$$

where

- h is the height of the fluid,
- ρ is the density of the fluid, and
- g is acceleration due to gravity.

Example 7.1.2: Calculation of Barometric Pressure

Show the calculation supporting the claim that atmospheric pressure near sea level corresponds to the pressure exerted by a column of mercury that is about 760 mm high. The density of mercury = $13.6\,g/cm^3$.

Solution

The hydrostatic pressure is given by Equation 7.1.5, with $h = 760\,mm$, $\rho = 13.6\,g/cm^3$, and $g = 9.81\,m/s^2$. Plugging these values into the Equation 7.1.5 and doing the necessary unit conversions will give us the value we seek. (Note: We are expecting to find a pressure of ~101,325 Pa:)

$$101,325\ N/\mathrm{m}^2 = 101,325\ \frac{\mathrm{kg}\cdot\mathrm{m}/\mathrm{s}^2}{\mathrm{m}^2} = 101,325\ \frac{\mathrm{kg}}{\mathrm{m}\cdot\mathrm{s}^2}$$

$$p = \left(760\ \text{mm} \times \frac{1\ \text{m}}{1000\ \text{mm}}\right) \times \left(\frac{13.6\ \text{g}}{1\ \text{cm}^3} \times \frac{1\ \text{kg}}{1000\ \text{g}} \times \frac{(100\ \text{cm})^3}{(1\ \text{m})^3}\right) \times \left(\frac{9.81\ \text{m}}{1\ \text{s}^2}\right)$$
$$= (0.760\ \text{m})(13,600\ \text{kg/m}^3)(9.81\ \text{m/s}^2) = 1.01 \times 10^5\ \text{kg/ms}^2 = 1.01 \times 10^5 N/\text{m}^2$$
$$= 1.01 \times 10^5\ \text{Pa}$$

Exercise 7.1.2

Calculate the height of a column of water at 25 °C that corresponds to normal atmospheric pressure. The density of water at this temperature is 1.0 g/cm^3.

Answer

10.3 m

A manometer is a device similar to a barometer that can be used to measure the pressure of a gas trapped in a container. A closed-end manometer is a U-shaped tube with one closed arm, one arm that connects to the gas to be measured, and a nonvolatile liquid (usually mercury) in between. As with a barometer, the distance between the liquid levels in the two arms of the tube (*h* in the diagram) is proportional to the pressure of the gas in the container. An open-end manometer (Figure **7.1.3**) is the same as a closed-end manometer, but one of its arms is open to the atmosphere. In this case, the distance between the liquid levels corresponds to the difference in pressure between the gas in the container and the atmosphere.

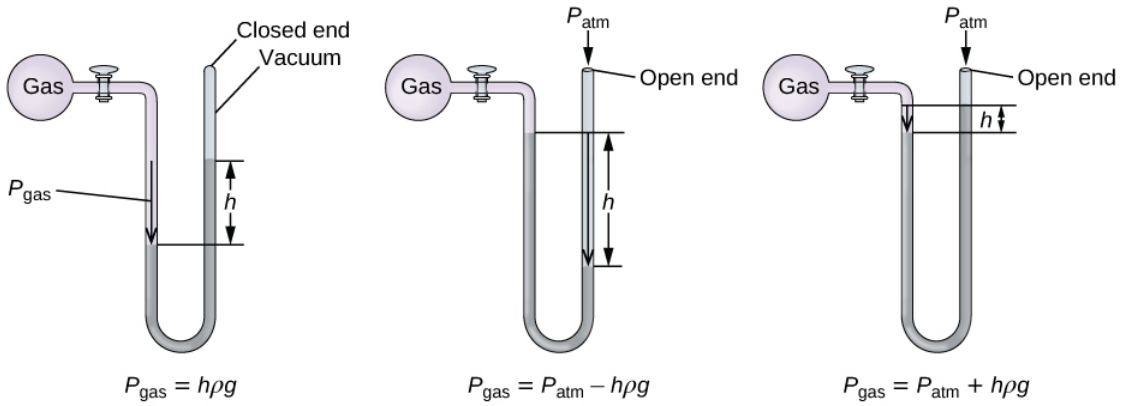


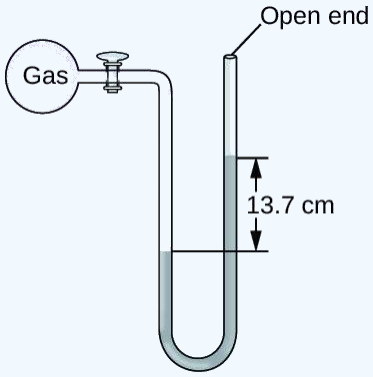
Figure **7.1.4**: A manometer can be used to measure the pressure of a gas. The (difference in) height between the liquid levels (h) is a measure of the pressure. Mercury is usually used because of its large density.

The first manometer is closed end. The gas in the bulb exerts a certain pressure on the liquid in the tube so that the height, h, between the two levels of liquid on both sides of the U tube is proportional to the pressure. The equation is P subscript gas equals to h rho g. The second manometer has an open end. The equation for P subscript gas is equals to P subscript atm minus h rho g. The final manometer is also open ended and has equation of P subscript gas equals to P subscript atm plus h rho g for cases where pressure of the gas is greater than atmospheric pressure.

Example 7.1.3: Calculation of Pressure Using an Open-End Manometer

The pressure of a sample of gas is measured at sea level with an open-end Hg (mercury) manometer, as shown below. Determine the pressure of the gas in:

a. mm Hg
b. atm
c. kPa



The height is the difference between the two levels of mercury on each side of the U tube and has a value of 13.7 centimeters. The level on the right side is higher than the left.

Solution

The pressure of the gas equals the hydrostatic pressure due to a column of mercury of height 13.7 cm plus the pressure of the atmosphere at sea level. (The pressure at the bottom horizontal line is equal on both sides of the tube. The pressure on the left is due to the gas and the pressure on the right is due to 13.7 cm of Hg plus atmospheric pressure.)

a. In mm Hg, this is: 137 mm Hg + 760 mm Hg = 897 mm Hg

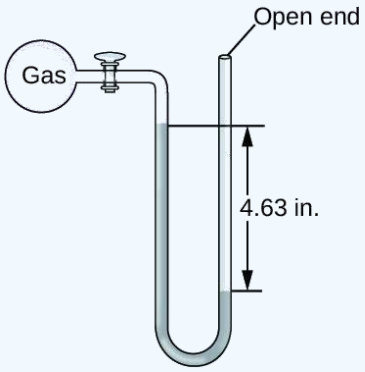
b. $897 \cancel{\text{ mmHg}} \times \dfrac{1 \text{ atm}}{760 \cancel{\text{ mmHg}}} = 1.18 \text{ atm}$

c. $1.18 \cancel{\text{ atm}} \times \dfrac{101.325 \text{ kPa}}{1 \cancel{\text{ atm}}} = 1.20 \times 10^2 \text{ kPa}$

Exercise 7.1.3

The pressure of a sample of gas is measured at sea level with an open-end Hg manometer, as shown below Determine the pressure of the gas in:

a. mm Hg
b. atm
c. kPa



The height is the difference between the two levels of mercury on each side of the U tube and has a value of 4.63 inches. The level on the left side is higher than the right.

Answer a

642 mm Hg

Answer b

0.845 atm

Answer c

85.6 kPa

Application: Measuring Blood Pressure

Blood pressure is measured using a device called a sphygmomanometer (Greek *sphygmos* = "pulse"). It consists of an inflatable cuff to restrict blood flow, a manometer to measure the pressure, and a method of determining when blood flow begins and when it becomes impeded (Figure **7.1.5**). Since its invention in 1881, it has been an essential medical device. There are many types of sphygmomanometers: manual ones that require a stethoscope and are used by medical professionals; mercury ones, used when the most accuracy is required; less accurate mechanical ones; and digital ones that can be used with little training but that have limitations. When using a sphygmomanometer, the cuff is placed around the upper arm and inflated until blood flow is completely blocked, then slowly released. As the heart beats, blood forced through the arteries causes a rise in pressure. This rise in pressure at which blood flow begins is the *systolic pressure*—the peak pressure in the cardiac cycle. When the cuff's pressure equals the arterial systolic pressure, blood flows past the cuff, creating audible sounds that can be heard using a stethoscope. This is followed by a decrease in pressure as the heart's ventricles prepare for another beat. As cuff pressure continues to decrease, eventually sound is no longer heard; this is the *diastolic pressure*—the lowest pressure (resting phase) in the cardiac cycle. Blood pressure units from a sphygmomanometer are in terms of millimeters of mercury (mm Hg).



Figure **7.1.5**: (a) A medical technician prepares to measure a patient's blood pressure with a sphygmomanometer. (b) A typical sphygmomanometer uses a valved rubber bulb to inflate the cuff and a diaphragm gauge to measure pressure. (credit a: modification of work by Master Sgt. Jeffrey Allen)

Meteorology, Climatology, and Atmospheric Science

Throughout the ages, people have observed clouds, winds, and precipitation, trying to discern patterns and make predictions: when it is best to plant and harvest; whether it is safe to set out on a sea voyage; and much more. We now face complex weather and atmosphere-related challenges that will have a major impact on our civilization and the ecosystem. Several different scientific disciplines use chemical principles to help us better understand weather, the atmosphere, and climate. These are meteorology, climatology, and atmospheric science. Meteorology is the study of the atmosphere, atmospheric phenomena, and atmospheric effects on earth's weather. Meteorologists seek to understand and predict the weather in the short term, which can save lives and benefit the economy. Weather forecasts (Figure **7.1.5**) are the result of thousands of measurements of air pressure, temperature, and the like, which are compiled, modeled, and analyzed in weather centers worldwide.

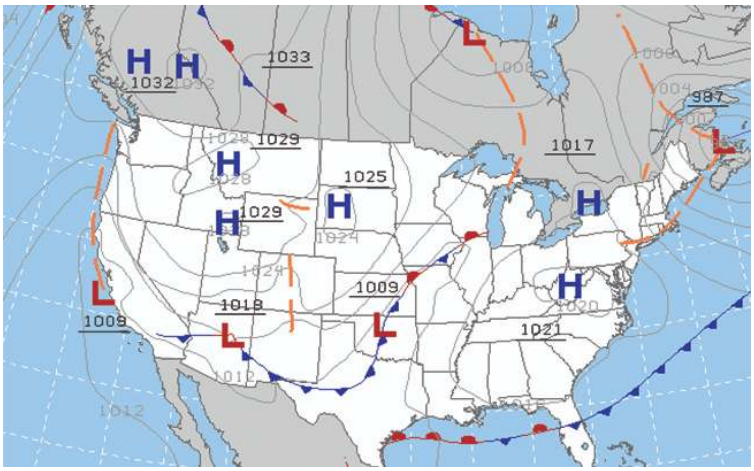


Figure **7.1.6**: Meteorologists use weather maps to describe and predict weather. Regions of high (H) and low (L) pressure have large effects on weather conditions. The gray lines represent locations of constant pressure known as isobars. (credit: modification of work by National Oceanic and Atmospheric Administration)

A weather map of the United States is shown which points out areas of high and low pressure with the letters H in blue and L in red. There are curved grey lines throughout the United States region as well as beyond it around area of Canada and the oceans.

In terms of weather, low-pressure systems occur when the earth's surface atmospheric pressure is lower than the surrounding environment: Moist air rises and condenses, producing clouds. Movement of moisture and air within various weather fronts instigates most weather events.

The atmosphere is the gaseous layer that surrounds a planet. Earth's atmosphere, which is roughly 100–125 km thick, consists of roughly 78.1% nitrogen and 21.0% oxygen, and can be subdivided further into the regions shown in Figure **7.1.7**: the exosphere (furthest from earth, > 700 km above sea level), the thermosphere (80–700 km), the mesosphere (50–80 km), the stratosphere (second lowest level of our atmosphere, 12–50 km above sea level), and the troposphere (up to 12 km above sea level, roughly 80% of the earth's atmosphere by mass and the layer where most weather events originate). As you go higher in the troposphere, air density and temperature both decrease.

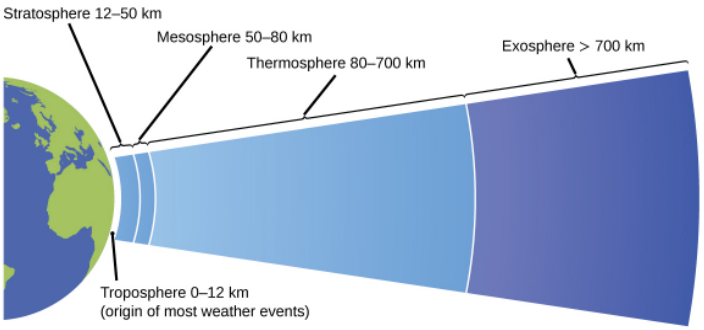


Figure **7.1.7**: Earth's atmosphere has five layers: the troposphere, the stratosphere, the mesosphere, the thermosphere, and the exosphere.

The different layers of the atmosphere is illustrated as a cross sectional slice of the Earth's atmosphere. The different thickness of each layer is shown. The thermosphere has the largest portion, followed by the exosphere, stratosphere, mesosphere, and troposphere.

Climatology is the study of the climate, averaged weather conditions over long time periods, using atmospheric data. However, climatologists study patterns and effects that occur over decades, centuries, and millennia, rather than shorter time frames of hours, days, and weeks like meteorologists. Atmospheric science is an even broader field, combining meteorology, climatology, and other scientific disciplines that study the atmosphere.

Summary

Gases exert pressure, which is force per unit area. The pressure of a gas may be expressed in the SI unit of pascal or kilopascal, as well as in many other units including torr, atmosphere, and bar. Atmospheric pressure is measured using a barometer; other gas

pressures can be measured using one of several types of manometers.

Key Equations

- $P = \frac{F}{A}$
- $p = h\rho g$

Glossary

atmosphere (atm)
unit of pressure; 1 atm = 101,325 Pa

bar
(bar or b) unit of pressure; 1 bar = 100,000 Pa

barometer
device used to measure atmospheric pressure

hydrostatic pressure
pressure exerted by a fluid due to gravity

manometer
device used to measure the pressure of a gas trapped in a container

pascal (Pa)
SI unit of pressure; 1 Pa = 1 N/m^2

pounds per square inch (psi)
unit of pressure common in the US

pressure
force exerted per unit area

torr
unit of pressure; $1\ \text{torr} = \frac{1}{760}\ \text{atm}$

This page titled 7.1: Gas Pressure is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

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

7.2: Relating Pressure, Volume, Amount, and Temperature- The Ideal Gas Law

Learning Objectives

- Identify the mathematical relationships between the various properties of gases
- Use the ideal gas law, and related gas laws, to compute the values of various gas properties under specified conditions

During the seventeenth and especially eighteenth centuries, driven both by a desire to understand nature and a quest to make balloons in which they could fly (Figure **7.2.1**), a number of scientists established the relationships between the macroscopic physical properties of gases, that is, pressure, volume, temperature, and amount of gas. Although their measurements were not precise by today's standards, they were able to determine the mathematical relationships between pairs of these variables (e.g., pressure and temperature, pressure and volume) that hold for an *ideal* gas—a hypothetical construct that real gases approximate under certain conditions. Eventually, these individual laws were combined into a single equation—the *ideal gas law*—that relates gas quantities for gases and is quite accurate for low pressures and moderate temperatures. We will consider the key developments in individual relationships (for pedagogical reasons not quite in historical order), then put them together in the ideal gas law.



Figure **7.2.1**: In 1783, the first (a) hydrogen-filled balloon flight, (b) manned hot air balloon flight, and (c) manned hydrogen-filled balloon flight occurred. When the hydrogen-filled balloon depicted in (a) landed, the frightened villagers of Gonesse reportedly destroyed it with pitchforks and knives. The launch of the latter was reportedly viewed by 400,000 people in Paris.

This figure includes three images. Image a is a black and white image of a hydrogen balloon apparently being deflated by a mob of people. In image b, a blue, gold, and red balloon is being held to the ground with ropes while positioned above a platform from which smoke is rising beneath the balloon. In c, an image is shown in grey on a peach-colored background of an inflated balloon with vertical striping in the air. It appears to have a basket attached to its lower side. A large stately building appears in the background.

Pressure and Temperature: Amontons's Law

Imagine filling a rigid container attached to a pressure gauge with gas and then sealing the container so that no gas may escape. If the container is cooled, the gas inside likewise gets colder and its pressure is observed to decrease. Since the container is rigid and tightly sealed, both the volume and number of moles of gas remain constant. If we heat the sphere, the gas inside gets hotter (Figure **7.2.2**) and the pressure increases.

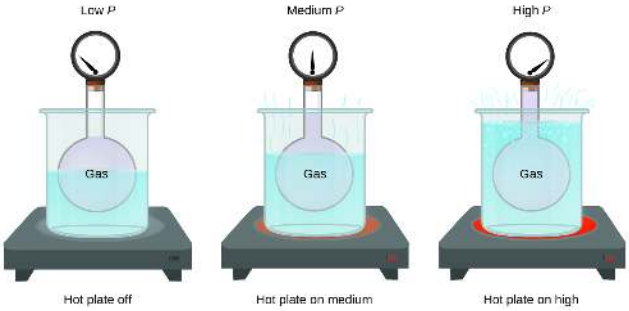


Figure **7.2.2**: The effect of temperature on gas pressure: When the hot plate is off, the pressure of the gas in the sphere is relatively low. As the gas is heated, the pressure of the gas in the sphere increases.

This figure includes three similar diagrams. In the first diagram to the left, a rigid spherical container of a gas to which a pressure gauge is attached at the top is placed in a large beaker of water, indicated in light blue, atop a hot plate. The needle on the pressure gauge points to the far left on the gauge. The diagram is labeled "low P" above and "hot plate off" below. The second similar diagram also has the rigid spherical container of gas placed in a large beaker from which light blue wavy line segments extend from the top of the liquid in the beaker. The beaker is situated on top of a slightly reddened circular area. The needle on the pressure gauge points straight up, or to the middle on the gauge. The diagram is labeled "medium P" above and "hot plate on medium" below. The third diagram also has the rigid spherical container of gas placed in a large beaker in which bubbles appear near the liquid surface and several wavy light blue line segments extend from the surface out of the beaker. The beaker is situated on top of a bright red circular area. The needle on the pressure gauge points to the far right on the gauge. The diagram is labeled "high P" above and "hot plate on high" below.

This relationship between temperature and pressure is observed for any sample of gas confined to a constant volume. An example of experimental pressure-temperature data is shown for a sample of air under these conditions in Figure **7.2.3**. We find that temperature and pressure are linearly related, and if the temperature is on the kelvin scale, then P and T are directly proportional (again, when *volume and moles of gas are held constant*); if the temperature on the kelvin scale increases by a certain factor, the gas pressure increases by the same factor.

Temperature (°C)	Temperature (K)	Pressure (kPa)
–150	173	36.0
–100	223	46.4
–50	273	56.7
0	323	67.1
50	373	77.5
100	423	88.0

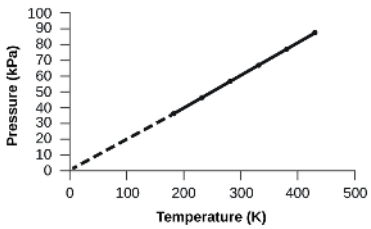


Figure **7.2.3**: For a constant volume and amount of air, the pressure and temperature are directly proportional, provided the temperature is in kelvin. (Measurements cannot be made at lower temperatures because of the condensation of the gas.) When this line is extrapolated to lower pressures, it reaches a pressure of 0 at –273 °C, which is 0 on the kelvin scale and the lowest possible temperature, called absolute zero.

This figure includes a table and a graph. The table has 3 columns and 7 rows. The first row is a header, which labels the columns "Temperature, degrees C," "Temperature, K," and "Pressure, k P a." The first column contains the values from top to bottom negative 150, negative 100, negative 50, 0, 50, and 100. The second column contains the values from top to bottom 173, 223, 273, 323, 373, and 423. The third column contains the values 36.0, 46.4, 56.7, 67.1, 77.5, and 88.0. A graph appears to the right of the table. The horizontal axis is labeled "Temperature (K)." with markings and labels provided for multiples of 100 beginning at 0 and ending at 500. The vertical axis is labeled "Pressure (k P a)" with markings and labels provided for multiples of 10, beginning at 0 and ending at 100. Six data points from the table are plotted on the graph with black dots. These dots are connected with a solid black line. A dashed line extends from the data point furthest to the left to the origin. The graph shows a positive linear trend.

Guillaume Amontons was the first to empirically establish the relationship between the pressure and the temperature of a gas (~1700), and Joseph Louis Gay-Lussac determined the relationship more precisely (~1800). Because of this, the *P-T* relationship for gases is known as either Amontons's law or Gay-Lussac's law. Under either name, it states that *the pressure of a given amount of*

gas is directly proportional to its temperature on the kelvin scale when the volume is held constant. Mathematically, this can be written:

$$P \propto T \text{ or } P = \text{constant} \times T \text{ or } P = k \times T$$

where ∝ means "is proportional to," and k is a proportionality constant that depends on the identity, amount, and volume of the gas.

For a confined, constant volume of gas, the ratio $\frac{P}{T}$ is therefore constant (i.e., $\frac{P}{T} = k$). If the gas is initially in "Condition 1" (with $P = P_1$ and $T = T_1$), and then changes to "Condition 2" (with $P = P_2$ and $T = T_2$), we have that $\frac{P_1}{T_1} = k$ and $\frac{P_2}{T_2} = k$, which reduces to $\frac{P_1}{T_1} = \frac{P_2}{T_2}$. This equation is useful for pressure-temperature calculations for a confined gas at constant volume. Note that temperatures must be on the kelvin scale for any gas law calculations (0 on the kelvin scale and the lowest possible temperature is called absolute zero). (Also note that there are at least three ways we can describe how the pressure of a gas changes as its temperature changes: We can use a table of values, a graph, or a mathematical equation.)

Example 7.2.1: Predicting Change in Pressure with Temperature

A can of hair spray is used until it is empty except for the propellant, isobutane gas.

a. On the can is the warning "Store only at temperatures below 120 °F (48.8 °C). Do not incinerate." Why?
b. The gas in the can is initially at 24 °C and 360 kPa, and the can has a volume of 350 mL. If the can is left in a car that reaches 50 °C on a hot day, what is the new pressure in the can?

Solution

a. The can contains an amount of isobutane gas at a constant volume, so if the temperature is increased by heating, the pressure will increase proportionately. High temperature could lead to high pressure, causing the can to burst. (Also, isobutane is combustible, so incineration could cause the can to explode.)
b. We are looking for a pressure change due to a temperature change at constant volume, so we will use Amontons's/Gay-Lussac's law. Taking P_1 and T_1 as the initial values, T_2 as the temperature where the pressure is unknown and P_2 as the unknown pressure, and converting °C to K, we have:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ which means that } \frac{360\ k\text{Pa}}{297\ \text{K}} = \frac{P_2}{323\ \text{K}}$$

Rearranging and solving gives:

$$P_2 = \frac{360\ \text{kPa} \times 323\ \cancel{\text{K}}}{297\ \cancel{\text{K}}} = 390\ \text{kPa}$$

Exercise 7.2.1

A sample of nitrogen, N_2, occupies 45.0 mL at 27 °C and 600 torr. What pressure will it have if cooled to –73 °C while the volume remains constant?

Answer

400 torr

Volume and Temperature: Charles's Law

If we fill a balloon with air and seal it, the balloon contains a specific amount of air at atmospheric pressure, let's say 1 atm. If we put the balloon in a refrigerator, the gas inside gets cold and the balloon shrinks (although both the amount of gas and its pressure remain constant). If we make the balloon very cold, it will shrink a great deal, and it expands again when it warms up.



Video **7.2.1**: This video shows how cooling and heating a gas causes its volume to decrease or increase, respectively.

These examples of the effect of temperature on the volume of a given amount of a confined gas at constant pressure are true in general: The volume increases as the temperature increases, and decreases as the temperature decreases. Volume-temperature data for a 1-mole sample of methane gas at 1 atm are listed and graphed in Figure **7.2.2**.

Temperature (°C)	Temperature (K)	Volume (L)
−3	270	22
−23	250	21
−53	220	18
−162	111	9

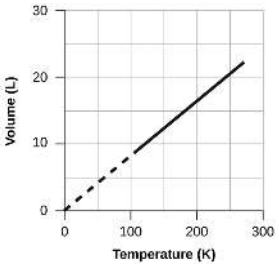


Figure **7.2.4**: The volume and temperature are linearly related for 1 mole of methane gas at a constant pressure of 1 atm. If the temperature is in kelvin, volume and temperature are directly proportional. The line stops at 111 K because methane liquefies at this temperature; when extrapolated, it intersects the graph's origin, representing a temperature of absolute zero.

This figure includes a table and a graph. The table has 3 columns and 6 rows. The first row is a header, which labels the columns "Temperature, degrees C," "Temperature, K," and "Pressure, k P a." The first column contains the values from top to bottom negative 100, negative 50, 0, 100, and 200. The second column contains the values from top to bottom 173, 223, 273, 373, and 473. The third column contains the values 14.10, 18.26, 22.40, 30.65, and 38.88. A graph appears to the right of the table. The horizontal axis is labeled "Temperature (K)." with markings and labels provided for multiples of 100 beginning at 0 and ending at 300. The vertical axis is labeled "Volume (L)" with marking and labels provided for multiples of 10, beginning at 0 and ending at 30. Five data points from the table are plotted on the graph with black dots. These dots are connected with a solid black line. The graph shows a positive linear trend.

The relationship between the volume and temperature of a given amount of gas at constant pressure is known as Charles's law in recognition of the French scientist and balloon flight pioneer Jacques Alexandre César Charles. Charles's law states that *the volume of a given amount of gas is directly proportional to its temperature on the kelvin scale when the pressure is held constant*.

Mathematically, this can be written as:

$$V \alpha T \text{ or } V = \text{constant} \cdot T \text{ or } V = k \cdot T$$

with k being a proportionality constant that depends on the amount and pressure of the gas.

For a confined, constant pressure gas sample, $\frac{V}{T}$ is constant (i.e., the ratio = k), and as seen with the P-T relationship, this leads to another form of Charles's law: $\frac{V_1}{T_1} = \frac{V_2}{T_2}$.

Example 7.2.2: Predicting Change in Volume with Temperature

A sample of carbon dioxide, CO_2, occupies 0.300 L at 10 °C and 750 torr. What volume will the gas have at 30 °C and 750 torr?

Solution

Because we are looking for the volume change caused by a temperature change at constant pressure, this is a job for Charles's law. Taking V_1 and T_1 as the initial values, T_2 as the temperature at which the volume is unknown and V_2 as the unknown volume, and converting °C into K we have:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ which means that } \frac{0.300\ \text{L}}{283\ \text{K}} = \frac{V_2}{303\ \text{K}}$$

Rearranging and solving gives: $V_2 = \frac{0.300\ \text{L} \times 303\ \cancel{\text{K}}}{283\ \cancel{\text{K}}} = 0.321\ \text{L}$

This answer supports our expectation from Charles's law, namely, that raising the gas temperature (from 283 K to 303 K) at a constant pressure will yield an increase in its volume (from 0.300 L to 0.321 L).

Exercise 7.2.2

A sample of oxygen, O_2, occupies 32.2 mL at 30 °C and 452 torr. What volume will it occupy at –70 °C and the same pressure?

Answer

21.6 mL

Example 7.2.3: Measuring Temperature with a Volume

Change Temperature is sometimes measured with a gas thermometer by observing the change in the volume of the gas as the temperature changes at constant pressure. The hydrogen in a particular hydrogen gas thermometer has a volume of 150.0 cm^3 when immersed in a mixture of ice and water (0.00 °C). When immersed in boiling liquid ammonia, the volume of the hydrogen, at the same pressure, is 131.7 cm^3. Find the temperature of boiling ammonia on the kelvin and Celsius scales.

Solution

A volume change caused by a temperature change at constant pressure means we should use Charles's law. Taking V_1 and T_1 as the initial values, T_2 as the temperature at which the volume is unknown and V_2 as the unknown volume, and converting °C into K we have:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ which means that } \frac{150.0\ \text{cm}^3}{273.15\ \text{K}} = \frac{131.7\ \text{cm}^3}{T_2}$$

Rearrangement gives $T_2 = \frac{131.7\ \cancel{\text{cm}^3} \times 273.15\ \text{K}}{150.0\ \cancel{\text{cm}^3}} = 239.8\ \text{K}$

Subtracting 273.15 from 239.8 K, we find that the temperature of the boiling ammonia on the Celsius scale is –33.4 °C.

Exercise 7.2.3

What is the volume of a sample of ethane at 467 K and 1.1 atm if it occupies 405 mL at 298 K and 1.1 atm?

Answer

635 mL

Volume and Pressure: Boyle's Law

If we partially fill an airtight syringe with air, the syringe contains a specific amount of air at constant temperature, say 25 °C. If we slowly push in the plunger while keeping temperature constant, the gas in the syringe is compressed into a smaller volume and its pressure increases; if we pull out the plunger, the volume increases and the pressure decreases. This example of the effect of volume on the pressure of a given amount of a confined gas is true in general. Decreasing the volume of a contained gas will increase its pressure, and increasing its volume will decrease its

pressure. In fact, if the volume increases by a certain factor, the pressure decreases by the same factor, and vice versa. Volume-pressure data for an air sample at room temperature are graphed in Figure **7.2.5**.

Figure **7.2.5**: When a gas occupies a smaller volume, it exerts a higher pressure; when it occupies a larger volume, it exerts a lower pressure (assuming the amount of gas and the temperature do not change). Since P and V are inversely proportional, a graph of $\frac{1}{P}$ vs. V is linear.

This figure contains a diagram and two graphs. The diagram shows a syringe labeled with a scale in m l or c c with multiples of 5 labeled beginning at 5 and ending at 30. The markings halfway between these measurements are also provided. Attached at the top of the syringe is a pressure gauge with a scale marked by fives from 40 on the left to 5 on the right. The gauge needle rests between 10 and 15, slightly closer to 15. The syringe plunger position indicates a volume measurement about halfway between 10 and 15 m l or c c. The first graph is labeled “V (m L)” on the horizontal axis and “P (p s i)” on the vertical axis. Points are labeled at 5, 10, 15, 20, and 25 m L with corresponding values of 39.0, 19.5, 13.0, 9.8, and 6.5 p s i. The points are connected with a smooth curve that is declining at a decreasing rate of change. The second graph is labeled “V (m L)” on the horizontal axis and “1 divided by P (p s i)” on the vertical axis. The horizontal axis is labeled at multiples of 5, beginning at zero and extending up to 35 m L. The vertical axis is labeled by multiples of 0.02, beginning at 0 and extending up to 0.18. Six points indicated by black dots on this graph are connected with a black line segment showing a positive linear trend.

Unlike the *P*-*T* and *V*-*T* relationships, pressure and volume are not directly proportional to each other. Instead, P and V exhibit inverse proportionality: Increasing the pressure results in a decrease of the volume of the gas. Mathematically this can be written:

$$P \propto \frac{1}{V}$$

or

$$P = k \cdot \frac{1}{V}$$

or

$$PV = k$$

or

$$P_1V_1 = P_2V_2$$

with k being a constant. Graphically, this relationship is shown by the straight line that results when plotting the inverse of the pressure $\left(\frac{1}{P}\right)$ versus the volume (V), or the inverse of volume $\left(\frac{1}{V}\right)$ versus the pressure (P). Graphs with curved lines are difficult to read accurately at low or high values of the variables, and they are more difficult to use in fitting theoretical equations and parameters to experimental data. For those reasons, scientists often try to find a way to “linearize” their data. If we plot P versus V, we obtain a hyperbola (Figure **7.2.6**).

Figure **7.2.6**: The relationship between pressure and volume is inversely proportional. (a) The graph of P vs. V is a hyperbola, whereas (b) the graph of $\left(\frac{1}{P}\right)$ vs. V is linear.

This diagram shows two graphs. In a, a graph is shown with volume on the horizontal axis and pressure on the vertical axis. A curved line is shown on the graph showing a decreasing trend with a decreasing rate of change. In b, a graph is shown with volume on the horizontal axis and one divided by pressure on the vertical axis. A line segment, beginning at the origin of the graph, shows a positive, linear trend.

The relationship between the volume and pressure of a given amount of gas at constant temperature was first published by the English natural philosopher Robert Boyle over 300 years ago. It is summarized in the statement now known as **Boyle’s law**: *The volume of a given amount of gas held at constant temperature is inversely proportional to the pressure under which it is measured.*

Example **7.2.4**: Volume of a Gas Sample

The sample of gas has a volume of 15.0 mL at a pressure of 13.0 psi. Determine the pressure of the gas at a volume of 7.5 mL, using:

a. the *P*-*V* graph in Figure **7.2.6***a*
b. the $\frac{1}{P}$ vs. V graph in Figure **7.2.6***b*
c. the Boyle’s law equation

Comment on the likely accuracy of each method.

Solution

a. Estimating from the *P*-*V* graph gives a value for P somewhere around 27 psi.
b. Estimating from the $\frac{1}{P}$ versus V graph give a value of about 26 psi.
c. From Boyle’s law, we know that the product of pressure and volume (PV) for a given sample of gas at a constant temperature is always equal to the same value. Therefore we have $P_1V_1 = k$ and $P_2V_2 = k$ which means that $P_1V_1 = P_2V_2$.

Using P_1 and V_1 as the known values 13.0 psi and 15.0 mL, P_2 as the pressure at which the volume is unknown, and V_2 as the unknown volume, we have:

$$P_1V_1 = P_2V_2 \text{ or } 13.0 \text{ psi} \times 15.0 \text{ mL} = P_2 \times 7.5 \text{ mL}$$

Solving:

$$P_2 = \frac{13.0 \text{ psi} \times 15.0 \cancel{\text{mL}}}{7.5 \cancel{\text{mL}}} = 26 \text{ psi}$$

It was more difficult to estimate well from the *P*-*V* graph, so (a) is likely more inaccurate than (b) or (c). The calculation will be as accurate as the equation and measurements allow.

Exercise **7.2.4**

The sample of gas has a volume of 30.0 mL at a pressure of 6.5 psi. Determine the volume of the gas at a pressure of 11.0 psi, using:

a. the *P*-*V* graph in Figure **7.2.6***a*
b. the $\frac{1}{P}$ vs. V graph in Figure **7.2.6***b*
c. the Boyle’s law equation

Comment on the likely accuracy of each method.

Answer a

about 17–18 mL

Answer b

~18 mL

Answer c

17.7 mL; it was more difficult to estimate well from the *P*-*V* graph, so (a) is likely more inaccurate than (b); the calculation will be as accurate as the equation and measurements allow

Breathing and Boyle's Law

What do you do about 20 times per minute for your whole life, without break, and often without even being aware of it? The answer, of course, is respiration, or breathing. How does it work? It turns out that the gas laws apply here. Your lungs take in gas that your body needs (oxygen) and get rid of waste gas (carbon dioxide). Lungs are made of spongy, stretchy tissue that expands and contracts while you breathe. When you inhale, your diaphragm and intercostal muscles (the muscles between your ribs) contract, expanding your chest cavity and making your lung volume larger. The increase in volume leads to a decrease in pressure (Boyle's law). This causes air to flow into the lungs (from high pressure to low pressure). When you exhale, the process reverses: Your diaphragm and rib muscles relax, your chest cavity contracts, and your lung volume decreases, causing the pressure to increase (Boyle's law again), and air flows out of the lungs (from high pressure to low pressure). You then breathe in and out again, and again, repeating this Boyle's law cycle for the rest of your life (Figure **7.2.7**).

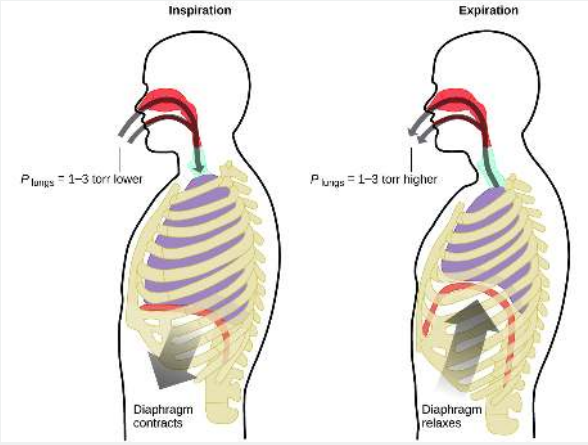


Figure **7.2.7**: Breathing occurs because expanding and contracting lung volume creates small pressure differences between your lungs and your surroundings, causing air to be drawn into and forced out of your lungs.

This figure contains two diagrams of a cross section of the human head and torso. The first diagram on the left is labeled "Inspiration." It shows curved arrows in gray proceeding through the nasal passages and mouth to the lungs. An arrow points downward from the diaphragm, which is relatively flat, just beneath the lungs. This arrow is labeled "Diaphragm contracts." At the entrance to the mouth and nasal passages, a label of P subscript lungs equals 1 dash 3 torr lower" is provided. The second, similar diagram, which is labeled "Expiration," reverses the direction of both arrows. Arrows extend from the lungs out through the nasal passages and mouth. Similarly, an arrow points up to the diaphragm, showing a curved diaphragm and lungs reduced in size from the previous image. This arrow is labeled "Diaphragm relaxes." At the entrance to the mouth and nasal passages, a label of P subscript lungs equals 1 dash 3 torr higher" is provided.

Moles of Gas and Volume: Avogadro's Law

The Italian scientist Amedeo Avogadro advanced a hypothesis in 1811 to account for the behavior of gases, stating that equal volumes of all gases, measured under the same conditions of temperature and pressure, contain the same number of molecules. Over time, this relationship was supported by many experimental observations as expressed by Avogadro's law: *For a confined gas, the volume (V) and number of moles (n) are directly proportional if the pressure and temperature both remain constant*.

In equation form, this is written as:

$$V \propto n \text{ or } V = k \times n \text{ or } \frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Mathematical relationships can also be determined for the other variable pairs, such as P versus n, and n versus T.

> *Visit this interactive PhET simulation to investigate the relationships between pressure, volume, temperature, and amount of gas. Use the simulation to examine the effect of changing one parameter on another while holding the other parameters constant (as described in the preceding sections on the various gas laws).*

The Ideal Gas Law

To this point, four separate laws have been discussed that relate pressure, volume, temperature, and the number of moles of the gas:

- Boyle's law: PV = constant at constant T and n
- Amontons's law: $\frac{P}{T}$ = constant at constant V and n
- Charles's law: $\frac{V}{T}$ = constant at constant P and n
- Avogadro's law: $\frac{V}{n}$ = constant at constant P and T

Combining these four laws yields the ideal gas law, a relation between the pressure, volume, temperature, and number of moles of a gas:

$$PV = nRT$$

where P is the pressure of a gas, V is its volume, n is the number of moles of the gas, T is its temperature on the kelvin scale, and R is a constant called the ideal gas constant or the universal gas constant. The units used to express pressure, volume, and temperature will determine the proper form of the gas constant as required by dimensional analysis, the most commonly encountered values being 0.08206 L atm mol^{-1} K^{-1} and 8.3145 kPa L mol^{-1} K^{-1}.

> *The ideal gas law is easy to remember and apply in solving problems, as long as you use the* ***proper values*** *and units for the gas constant, R.*

Gases whose properties of P, V, and T are accurately described by the ideal gas law (or the other gas laws) are said to exhibit *ideal behavior* or to approximate the traits of an ideal gas. An ideal gas is a hypothetical construct that may be used along with *kinetic molecular theory* to effectively explain the gas laws as will be described in a later module of this chapter. Although all the calculations presented in this module assume ideal behavior, this assumption is only reasonable for gases under conditions of relatively low pressure and high temperature. In the final module of this chapter, a modified gas law will be introduced that accounts for the *non-ideal* behavior observed for many gases at relatively high pressures and low temperatures.

The ideal gas equation contains five terms, the gas constant R and the variable properties P, V, n, and T. Specifying any four of these terms will permit use of the ideal gas law to calculate the fifth term as demonstrated in the following example exercises.

Example 7.2.5: Using the Ideal Gas Law

Methane, CH_4, is being considered for use as an alternative automotive fuel to replace gasoline. One gallon of gasoline could be replaced by 655 g of CH_4. What is the volume of this much methane at 25 °C and 745 torr?

Solution

Exercise 7.2.5

Calculate the pressure in bar of 2520 moles of hydrogen gas stored at 27 °C in the 180-L storage tank of a modern hydrogen-powered car.

Answer

350 bar

If the number of moles of an ideal gas are kept constant under two different sets of conditions, a useful mathematical relationship called the combined gas law is obtained: $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ using units of atm, L, and K. Both sets of conditions are equal to the product of $n \times R$ (where n = the number of moles of the gas and R is the ideal gas law constant).

Example 7.2.6: Using the Combined Gas Law

When filled with air, a typical scuba tank with a volume of 13.2 L has a pressure of 153 atm (Figure **7.2.8**). If the water temperature is 27 °C, how many liters of air will such a tank provide to a diver's lungs at a depth of approximately 70 feet in the ocean where the pressure is 3.13 atm?



Figure **7.2.8**: Scuba divers use compressed air to breathe while underwater. (credit: modification of work by Mark Goodchild)

This photograph shows a scuba diver underwater with a tank on his or her back and bubbles ascending from the breathing apparatus.

Letting *1* represent the air in the scuba tank and *2* represent the air in the lungs, and noting that body temperature (the temperature the air will be in the lungs) is 37 °C, we have:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \longrightarrow \frac{(153\ \text{atm})(13.2\ \text{L})}{(300\ \text{K})} = \frac{(3.13\ \text{atm})(V_2)}{(310\ \text{K})}$$

Solving for V_2:

$$V_2 = \frac{(153\ \cancel{\text{atm}})(13.2\ \text{L})(310\ \cancel{\text{K}})}{(300\ \cancel{\text{K}})(3.13\ \cancel{\text{atm}})} = 667\ \text{L}$$

(Note: Be advised that this particular example is one in which the assumption of ideal gas behavior is not very reasonable, since it involves gases at relatively high pressures and low temperatures. Despite this limitation, the calculated volume can be viewed as a good "ballpark" estimate.)

Exercise 7.2.6

A sample of ammonia is found to occupy 0.250 L under laboratory conditions of 27 °C and 0.850 atm. Find the volume of this sample at 0 °C and 1.00 atm.

Answer

0.193 L

The Interdependence between Ocean Depth and Pressure in Scuba Diving

Whether scuba diving at the Great Barrier Reef in Australia (shown in Figure **7.2.9**) or in the Caribbean, divers must understand how pressure affects a number of issues related to their comfort and safety.



Figure **7.2.9**: Scuba divers, whether at the Great Barrier Reef or in the Caribbean, must be aware of buoyancy, pressure equalization, and the amount of time they spend underwater, to avoid the risks associated with pressurized gases in the body. (credit: Kyle Taylor).

This picture shows colorful underwater corals and anemones in hues of yellow, orange, green, and brown, surrounded by water that appears blue in color.

Pressure increases with ocean depth, and the pressure changes most rapidly as divers reach the surface. The pressure a diver experiences is the sum of all pressures above the diver (from the water and the air). Most pressure measurements are given in units of atmospheres, expressed as "atmospheres absolute" or ATA in the diving community: Every 33 feet of salt water represents 1 ATA of pressure in addition to 1 ATA of pressure from the atmosphere at sea level. As a diver descends, the increase in pressure causes the body's air pockets in the ears and lungs to compress; on the ascent, the decrease in pressure causes these air pockets to expand, potentially rupturing eardrums or bursting the lungs. Divers must therefore undergo equalization by adding air to body

airspaces on the descent by breathing normally and adding air to the mask by breathing out of the nose or adding air to the ears and sinuses by equalization techniques; the corollary is also true on ascent, divers must release air from the body to maintain equalization. Buoyancy, or the ability to control whether a diver sinks or floats, is controlled by the buoyancy compensator (BCD). If a diver is ascending, the air in his BCD expands because of lower pressure according to Boyle's law (decreasing the pressure of gases increases the volume). The expanding air increases the buoyancy of the diver, and she or he begins to ascend. The diver must vent air from the BCD or risk an uncontrolled ascent that could rupture the lungs. In descending, the increased pressure causes the air in the BCD to compress and the diver sinks much more quickly; the diver must add air to the BCD or risk an uncontrolled descent, facing much higher pressures near the ocean floor. The pressure also impacts how long a diver can stay underwater before ascending. The deeper a diver dives, the more compressed the air that is breathed because of increased pressure: If a diver dives 33 feet, the pressure is 2 ATA and the air would be compressed to one-half of its original volume. The diver uses up available air twice as fast as at the surface.

Standard Conditions of Temperature and Pressure

We have seen that the volume of a given quantity of gas and the number of molecules (moles) in a given volume of gas vary with changes in pressure and temperature. Chemists sometimes make comparisons against a standard temperature and pressure (STP) for reporting properties of gases: 273.15 K (0.00 °C) and 1 atm (101.325 kPa). At STP, an ideal gas has a volume of about 22.4 L—this is referred to as the standard molar volume (Figure **7.2.10**).

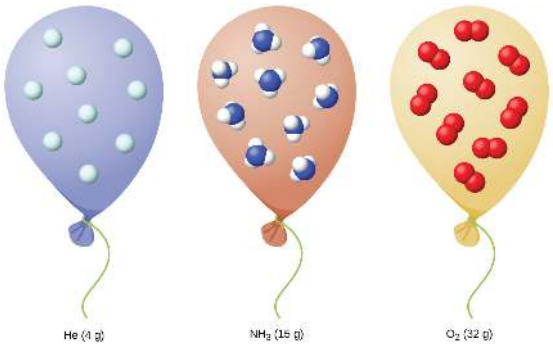


Figure **7.2.10**: Since the number of moles in a given volume of gas varies with pressure and temperature changes, chemists use standard temperature and pressure (273.15 K and 1 atm or 101.325 kPa) to report properties of gases.

This figure shows three balloons each filled with H e, N H subscript 2, and O subscript 2 respectively. Beneath the first balloon is the label "4 g of He" Beneath the second balloon is the label, "15 g of N H subscript 2." Beneath the third balloon is the label "32 g of O subscript 2." Each balloon contains the same number of molecules of their respective gases.

Summary

The behavior of gases can be described by several laws based on experimental observations of their properties. The pressure of a given amount of gas is directly proportional to its absolute temperature, provided that the volume does not change (Amontons's law). The volume of a given gas sample is directly proportional to its absolute temperature at constant pressure (Charles's law). The volume of a given amount of gas is inversely proportional to its pressure when temperature is held constant (Boyle's law). Under the same conditions of temperature and pressure, equal volumes of all gases contain the same number of molecules (Avogadro's law).

The equations describing these laws are special cases of the ideal gas law, $PV = nRT$, where P is the pressure of the gas, V is its volume, n is the number of moles of the gas, T is its kelvin temperature, and R is the ideal (universal) gas constant.

Key Equations

- $PV = nRT$

Summary

absolute zero
temperature at which the volume of a gas would be zero according to Charles's law.

Amontons's law
(also, Gay-Lussac's law) pressure of a given number of moles of gas is directly proportional to its kelvin temperature when the volume is held constant

Avogadro's law
volume of a gas at constant temperature and pressure is proportional to the number of gas molecules

Boyle's law
volume of a given number of moles of gas held at constant temperature is inversely proportional to the pressure under which it is measured

Charles's law
volume of a given number of moles of gas is directly proportional to its kelvin temperature when the pressure is held constant

ideal gas
hypothetical gas whose physical properties are perfectly described by the gas laws

ideal gas constant (R)
constant derived from the ideal gas equation $R = 0.08226$ L atm mol^{-1} K^{-1} or 8.314 L kPa mol^{-1} K^{-1}

ideal gas law
relation between the pressure, volume, amount, and temperature of a gas under conditions derived by combination of the simple gas laws

standard conditions of temperature and pressure (STP)
273.15 K (0 °C) and 1 atm (101.325 kPa)

standard molar volume
volume of 1 mole of gas at STP, approximately 22.4 L for gases behaving ideally

This page titled 7.2: Relating Pressure, Volume, Amount, and Temperature- The Ideal Gas Law is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

- **9.2: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

https://chem.libretexts.org/@go/page/216763

https://chem.libretexts.org/@go/page/216763

https://chem.libretexts.org/@go/page/216763

https://chem.libretexts.org/@go/page/216763

7.3: Stoichiometry of Gaseous Substances, Mixtures, and Reactions

Learning Objectives

- Use the ideal gas law to compute gas densities and molar masses
- Perform stoichiometric calculations involving gaseous substances
- State Dalton's law of partial pressures and use it in calculations involving gaseous mixtures

The study of the chemical behavior of gases was part of the basis of perhaps the most fundamental chemical revolution in history. French nobleman Antoine Lavoisier, widely regarded as the "father of modern chemistry," changed chemistry from a qualitative to a quantitative science through his work with gases. He discovered the law of conservation of matter, discovered the role of oxygen in combustion reactions, determined the composition of air, explained respiration in terms of chemical reactions, and more. He was a casualty of the French Revolution, guillotined in 1794. Of his death, mathematician and astronomer Joseph-Louis Lagrange said, "It took the mob only a moment to remove his head; a century will not suffice to reproduce it."

As described in an earlier chapter of this text, we can turn to chemical stoichiometry for answers to many of the questions that ask "How much?" We can answer the question with masses of substances or volumes of solutions. However, we can also answer this question another way: with volumes of gases. We can use the ideal gas equation to relate the pressure, volume, temperature, and number of moles of a gas. Here we will combine the ideal gas equation with other equations to find gas density and molar mass. We will deal with mixtures of different gases, and calculate amounts of substances in reactions involving gases. This section will not introduce any new material or ideas, but will provide examples of applications and ways to integrate concepts we have already discussed.

Density of a Gas

Recall that the density of a gas is its mass to volume ratio, $\rho = \frac{m}{V}$. Therefore, if we can determine the mass of some volume of a gas, we will get its density. The density of an unknown gas can used to determine its molar mass and thereby assist in its identification. The ideal gas law, $PV = nRT$, provides us with a means of deriving such a mathematical formula to relate the density of a gas to its volume in the proof shown in Example **7.3.1**.

Example 7.3.1: Derivation of a Density Formula from the Ideal Gas Law

Use $PV = nRT$ to derive a formula for the density of gas in g/L

Solution

$$PV = nRT$$

Rearrange to get (mol/L):

$$\frac{n}{v} = \frac{P}{RT}$$

Multiply each side of the equation by the molar mass, $\mathcal{M}$. When moles are multiplied by $\mathcal{M}$ in g/mol, g are obtained:

$$(\mathcal{M})\left(\frac{n}{V}\right) = \left(\frac{P}{RT}\right)(\mathcal{M})$$

$$\mathcal{M}/V = \rho = \frac{P\mathcal{M}}{RT}$$

Exercise 7.3.1

A gas was found to have a density of 0.0847 g/L at 17.0 °C and a pressure of 760 torr. What is its molar mass? What is the gas?

Answer

$$\rho = \frac{P\mathcal{M}}{RT}$$

$$0.0847\ \text{g/L} = 760\ \cancel{\text{torr}} \times \frac{1\ \cancel{\text{atm}}}{760\ \cancel{\text{torr}}} \times \frac{\mathcal{M}}{0.0821\ \text{L}\ \cancel{\text{atm}}/\text{mol K}} \times 290\ \text{K}$$

$\mathcal{M}$ = 2.02 g/mol; therefore, the gas must be hydrogen (H_2, 2.02 g/mol)

We must specify both the temperature and the pressure of a gas when calculating its density because the number of moles of a gas (and thus the mass of the gas) in a liter changes with temperature or pressure. Gas densities are often reported at STP.

Example 7.3.2: Empirical/Molecular Formula Problems

Using the Ideal Gas Law and Density of a Gas Cyclopropane, a gas once used with oxygen as a general anesthetic, is composed of 85.7% carbon and 14.3% hydrogen by mass. Find the empirical formula. If 1.56 g of cyclopropane occupies a volume of 1.00 L at 0.984 atm and 50 °C, what is the molecular formula for cyclopropane?

Solution

Strategy:

First solve the empirical formula problem using methods discussed earlier. Assume 100 g and convert the percentage of each element into grams. Determine the number of moles of carbon and hydrogen in the 100-g sample of cyclopropane. Divide by the smallest number of moles to relate the number of moles of carbon to the number of moles of hydrogen. In the last step, realize that the smallest whole number ratio is the empirical formula:

$$85.7\ \text{g C} \times \frac{1\ \text{mol C}}{12.01\ \text{g C}} = 7.136\ \text{mol C} \quad \frac{7.136}{7.136} = 1.00\ \text{mol C}$$

$$14.3\ \text{g H} \times \frac{1\ \text{mol H}}{1.01\ \text{g H}} = 14.158\ \text{mol H} \quad \frac{14.158}{7.136} = 1.98\ \text{mol H}$$

Empirical formula is CH_2 [empirical mass (EM) of 14.03 g/empirical unit].

Next, use the density equation related to the ideal gas law to determine the molar mass:

$$d = \frac{P\mathcal{M}}{RT} \quad \frac{1.56\ \text{g}}{1.00\ \text{L}} = 0.984\ \text{atm} \times \frac{\mathcal{M}}{0.0821\ \text{L atm/mol K}} \times 323\ \text{K}$$

$\mathcal{M}$ = 42.0 g/mol, $\frac{\mathcal{M}}{E\mathcal{M}} = \frac{42.0}{14.03} = 2.99$, so (3)($CH_2$) = C_3H_6 (molecular formula)

Exercise 7.3.2

Acetylene, a fuel used welding torches, is comprised of 92.3% C and 7.7% H by mass. Find the empirical formula. If 1.10 g of acetylene occupies of volume of 1.00 L at 1.15 atm and 59.5 °C, what is the molecular formula for acetylene?

Answer

Empirical formula, CH; Molecular formula, C_2H_2

Molar Mass of a Gas

Another useful application of the ideal gas law involves the determination of molar mass. By definition, the molar mass of a substance is the ratio of its mass in grams, *m*, to its amount in moles, *n*:

$$\mathcal{M} = \frac{\text{grams of substance}}{\text{moles of substance}} = \frac{m}{n}$$

The ideal gas equation can be rearranged to isolate n:

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

and then combined with the molar mass equation to yield:

$$\mathcal{M} = \frac{mRT}{PV}$$

This equation can be used to derive the molar mass of a gas from measurements of its pressure, volume, temperature, and mass.

Example 7.3.3: Determining the Molar Mass of a Volatile Liquid

The approximate molar mass of a volatile liquid can be determined by:

1. Heating a sample of the liquid in a flask with a tiny hole at the top, which converts the liquid into gas that may escape through the hole
2. Removing the flask from heat at the instant when the last bit of liquid becomes gas, at which time the flask will be filled with only gaseous sample at ambient pressure
3. Sealing the flask and permitting the gaseous sample to condense to liquid, and then weighing the flask to determine the sample's mass (Figure **7.3.1**)

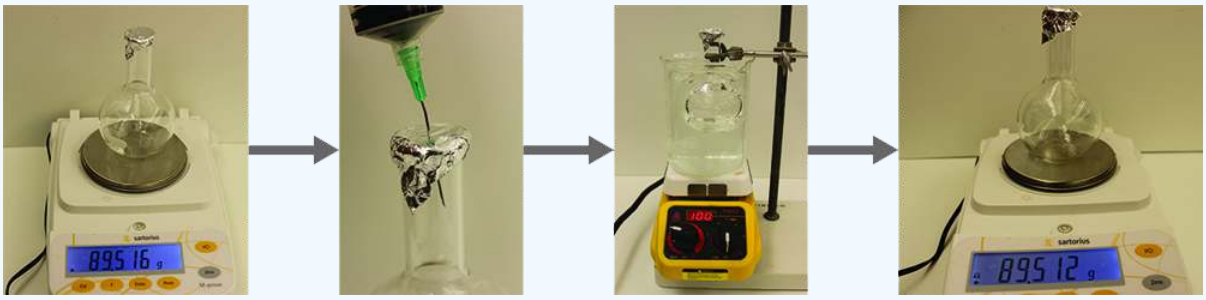


Figure **7.3.1**: When the volatile liquid in the flask is heated past its boiling point, it becomes gas and drives air out of the flask. At $t_{l \longrightarrow g}$, *the flask is filled with volatile liquid gas at the same pressure as the atmosphere. If the flask is then cooled to room temperature, the gas condenses and the mass of the gas that filled the flask, and is now liquid, can be measured. (credit: modification of work by Mark Ott)*

Using this procedure, a sample of chloroform gas weighing 0.494 g is collected in a flask with a volume of 129 cm^3 at 99.6 °C when the atmospheric pressure is 742.1 mm Hg. What is the approximate molar mass of chloroform?

Solution

Since

$$\mathcal{M} = \frac{m}{n}$$

and

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

substituting and rearranging gives

$$\mathcal{M} = \frac{mRT}{PV}$$

then

$$\mathcal{M} = \frac{mRT}{PV} = \frac{(0.494\ \text{g}) \times 0.08206\ \text{L} \cdot \text{atm/mol K} \times 372.8\ \text{K}}{0.976\ \text{atm} \times 0.129\ \text{L}} = 120\ \text{g/mol}$$

Exercise 7.3.3

A sample of phosphorus that weighs 3.243×10^{-2} g exerts a pressure of 31.89 kPa in a 56.0-mL bulb at 550 °C. What are the molar mass and molecular formula of phosphorus vapor?

Answer

124 g/mol P_4

The Pressure of a Mixture of Gases: Dalton's Law

Unless they chemically react with each other, the individual gases in a mixture of gases do not affect each other's pressure. Each individual gas in a mixture exerts the same pressure that it would exert if it were present alone in the container (Figure **7.3.2**). The pressure exerted by each individual gas in a mixture is called its partial pressure. This observation is summarized by Dalton's law of partial pressures: *The total pressure of a mixture of ideal gases is equal to the sum of the partial pressures of the component gases*:

$$P_{Total} = P_A + P_B + P_C + ... = \sum_i P_i$$

In the equation P_{Total} is the total pressure of a mixture of gases, P_A is the partial pressure of gas A; P_B is the partial pressure of gas B; P_C is the partial pressure of gas C; and so on.

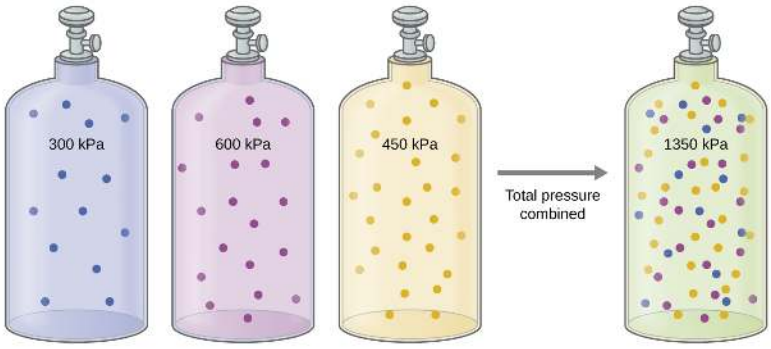


Figure **7.3.2**: If equal-volume cylinders containing gas A at a pressure of 300 kPa, gas B at a pressure of 600 kPa, and gas C at a pressure of 450 kPa are all combined in the same-size cylinder, the total pressure of the mixture is 1350 kPa.

This figure includes images of four gas-filled cylinders or tanks. Each has a valve at the top. The interior of the first cylinder is shaded blue. This region contains 5 small blue circles that are evenly distributed. The label "300 k P a" is on the cylinder. The second cylinder is shaded lavender. This region contains 8 small purple circles that are evenly distributed. The label "600 k P a" is on the cylinder. To the right of these cylinders is a third cylinder. Its interior is shaded pale yellow. This region contains 12 small yellow circles that are evenly distributed. The label "450 k P a" is on this region of the cylinder. An arrow labeled "Total pressure combined" appears to the right of these three cylinders. This arrow points to a fourth cylinder. The interior of this cylinder is shaded a pale green. It contains evenly distributed small circles in the following quantities and colors; 5 blue, 8 purple, and 12 yellow. This cylinder is labeled "1350 k P a."

The partial pressure of gas A is related to the total pressure of the gas mixture via its mole fraction (X), a unit of concentration defined as the number of moles of a component of a solution divided by the total number of moles of all components:

$$P_A = X_A \times P_{Total} \quad \text{where} \quad X_A = \frac{n_A}{n_{Total}}$$

where P_A, X_A, and n_A are the partial pressure, mole fraction, and number of moles of gas A, respectively, and n_{Total} is the number of moles of all components in the mixture.

Example **7.3.2**: The Pressure of a Mixture of Gases

A 10.0-L vessel contains 2.50×10^{-3} mol of H_2, 1.00×10^{-3} mol of He, and 3.00×10^{-4} mol of Ne at 35 °C.

a. What are the partial pressures of each of the gases?
b. What is the total pressure in atmospheres?

Solution

The gases behave independently, so the partial pressure of each gas can be determined from the ideal gas equation, using $P = \frac{nRT}{V}$:

$$P_{H_2} = \frac{(2.50 \times 10^{-3}\ \text{mol})(0.08206\ \cancel{L}\ \cancel{\text{atm mol}^{-1}\ \text{K}^{-1}})(308\ \cancel{K})}{10.0\ \cancel{L}} = 6.32 \times 10^{-3}\ \text{atm}$$

$$P_{He} = \frac{(1.00 \times 10^{-3}\ \cancel{\text{mol}})(0.08206\ \cancel{L}\ \cancel{\text{atm mol}^{-1}\ \text{K}^{-1}})(308\ \cancel{K})}{10.0\ \cancel{L}} = 2.53 \times 10^{-3}\ \text{atm}$$

$$P_{Ne} = \frac{(3.00 \times 10^{-4}\ \cancel{\text{mol}})(0.08206\ \cancel{L}\ \cancel{\text{atm mol}^{-1}\ \text{K}^{-1}})(308\ \cancel{K})}{10.0\ \cancel{L}} = 7.58 \times 10^{-4}\ \text{atm}$$

The total pressure is given by the sum of the partial pressures:

$$P_T = P_{H_2} + P_{He} + P_{Ne} = (0.00632 + 0.00253 + 0.00076)\ \text{atm} = 9.61 \times 10^{-3}\ \text{atm}$$

? Exercise 7.3.2

A 5.73-L flask at 25 °C contains 0.0388 mol of N_2, 0.147 mol of CO, and 0.0803 mol of H_2. What is the total pressure in the flask in atmospheres?

Answer

1.137 atm

Here is another example of this concept, but dealing with mole fraction calculations.

✔ Example 7.3.3: The Pressure of a Mixture of Gases

A gas mixture used for anesthesia contains 2.83 mol oxygen, O_2, and 8.41 mol nitrous oxide, N_2O. The total pressure of the mixture is 192 kPa.

a. What are the mole fractions of O_2 and N_2O?
b. What are the partial pressures of O_2 and N_2O?

Solution

The mole fraction is given by

$$X_A = \frac{n_A}{n_{Total}}$$

and the partial pressure is

$$P_A = X_A \times P_{Total}$$

For O_2,

$$X_{O_2} = \frac{n_{O_2}}{n_{Total}} = \frac{2.83\text{mol}}{(2.83 + 8.41)\ \text{mol}} = 0.252$$

and

$$P_{O_2} = X_{O_2} \times P_{Total} = 0.252 \times 192\ \text{kPa} = 48.4\ \text{kPa}$$

For N_2O,

$$X_{N_2O} = \frac{n_{N_2O}}{n_{Total}} = \frac{8.41\ \text{mol}}{(2.83 + 8.41)\ \text{mol}} = 0.748$$

and

$$P_{N_2O} = X_{N_2O} \times P_{Total} = (0.748) \times 192\ \text{kPa} = 143.6\ \text{kPa}$$

? Exercise 7.3.3

What is the pressure of a mixture of 0.200 g of H_2, 1.00 g of N_2, and 0.820 g of Ar in a container with a volume of 2.00 L at 20 °C?

Answer

1.87 atm

Collection of Gases over Water

A simple way to collect gases that do not react with water is to capture them in a bottle that has been filled with water and inverted into a dish filled with water. The pressure of the gas inside the bottle can be made equal to the air pressure outside by raising or lowering the bottle. When the water level is the same both inside and outside the bottle (Figure **7.3.3**), the pressure of the gas is equal to the atmospheric pressure, which can be measured with a barometer.

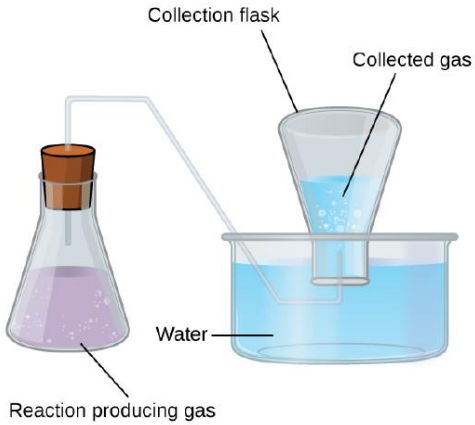


Figure **7.3.3**: When a reaction produces a gas that is collected above water, the trapped gas is a mixture of the gas produced by the reaction and water vapor. If the collection flask is appropriately positioned to equalize the water levels both within and outside the flask, the pressure of the trapped gas mixture will equal the atmospheric pressure outside the flask (see the earlier discussion of manometers).

This figure shows a diagram of equipment used for collecting a gas over water. To the left is an Erlenmeyer flask. It is approximately two thirds full of a lavender colored liquid. Bubbles are evident in the liquid. The label “Reaction Producing Gas” appears below the flask. A line segment connects this label to the liquid in the flask. The flask has a stopper in it through which a single glass tube extends from the open region above the liquid in the flask up, through the stopper, to the right, then angles down into a pan that is nearly full of light blue water. This tube again extends right once it is well beneath the water’s surface. It then bends up into an inverted flask which is labeled “Collection Flask.” This collection flask is positioned with its mouth beneath the surface of the light blue water and appears approximately half full. Bubbles are evident in the water in the inverted flask. The open space above the water in the inverted flask is labeled “collected gas.”

However, there is another factor we must consider when we measure the pressure of the gas by this method. Water evaporates and there is always gaseous water (water vapor) above a sample of liquid water. As a gas is collected over water, it becomes saturated with water vapor and the total pressure of the mixture equals the partial pressure of the gas plus the partial pressure of the water vapor. The pressure of the pure gas is therefore equal to the total pressure minus the pressure of the water vapor—this is referred to as the “dry” gas pressure, that is, the pressure of the gas only, without water vapor.

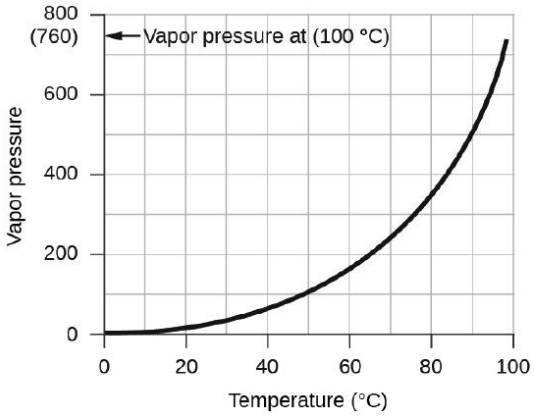


Figure **7.3.4**: This graph shows the vapor pressure of water at sea level as a function of temperature.

A graph is shown. The horizontal axis is labeled “Temperature (degrees C)” with markings and labels provided for multiples of 20 beginning at 0 and ending at 100. The vertical axis is labeled “Vapor pressure (torr)” with marking and labels provided for multiples of 200, beginning at 0 and ending at 800. A smooth solid black curve extends from the origin up and to the right across the graph. The graph shows a positive trend with an increasing rate of change. On the vertical axis is (7 60) and an arrow pointing to it. The arrow is labeled, “Vapor pressure at (100 degrees C).”

The vapor pressure of water, which is the pressure exerted by water vapor in equilibrium with liquid water in a closed container, depends on the temperature (Figure **7.3.4**); more detailed information on the temperature dependence of water vapor can be found in Table **7.3.1**, and vapor pressure will be discussed in more detail in the next chapter on liquids.

Table **7.3.1**: *Vapor Pressure of Ice and Water in Various Temperatures at Sea Level*

Temperature (°C)	Pressure (torr)	Temperature (°C)	Pressure (torr)	Temperature (°C)	Pressure (torr)
–10	1.95	18	15.5	30	31.8
–5	3.0	19	16.5	35	42.2
–2	3.9	20	17.5	40	55.3
0	4.6	21	18.7	50	92.5
2	5.3	22	19.8	60	149.4
4	6.1	23	21.1	70	233.7
6	7.0	24	22.4	80	355.1
8	8.0	25	23.8	90	525.8
10	9.2	26	25.2	95	633.9
12	10.5	27	26.7	99	733.2
14	12.0	28	28.3	100.0	760.0
16	13.6	29	30.0	101.0	787.6

Example 7.3.4: Pressure of a Gas Collected Over Water

If 0.200 L of argon is collected over water at a temperature of 26 °C and a pressure of 750 torr in a system like that shown in Figure **7.3.3**, what is the partial pressure of argon?

Solution

According to Dalton’s law, the total pressure in the bottle (750 torr) is the sum of the partial pressure of argon and the partial pressure of gaseous water:

$$P_T = P_{Ar} + P_{H_2O}$$

Rearranging this equation to solve for the pressure of argon gives:

$$P_{Ar} = P_T - P_{H_2O}$$

The pressure of water vapor above a sample of liquid water at 26 °C is 25.2 torr (Appendix E), so:

$$P_{Ar} = 750 \text{ torr} - 25.2 \text{ torr} = 725 \text{ torr}$$

? Exercise 7.3.4

A sample of oxygen collected over water at a temperature of 29.0 °C and a pressure of 764 torr has a volume of 0.560 L. What volume would the dry oxygen have under the same conditions of temperature and pressure?

Answer

0.583 L

Chemical Stoichiometry and Gases

Chemical stoichiometry describes the quantitative relationships between reactants and products in chemical reactions. We have previously measured quantities of reactants and products using masses for solids and volumes in conjunction with the molarity for solutions; now we can also use gas volumes to indicate quantities. If we know the volume, pressure, and temperature of a gas, we can use the ideal gas equation to calculate how many moles of the gas are present. If we know how many moles of a gas are involved, we can calculate the volume of a gas at any temperature and pressure.

Avogadro's Law Revisited

Sometimes we can take advantage of a simplifying feature of the stoichiometry of gases that solids and solutions do not exhibit: All gases that show ideal behavior contain the same number of molecules in the same volume (at the same temperature and pressure). Thus, the ratios of volumes of gases involved in a chemical reaction are given by the coefficients in the equation for the reaction, provided that the gas volumes are measured at the same temperature and pressure.

We can extend Avogadro's law (that the volume of a gas is directly proportional to the number of moles of the gas) to chemical reactions with gases: Gases combine, or react, in definite and simple proportions by volume, provided that all gas volumes are measured at the same temperature and pressure. For example, since nitrogen and hydrogen gases react to produce ammonia gas according to

$$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$$

a given volume of nitrogen gas reacts with three times that volume of hydrogen gas to produce two times that volume of ammonia gas, if pressure and temperature remain constant.

The explanation for this is illustrated in Figure **7.3.4**. According to Avogadro's law, equal volumes of gaseous N_2, H_2, and NH_3, at the same temperature and pressure, contain the same number of molecules. Because one molecule of N_2 reacts with three molecules of H_2 to produce two molecules of NH_3, the volume of H_2 required is three times the volume of N_2, and the volume of NH_3 produced is two times the volume of N_2.

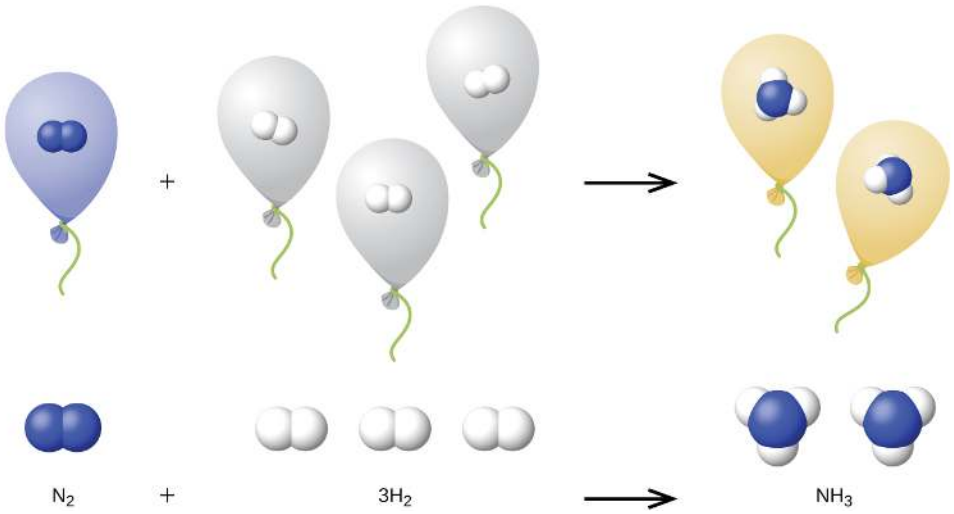


Figure **7.3.5**: *One volume of N_2 combines with three volumes of H_2 to form two volumes of NH_3.*

This diagram provided models the chemical reaction written with formulas across the bottom of the figure. The reaction is written; N subscript 2 plus 3 H subscript 2 followed by an arrow pointing right to N H subscript 3. Just above the formulas, space-filling models are provided. Above N H subscript 2, two blue spheres are bonded. Above 3 H subscript 2, three pairs of two slightly smaller white spheres are bonded. Above N H subscript 3, two molecules are shown composed each of a central blue sphere to which three slightly smaller white spheres are bonded. Across the top of the diagram, the reaction is illustrated with balloons. To the left is a light blue balloon which is labeled "N subscript 2". This balloon contains a single space-filling model composed of two bonded blue spheres. This balloon is followed by a plus sign, then three grey balloons which are each labeled "H subscript 2." Each of these balloons similarly contain a single space-filling model composed of two bonded white spheres. These white spheres are slightly smaller than the blue spheres. An arrow follows which points right to two light green balloons which are each labeled "N H subscript 3." Each light green balloon contains a space-filling model composed of a single central blue sphere to which three slightly smaller white spheres are bonded.

Example 7.3.5: Reaction of Gases

Propane, $C_3H_8(g)$, is used in gas grills to provide the heat for cooking. What volume of $O_2(g)$ measured at 25 °C and 760 torr is required to react with 2.7 L of propane measured under the same conditions of temperature and pressure? Assume that the propane undergoes complete combustion.

Solution

The ratio of the volumes of C_3H_8 and O_2 will be equal to the ratio of their coefficients in the balanced equation for the reaction:

$$\begin{array}{ll} \mathrm{C_3H_8}(g) + 5\,\mathrm{O_2}(g) \longrightarrow & 3\,\mathrm{CO_2}(g) + 4\,\mathrm{H_2O}(l) \quad (7.3.1) \\ 1\ \text{volume} + 5\ \text{volumes} & 3\ \text{volumes} + 4\ \text{volumes} \quad (7.3.2) \end{array}$$

From the equation, we see that one volume of C_3H_8 will react with five volumes of O_2:

$$2.7\ \cancel{\mathrm{L\ C_3H_8}} \times \frac{5\ \mathrm{L\ O_2}}{1\ \cancel{\mathrm{L\ C_3H_8}}} = 13.5\ \mathrm{L\ O_2}$$

A volume of 13.5 L of O_2 will be required to react with 2.7 L of C_3H_8.

Exercise 7.3.5

An acetylene tank for an oxyacetylene welding torch provides 9340 L of acetylene gas, C_2H_2, at 0 °C and 1 atm. How many tanks of oxygen, each providing 7.00×10^3 L of O_2 at 0 °C and 1 atm, will be required to burn the acetylene?

$$2\,\mathrm{C_2H_2} + 5\,\mathrm{O_2} \longrightarrow 4\,\mathrm{CO_2} + 2\,\mathrm{H_2O}$$

Answer

3.34 tanks (2.34×10^4 L)

Example 7.3.6: Volumes of Reacting Gases

Ammonia is an important fertilizer and industrial chemical. Suppose that a volume of 683 billion cubic feet of gaseous ammonia, measured at 25 °C and 1 atm, was manufactured. What volume of $H_2(g)$, measured under the same conditions, was required to prepare this amount of ammonia by reaction with N_2?

$$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$$

Solution

Because equal volumes of H_2 and NH_3 contain equal numbers of molecules and each three molecules of H_2 that react produce two molecules of NH_3, the ratio of the volumes of H_2 and NH_3 will be equal to 3:2. Two volumes of NH_3, in this case in units of billion ft^3, will be formed from three volumes of H_2:

$$683 \text{ billion ft}^3 \text{ NH}_3 \times \frac{3 \text{ billion ft}^3 \text{ H}_2}{2 \text{ billion ft}^3 \text{ NH}_3} = 1.02 \times 10^3 \text{ billion ft}^3 \text{ H}_2$$

The manufacture of 683 billion ft^3 of NH_3 required 1020 billion ft^3 of H_2. (At 25 °C and 1 atm, this is the volume of a cube with an edge length of approximately 1.9 miles.)

Exercise 7.3.6

What volume of $O_2(g)$ measured at 25 °C and 760 torr is required to react with 17.0 L of ethylene, $C_2H_4(g)$, measured under the same conditions of temperature and pressure? The products are CO_2 and water vapor.

Answer

51.0 L

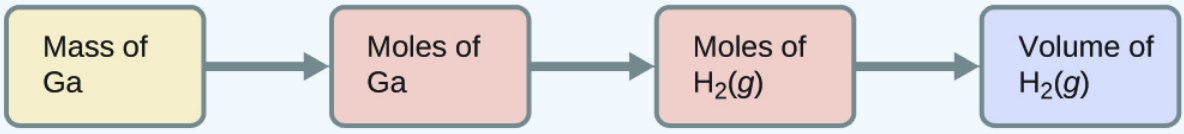
Example 7.3.7: Volume of Gaseous Product

What volume of hydrogen at 27 °C and 723 torr may be prepared by the reaction of 8.88 g of gallium with an excess of hydrochloric acid?

$$2\,Ga(s) + 6\,HCl(aq) \longrightarrow 2\,GaCl_3(aq) + 3\,H_2(g)$$

Solution

To convert from the mass of gallium to the volume of $H_2(g)$, we need to do something like this:



The first two conversions are:

$$8.88 \text{ g Ga} \times \frac{1 \text{ mol Ga}}{69.723 \text{ g Ga}} \times \frac{3 \text{ mol H}_2}{2 \text{ mol Ga}} = 0.191 \text{ mol H}_2$$

Finally, we can use the ideal gas law:

$$V_{H_2} = \left(\frac{nRT}{P}\right)_{H_2} = \frac{0.191 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{0.951 \text{ atm}} = 4.94 \text{ L}$$

https://chem.libretexts.org/@go/page/216764

Exercise 7.3.7

Sulfur dioxide is an intermediate in the preparation of sulfuric acid. What volume of SO_2 at 343 °C and 1.21 atm is produced by burning l.00 kg of sulfur in oxygen?

Answer

1.30×10^3 L

Greenhouse Gases and Climate Change

The thin skin of our atmosphere keeps the earth from being an ice planet and makes it habitable. In fact, this is due to less than 0.5% of the air molecules. Of the energy from the sun that reaches the earth, almost $\frac{1}{3}$ is reflected back into space, with the rest absorbed by the atmosphere and the surface of the earth. Some of the energy that the earth absorbs is re-emitted as infrared (IR) radiation, a portion of which passes back out through the atmosphere into space. However, most of this IR radiation is absorbed by certain substances in the atmosphere, known as greenhouse gases, which re-emit this energy in all directions, trapping some of the heat. This maintains favorable living conditions—without atmosphere, the average global average temperature of 14 °C (57 °F) would be about –19 °C (–2 °F). The major greenhouse gases (GHGs) are water vapor, carbon dioxide, methane, and ozone. Since the Industrial Revolution, human activity has been increasing the concentrations of GHGs, which have changed the energy balance and are significantly altering the earth's climate (Figure **7.3.6**).

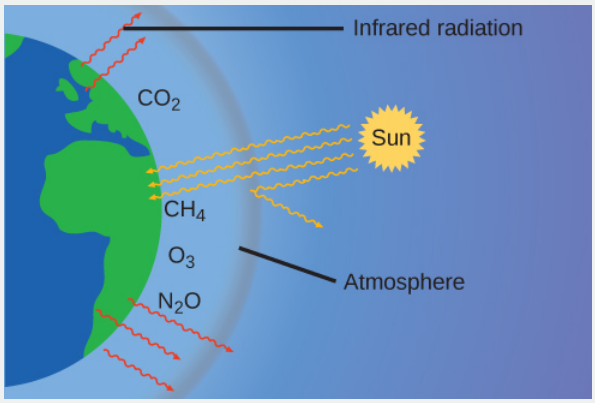


Figure **7.3.6**: Greenhouse gases trap enough of the sun's energy to make the planet habitable—this is known as the greenhouse effect. Human activities are increasing greenhouse gas levels, warming the planet and causing more extreme weather events.

There is strong evidence from multiple sources that higher atmospheric levels of CO_2 are caused by human activity, with fossil fuel burning accounting for about $\frac{3}{4}$ of the recent increase in CO_2. Reliable data from ice cores reveals that CO_2 concentration in the atmosphere is at the highest level in the past 800,000 years; other evidence indicates that it may be at its highest level in 20 million years. In recent years, the CO_2 concentration has increased from historical levels of below 300 ppm to almost 400 ppm today (Figure **7.3.7**).

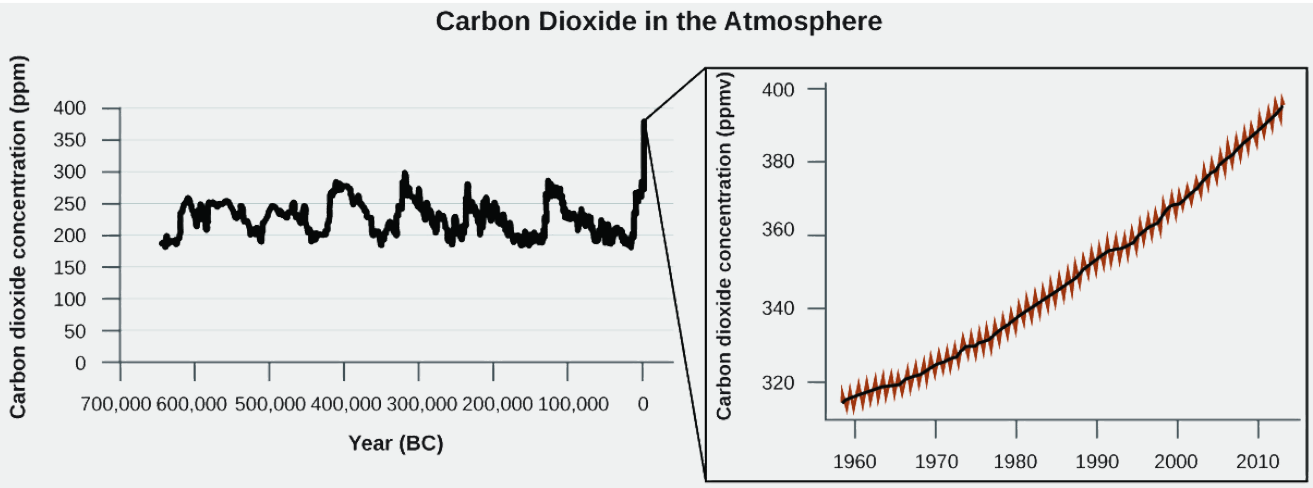


Figure **7.3.7**: Figure CO_2 levels over the past 700,000 years were typically from 200–300 ppm, with a steep, unprecedented increase over the past 50 years.

Summary

The ideal gas law can be used to derive a number of convenient equations relating directly measured quantities to properties of interest for gaseous substances and mixtures. Appropriate rearrangement of the ideal gas equation may be made to permit the calculation of gas densities and molar masses. Dalton's law of partial pressures may be used to relate measured gas pressures for gaseous mixtures to their compositions. Avogadro's law may be used in stoichiometric computations for chemical reactions involving gaseous reactants or products.

Key Equations

- $P_{Total} = P_A + P_B + P_C + \ldots = \Sigma_i P_i$
- $P_A = X_A P_{Total}$
- $X_A = \frac{n_A}{n_{Total}}$

Footnotes

1. "Quotations by Joseph-Louis Lagrange," last modified February 2006, accessed February 10, 2015, www-history.mcs.st-andrews.ac.../Lagrange.html

Summary

Dalton's law of partial pressures

total pressure of a mixture of ideal gases is equal to the sum of the partial pressures of the component gases.

mole fraction (*X*)

concentration unit defined as the ratio of the molar amount of a mixture component to the total number of moles of all mixture components

partial pressure

pressure exerted by an individual gas in a mixture

vapor pressure of water

pressure exerted by water vapor in equilibrium with liquid water in a closed container at a specific temperature

This page titled 7.3: Stoichiometry of Gaseous Substances, Mixtures, and Reactions is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

- **9.3: Stoichiometry of Gaseous Substances, Mixtures, and Reactions** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

https://chem.libretexts.org/@go/page/216764

https://chem.libretexts.org/@go/page/216764

https://chem.libretexts.org/@go/page/216764



https://chem.libretexts.org/@go/page/216764

7.4: The Kinetic-Molecular Theory

Learning Objectives

- State the postulates of the kinetic-molecular theory
- Use this theory's postulates to explain the gas laws

The gas laws that we have seen to this point, as well as the ideal gas equation, are empirical, that is, they have been derived from experimental observations. The mathematical forms of these laws closely describe the macroscopic behavior of most gases at pressures less than about 1 or 2 atm. Although the gas laws describe relationships that have been verified by many experiments, they do not tell us why gases follow these relationships.

The kinetic molecular theory (KMT) is a simple microscopic model that effectively explains the gas laws described in previous modules of this chapter. This theory is based on the following five postulates described here. (Note: The term "molecule" will be used to refer to the individual chemical species that compose the gas, although some gases are composed of atomic species, for example, the noble gases.)

1. Gases are composed of molecules that are in continuous motion, travelling in straight lines and changing direction only when they collide with other molecules or with the walls of a container.
2. The molecules composing the gas are negligibly small compared to the distances between them.
3. The pressure exerted by a gas in a container results from collisions between the gas molecules and the container walls.
4. Gas molecules exert no attractive or repulsive forces on each other or the container walls; therefore, their collisions are *elastic* (do not involve a loss of energy).
5. The average kinetic energy of the gas molecules is proportional to the kelvin temperature of the gas.

The test of the KMT and its postulates is its ability to explain and describe the behavior of a gas. The various gas laws can be derived from the assumptions of the KMT, which have led chemists to believe that the assumptions of the theory accurately represent the properties of gas molecules. We will first look at the individual gas laws (Boyle's, Charles's, Amontons's, Avogadro's, and Dalton's laws) conceptually to see how the KMT explains them. Then, we will more carefully consider the relationships between molecular masses, speeds, and kinetic energies with temperature, and explain Graham's law.

The Kinetic-Molecular Theory Explains the Behavior of Gases, Part I

Recalling that gas pressure is exerted by rapidly moving gas molecules and depends directly on the number of molecules hitting a unit area of the wall per unit of time, we see that the KMT conceptually explains the behavior of a gas as follows:

- *Amontons's law.* If the temperature is increased, the average speed and kinetic energy of the gas molecules increase. If the volume is held constant, the increased speed of the gas molecules results in more frequent and more forceful collisions with the walls of the container, therefore increasing the pressure (Figure **7.4.1*a***).
- *Charles's law.* If the temperature of a gas is increased, a constant pressure may be maintained only if the volume occupied by the gas increases. This will result in greater average distances traveled by the molecules to reach the container walls, as well as increased wall surface area. These conditions will decrease both the frequency of molecule-wall collisions and the number of collisions per unit area, the combined effects of which balance the effect of increased collision forces due to the greater kinetic energy at the higher temperature.
- *Boyle's law.* If the gas volume is decreased, the container wall area decreases and the molecule-wall collision frequency increases, both of which increase the pressure exerted by the gas (Figure **7.4.1*b***).
- *Avogadro's law.* At constant pressure and temperature, the frequency and force of molecule-wall collisions are constant. Under such conditions, increasing the number of gaseous molecules will require a proportional increase in the container volume in order to yield a decrease in the number of collisions per unit area to compensate for the increased frequency of collisions (Figure **7.4.1*c***).
- *Dalton's Law.* Because of the large distances between them, the molecules of one gas in a mixture bombard the container walls with the same frequency whether other gases are present or not, and the total pressure of a gas mixture equals the sum of the (partial) pressures of the individual gases.

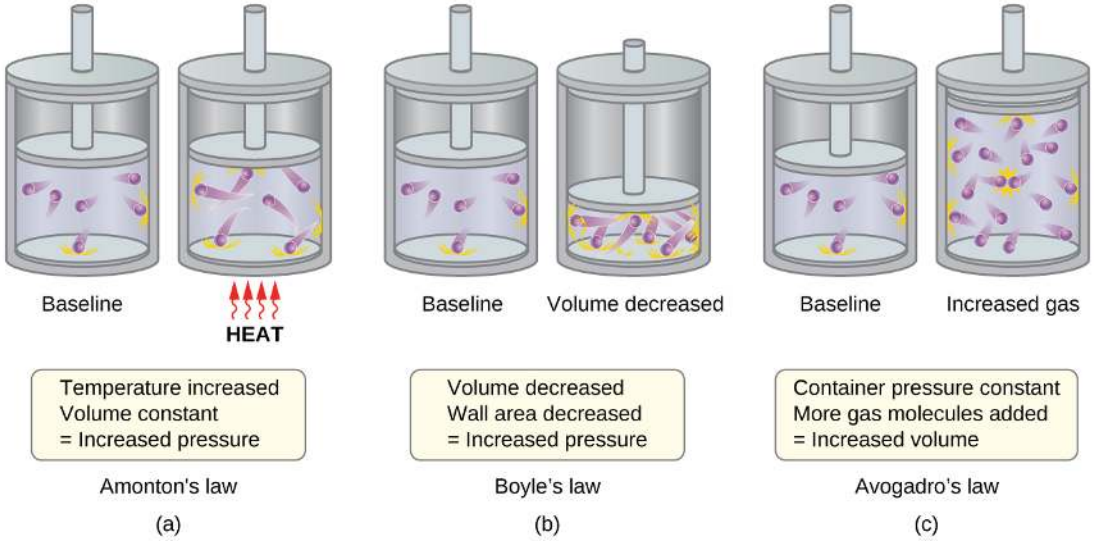


Figure 7.4.1: (a) When gas temperature increases, gas pressure increases due to increased force and frequency of molecular collisions. (b) When volume decreases, gas pressure increases due to increased frequency of molecular collisions. (c) When the amount of gas increases at a constant pressure, volume increases to yield a constant number of collisions per unit wall area per unit time.

This figure shows 3 pairs of pistons and cylinders. In a, which is labeled, “Charles’s Law,” the piston is positioned for the first cylinder so that just over half of the available volume contains 6 purple spheres with trails behind them. The trails indicate movement. Orange dashes extend from the interior surface of the cylinder where the spheres have collided. This cylinder is labeled, “Baseline.” In the second cylinder, the piston is in the same position, and the label, “Heat” is indicated in red capitalized text. Four red arrows with wavy stems are pointing upward to the base of the cylinder. The six purple spheres have longer trails behind them and the number of orange dashes indicating points of collision with the container walls has increased. A rectangle beneath the diagram states, “Temperature increased, Volume constant equals Increased pressure.” In b, which is labeled, “Boyle’s Law,” the first, baseline cylinder shown is identical to the first cylinder in a. In the second cylinder, the piston has been moved, decreasing the volume available to the 6 purple spheres to half of the initial volume. The six purple spheres have longer trails behind them and the number of orange dashes indicating points of collision with the container walls has increased. This second cylinder is labeled, “Volume decreased.” A rectangle beneath the diagram states, “Volume decreased, Wall area decreased equals Increased pressure.” In c, which is labeled “Avogadro’s Law,” the first, baseline cylinder shown is identical to the first cylinder in a. In the second cylinder, the number of purple spheres has changed from 6 to 12 and volume has doubled. This second cylinder is labeled “Increased gas.” A rectangle beneath the diagram states, “At constant pressure, More gas molecules added equals Increased volume.”

Molecular Velocities and Kinetic Energy

The previous discussion showed that the KMT qualitatively explains the behaviors described by the various gas laws. The postulates of this theory may be applied in a more quantitative fashion to derive these individual laws. To do this, we must first look at velocities and kinetic energies of gas molecules, and the temperature of a gas sample.

In a gas sample, individual molecules have widely varying speeds; however, because of the *vast* number of molecules and collisions involved, the molecular speed distribution and average speed are constant. This molecular speed distribution is known as a Maxwell-Boltzmann distribution, and it depicts the relative numbers of molecules in a bulk sample of gas that possesses a given speed (Figure 7.4.2).

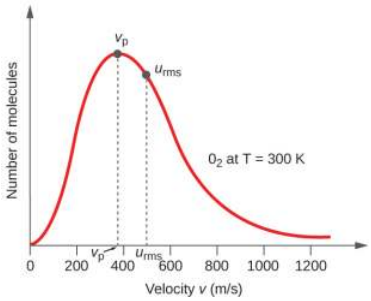


Figure **7.4.2**: The molecular speed distribution for oxygen gas at 300 K is shown here. Very few molecules move at either very low or very high speeds. The number of molecules with intermediate speeds increases rapidly up to a maximum, which is the most probable speed, then drops off rapidly. Note that the most probable speed, v_p, is a little less than 400 m/s, while the root mean square speed, u_{rms}, is closer to 500 m/s.

The kinetic energy (KE) of a particle of mass (m) and speed (u) is given by:

$$\mathrm{KE} = \frac{1}{2}mu^2$$

Expressing mass in kilograms and speed in meters per second will yield energy values in units of joules (J = kg m^2 s^{-2}). To deal with a large number of gas molecules, we use averages for both speed and kinetic energy. In the KMT, the root mean square velocity of a particle, u_{rms}, is defined as the square root of the average of the squares of the velocities with n = the number of particles:

$$u_{rms} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + u_4^2 + \ldots}{n}}$$

The average kinetic energy, KE_{avg}, is then equal to:

$$\mathrm{KE_{avg}} = \frac{1}{2}mu_{rms}^2$$

The KE_{avg} of a collection of gas molecules is also directly proportional to the temperature of the gas and may be described by the equation:

$$\mathrm{KE_{avg}} = \frac{3}{2}RT$$

where R is the gas constant and T is the kelvin temperature. When used in this equation, the appropriate form of the gas constant is 8.314 J $mol^{-1}K^{-1}$ (8.314 kg $m^2s^{-2}mol^{-1}K^{-1}$). These two separate equations for KE_{avg} may be combined and rearranged to yield a relation between molecular speed and temperature:

$$\frac{1}{2}mu_{rms}^2 = \frac{3}{2}RT$$

$$u_{rms} = \sqrt{\frac{3RT}{m}} \tag{7.4.1}$$

Example 7.4.1: Calculation of u_{rms}

Calculate the root-mean-square velocity for a nitrogen molecule at 30 °C.

Solution

Convert the temperature into Kelvin:

$$30°C + 273 = 303\ K$$

Determine the mass of a nitrogen molecule in kilograms:

$$\frac{28.0\ \cancel{g}}{1\ \mathrm{mol}} \times \frac{1\ \mathrm{kg}}{1000\ \cancel{g}} = 0.028\ \mathrm{kg/mol}$$

Replace the variables and constants in the root-mean-square velocity formula (Equation 7.4.1), replacing Joules with the equivalent kg m^2s^{-2}:

$$u_{rms} = \sqrt{\frac{3RT}{m}}$$

$$u_{rms} = \sqrt{\frac{3(8.314\ J/mol\ K)(303\ K)}{(0.028\ kg/mol)}}$$

$$= \sqrt{2.70 \times 10^5\ m^2s^{-2}}$$

$$= 519\ m/s$$

? Exercise 7.4.1

Calculate the root-mean-square velocity for an oxygen molecule at –23 °C.

Answer

441 m/s

If the temperature of a gas increases, its KE_{avg} increases, more molecules have higher speeds and fewer molecules have lower speeds, and the distribution shifts toward higher speeds overall, that is, to the right. If temperature decreases, KE_{avg} decreases, more molecules have lower speeds and fewer molecules have higher speeds, and the distribution shifts toward lower speeds overall, that is, to the left. This behavior is illustrated for nitrogen gas in Figure 7.4.3.

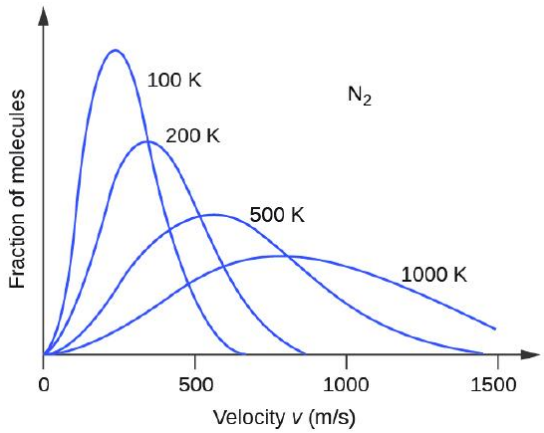


Figure 7.4.3: The molecular speed distribution for nitrogen gas (N_2) shifts to the right and flattens as the temperature increases; it shifts to the left and heightens as the temperature decreases.

A graph with four positively or right-skewed curves of varying heights is shown. The horizontal axis is labeled, “Velocity v (m divided by s).” This axis is marked by increments of 500 beginning at 0 and extending up to 1500. The vertical axis is labeled, “Fraction of molecules.” The label, “N subscript 2,” appears in the open space in the upper right area of the graph. The tallest and narrowest of these curves is labeled, “100 K.” Its right end appears to touch the horizontal axis around 700 m per s. It is followed by a slightly wider curve which is labeled, “200 K,” that is about three quarters of the height of the initial curve. Its right end appears to touch the horizontal axis around 850 m per s. The third curve is significantly wider and only about half the height of the initial curve. It is labeled, “500 K.” Its right end appears to touch the horizontal axis around 1450 m per s. The final curve is only about one third the height of the initial curve. It is much wider than the others, so much so that its right end has not yet reached the horizontal axis. This curve is labeled, “1000 K.”

At a given temperature, all gases have the same KE_{avg} for their molecules. Gases composed of lighter molecules have more high-speed particles and a higher u_{rms}, with a speed distribution that peaks at relatively higher velocities. Gases consisting of heavier molecules have more low-speed particles, a lower u_{rms}, and a speed distribution that peaks at relatively lower velocities. This trend is demonstrated by the data for a series of noble gases shown in Figure 7.4.4.

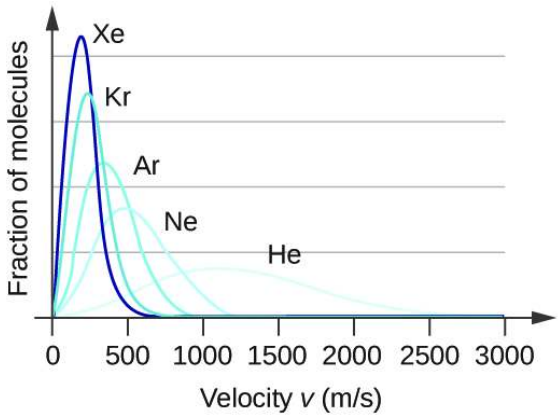


Figure **7.4.4**: Molecular velocity is directly related to molecular mass. At a given temperature, lighter molecules move faster on average than heavier molecules.

A graph is shown with four positively or right-skewed curves of varying heights. The horizontal axis is labeled, “Velocity v (m divided by s).” This axis is marked by increments of 500 beginning at 0 and extending up to 3000. The vertical axis is labeled, “Fraction of molecules.” The tallest and narrowest of these curves is labeled, “X e.” Its right end appears to touch the horizontal axis around 600 m per s. It is followed by a slightly wider curve which is labeled, “A r,” that is about half the height of the initial curve. Its right end appears to touch the horizontal axis around 900 m per s. The third curve is significantly wider and just over a third of the height of the initial curve. It is labeled, “N e.” Its right end appears to touch the horizontal axis around 1200 m per s. The final curve is only about one fourth the height of the initial curve. It is much wider than the others, so much so that its right reaches the horizontal axis around 2500 m per s. This curve is labeled, “H e.”

> *The gas simulator may be used to examine the effect of temperature on molecular velocities. Examine the simulator's "energy histograms" (molecular speed distributions) and "species information" (which gives average speed values) for molecules of different masses at various temperatures.*

The Kinetic-Molecular Theory Explains the Behavior of Gases, Part II

According to Graham's law, the molecules of a gas are in rapid motion and the molecules themselves are small. The average distance between the molecules of a gas is large compared to the size of the molecules. As a consequence, gas molecules can move past each other easily and diffuse at relatively fast rates.

The rate of effusion of a gas depends directly on the (average) speed of its molecules:

$$\text{effusion rate} \propto u_{\text{rms}}$$

Using this relation, and the equation relating molecular speed to mass, Graham's law may be easily derived as shown here:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{m}}$$

$$m = \frac{3RT}{u_{\text{rms}}^2} = \frac{3RT}{\overline{u}^2}$$

$$\frac{\text{effusion rate A}}{\text{effusion rate B}} = \frac{u_{\text{rms A}}}{u_{\text{rms B}}} = \frac{\sqrt{\frac{3RT}{m_{\text{A}}}}}{\sqrt{\frac{3RT}{m_{\text{B}}}}} = \sqrt{\frac{m_{\text{B}}}{m_{\text{A}}}}$$

The ratio of the rates of effusion is thus derived to be inversely proportional to the ratio of the square roots of their masses. This is the same relation observed experimentally and expressed as Graham's law.

Summary

The kinetic molecular theory is a simple but very effective model that effectively explains ideal gas behavior. The theory assumes that gases consist of widely separated molecules of negligible volume that are in constant motion, colliding elastically with one

another and the walls of their container with average velocities determined by their absolute temperatures. The individual molecules of a gas exhibit a range of velocities, the distribution of these velocities being dependent on the temperature of the gas and the mass of its molecules.

Key Equations

- $u_{\text{rms}} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + u_4^2 + \ldots}{n}}$
- $\text{KE}_{\text{avg}} = \frac{3}{2}RT$
- $u_{\text{rms}} = \sqrt{\frac{3RT}{m}}$

Summary

kinetic molecular theory

theory based on simple principles and assumptions that effectively explains ideal gas behavior

root mean square velocity (u_{rms})

measure of average velocity for a group of particles calculated as the square root of the average squared velocity

---

This page titled 7.4: The Kinetic-Molecular Theory is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

- **9.5: The Kinetic-Molecular Theory** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

7.E: Gases (Exercises)

9.1: Gas Pressure

Q9.1.1

Why are sharp knives more effective than dull knives (Hint: think about the definition of pressure)?

S9.1.1

The cutting edge of a knife that has been sharpened has a smaller surface area than a dull knife. Since pressure is force per unit area, a sharp knife will exert a higher pressure with the same amount of force and cut through material more effectively.

Q9.1.2

Why do some small bridges have weight limits that depend on how many wheels or axles the crossing vehicle has?

Q9.1.3

Why should you roll or belly-crawl rather than walk across a thinly-frozen pond?

S9.1.3

Lying down distributes your weight over a larger surface area, exerting less pressure on the ice compared to standing up. If you exert less pressure, you are less likely to break through thin ice.

Q9.1.4

A typical barometric pressure in Redding, California, is about 750 mm Hg. Calculate this pressure in atm and kPa.

Q9.1.5

A typical barometric pressure in Denver, Colorado, is 615 mm Hg. What is this pressure in atmospheres and kilopascals?

S9.1.5

0.809 atm; 82.0 kPa

Q9.1.6

A typical barometric pressure in Kansas City is 740 torr. What is this pressure in atmospheres, in millimeters of mercury, and in kilopascals?

Q9.1.7

Canadian tire pressure gauges are marked in units of kilopascals. What reading on such a gauge corresponds to 32 psi?

S9.1.7

2.2×10^2 kPa

Q9.1.8

During the Viking landings on Mars, the atmospheric pressure was determined to be on the average about 6.50 millibars (1 bar = 0.987 atm). What is that pressure in torr and kPa?

Q9.1.9

The pressure of the atmosphere on the surface of the planet Venus is about 88.8 atm. Compare that pressure in psi to the normal pressure on earth at sea level in psi.

S9.1.9

Earth: 14.7 lb in^{-2}; Venus: 13.1×10^3 lb in^{-2}

Q9.1.10

A medical laboratory catalog describes the pressure in a cylinder of a gas as 14.82 MPa. What is the pressure of this gas in atmospheres and torr?

Q9.1.11

Consider this scenario and answer the following questions: On a mid-August day in the northeastern United States, the following information appeared in the local newspaper: atmospheric pressure at sea level 29.97 in., 1013.9 mbar.

a. What was the pressure in kPa?
b. The pressure near the seacoast in the northeastern United States is usually reported near 30.0 in. Hg. During a hurricane, the pressure may fall to near 28.0 in. Hg. Calculate the drop in pressure in torr.

S9.1.11

(a) 101.5 kPa; (b) 51 torr drop

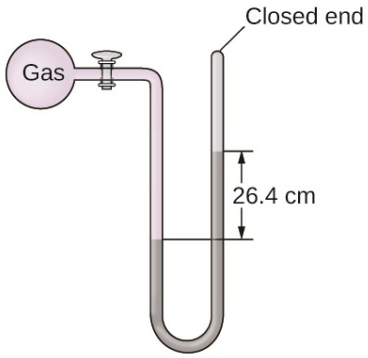
Q9.1.12

Why is it necessary to use a nonvolatile liquid in a barometer or manometer?

Q9.1.13

The pressure of a sample of gas is measured at sea level with a closed-end manometer. The liquid in the manometer is mercury. Determine the pressure of the gas in:

a. torr
b. Pa
c. bar



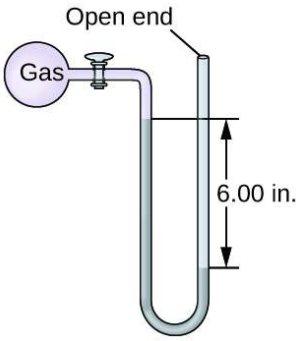
S9.1.13

(a) 264 torr; (b) 35,200 Pa; (c) 0.352 bar

Q9.1.14

The pressure of a sample of gas is measured with an open-end manometer, partially shown to the right. The liquid in the manometer is mercury. Assuming atmospheric pressure is 29.92 in. Hg, determine the pressure of the gas in:

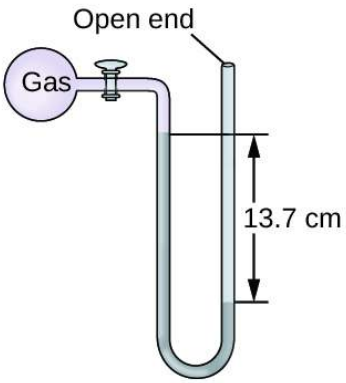
a. torr
b. Pa
c. bar



Q9.1.15

The pressure of a sample of gas is measured at sea level with an open-end mercury manometer. Assuming atmospheric pressure is 760.0 mm Hg, determine the pressure of the gas in:

a. mm Hg
b. atm
c. kPa



S9.1.15

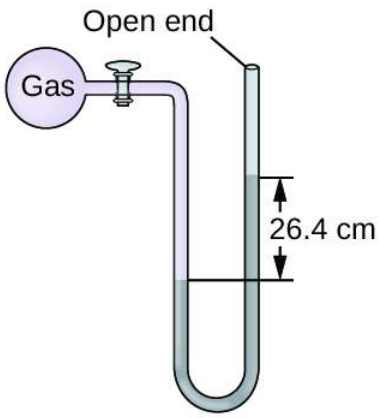
(a) 623 mm Hg; (b) 0.820 atm; (c) 83.1 kPa

Q9.1.16

The pressure of a sample of gas is measured at sea level with an open-end mercury manometer. Assuming atmospheric pressure is 760 mm Hg, determine the pressure of the gas in:

a. mm Hg
b. atm
c. kPa

https://chem.libretexts.org/@go/page/216766



Q9.1.17

How would the use of a volatile liquid affect the measurement of a gas using open-ended manometers vs. closed-end manometers?

S9.1.17

With a closed-end manometer, no change would be observed, since the vaporized liquid would contribute equal, opposing pressures in both arms of the manometer tube. However, with an open-ended manometer, a higher pressure reading of the gas would be obtained than expected, since $P_{gas} = P_{atm} + P_{vol\ liquid}$.

9.2: Relating Pressure, Volume, Amount, and Temperature: The Ideal Gas Law

Q9.2.1

Sometimes leaving a bicycle in the sun on a hot day will cause a blowout. Why?

Q9.2.2

Explain how the volume of the bubbles exhausted by a scuba diver (Figure) change as they rise to the surface, assuming that they remain intact.

S9.2.2

As the bubbles rise, the pressure decreases, so their volume increases as suggested by Boyle's law.

Q9.2.3

One way to state Boyle's law is "All other things being equal, the pressure of a gas is inversely proportional to its volume." (a) What is the meaning of the term "inversely proportional?" (b) What are the "other things" that must be equal?

Q9.2.4

An alternate way to state Avogadro's law is "All other things being equal, the number of molecules in a gas is directly proportional to the volume of the gas."

a. What is the meaning of the term "directly proportional?"
b. What are the "other things" that must be equal?

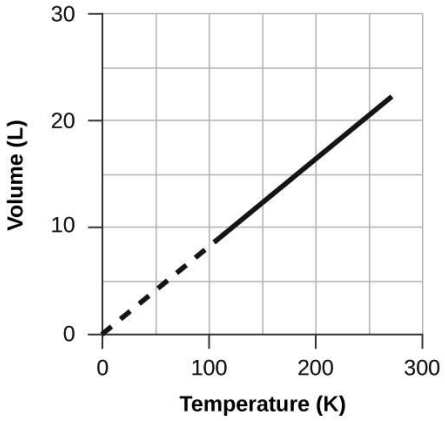
S9.2.4

(a) The number of particles in the gas increases as the volume increases. (b) temperature, pressure

Q9.2.5

How would the graph in Figure change if the number of moles of gas in the sample used to determine the curve were doubled?

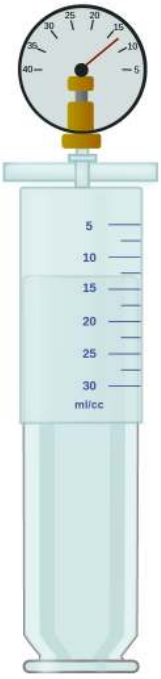
Temperature (°C)	Temperature (K)	Volume (L)
–3	270	22
–23	250	21
–53	220	18
–162	111	9

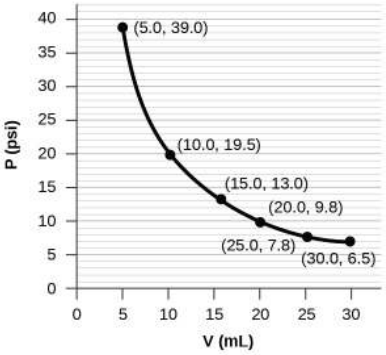


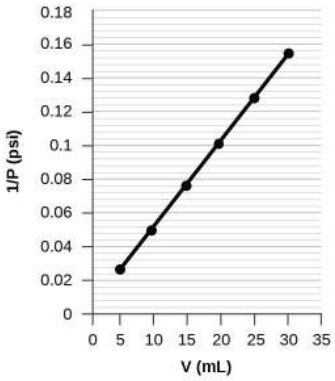
The volume and temperature are linearly related for 1 mole of methane gas at a constant pressure of 1 atm. If the temperature is in kelvin, volume and temperature are directly proportional. The line stops at 111 K because methane liquefies at this temperature; when extrapolated, it intersects the graph's origin, representing a temperature of absolute zero.

Q9.2.6

How would the graph in Figure change if the number of moles of gas in the sample used to determine the curve were doubled?







When a gas occupies a smaller volume, it exerts a higher pressure; when it occupies a larger volume, it exerts a lower pressure (assuming the amount of gas and the temperature do not change). Since P and V are inversely proportional, a graph of $1/P$ *vs. \ (V\) is linear.*

S9.2.6

The curve would be farther to the right and higher up, but the same basic shape.

Q9.2.7

In addition to the data found in Figure, what other information do we need to find the mass of the sample of air used to determine the graph?

https://chem.libretexts.org/@go/page/216766

Q9.2.8

Determine the volume of 1 mol of CH_4 gas at 150 K and 1 atm, using Figure.

S9.2.8

16.3 to 16.5 L

Q9.2.9

Determine the pressure of the gas in the syringe shown in Figure when its volume is 12.5 mL, using:

a. the appropriate graph
b. Boyle's law

Q9.2.10

A spray can is used until it is empty except for the propellant gas, which has a pressure of 1344 torr at 23 °C. If the can is thrown into a fire (T = 475 °C), what will be the pressure in the hot can?

S9.2.10

3.40×10^3 torr

Q9.2.11

What is the temperature of an 11.2-L sample of carbon monoxide, CO, at 744 torr if it occupies 13.3 L at 55 °C and 744 torr?

S9.2.11

we must use $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ and solve for T_1

$T_1 = \frac{P_1V_1T_2}{P_2V_2}$

Where:

$P_1 = 744\,torr$

$V_1 = 11.2\,L$

$P_2 = 744\,torr$

$V_2 = 13.3\,L$

$T_2 = 328.15°\,K$

$\frac{(744\,torr)(11.2\,L)(328.15°\,K)}{(744\,torr)(13.3\,L)} = 276°\,K$

276°K ; 3°C

Q9.2.12

A 2.50-L volume of hydrogen measured at –196 °C is warmed to 100 °C. Calculate the volume of the gas at the higher temperature, assuming no change in pressure.

S9.2.13

12.1 L

Q9.2.14

A balloon inflated with three breaths of air has a volume of 1.7 L. At the same temperature and pressure, what is the volume of the balloon if five more same-sized breaths are added to the balloon?

Q9.2.15

A weather balloon contains 8.80 moles of helium at a pressure of 0.992 atm and a temperature of 25 °C at ground level. What is the volume of the balloon under these conditions?



S9.2.15

217 L

Q9.2.16

The volume of an automobile air bag was 66.8 L when inflated at 25 °C with 77.8 g of nitrogen gas. What was the pressure in the bag in kPa?

Q9.2.17

How many moles of gaseous boron trifluoride, BF_3, are contained in a 4.3410-L bulb at 788.0 K if the pressure is 1.220 atm? How many grams of BF_3?

S9.2.17

8.190×10^{-2} mol; 5.553 g

Q9.2.18

Iodine, I_2, is a solid at room temperature but sublimes (converts from a solid into a gas) when warmed. What is the temperature in a 73.3-mL bulb that contains 0.292 g of I_2 vapor at a pressure of 0.462 atm?

S9.2.18

1.) Use the equation $PV = nRT$ and solve for T

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

2.) convert grams of I_2 to moles of I_2 and convert mL to L

$$0.292 g\ I_2 \times \frac{1\ mole\ I_2}{253.8 g\ I_2} = 1.15 \times 10^{-3}\ moles\ I_2$$

$$73.3\ mL = 0.0733\ L$$

3.) Use these values along with $R = 0.08206\ \frac{atm\ L}{mole\ °K}$ to solve for T

$$T = \frac{(0.462\ \cancel{atm})(0.0733\ \cancel{L})}{(1.15 \times 10^{-3}\ \cancel{moles})(0.08206\ \frac{\cancel{atm}\ \cancel{L}}{\cancel{mole}\ °K})} = 359\ °K$$

359°K ; 86°C

Q9.2.19

How many grams of gas are present in each of the following cases?

a. 0.100 L of CO_2 at 307 torr and 26 °C
b. 8.75 L of C_2H_4, at 378.3 kPa and 483 K
c. 221 mL of Ar at 0.23 torr and –54 °C

S9.2.19

(a) 7.24×10^{-2} g; (b) 23.1 g; (c) 1.5×10^{-4} g

Q9.2.20

A high altitude balloon is filled with 1.41×10^4 L of hydrogen at a temperature of 21 °C and a pressure of 745 torr. What is the volume of the balloon at a height of 20 km, where the temperature is –48 °C and the pressure is 63.1 torr?

Q9.2.21

A cylinder of medical oxygen has a volume of 35.4 L, and contains O_2 at a pressure of 151 atm and a temperature of 25 °C. What volume of O_2 does this correspond to at normal body conditions, that is, 1 atm and 37 °C?

S9.2.21

5561 L

Q9.2.22

A large scuba tank (Figure) with a volume of 18 L is rated for a pressure of 220 bar. The tank is filled at 20 °C and contains enough air to supply 1860 L of air to a diver at a pressure of 2.37 atm (a depth of 45 feet). Was the tank filled to capacity at 20 °C?

Q9.2.23

A 20.0-L cylinder containing 11.34 kg of butane, C_4H_{10}, was opened to the atmosphere. Calculate the mass of the gas remaining in the cylinder if it were opened and the gas escaped until the pressure in the cylinder was equal to the atmospheric pressure, 0.983 atm, and a temperature of 27 °C.

S9.2.23

46.4 g

Q9.2.24

While resting, the average 70-kg human male consumes 14 L of pure O_2 per hour at 25 °C and 100 kPa. How many moles of O_2 are consumed by a 70 kg man while resting for 1.0 h?

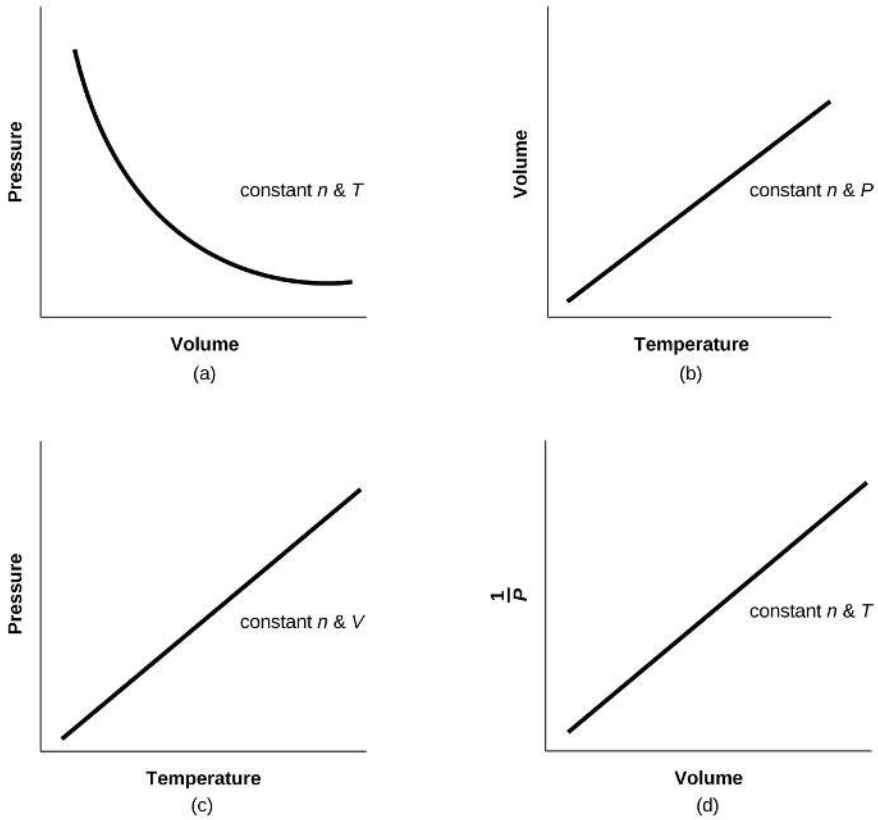
Q9.2.25

For a given amount of gas showing ideal behavior, draw labeled graphs of:

a. the variation of P with V
b. the variation of V with T
c. the variation of P with T
d. the variation of $\frac{1}{P}$ with V

Q9.2.26

For a gas exhibiting ideal behavior:



Q9.2.27

A liter of methane gas, CH_4, at STP contains more atoms of hydrogen than does a liter of pure hydrogen gas, H_2, at STP. Using Avogadro's law as a starting point, explain why.

Q9.2.28

The effect of chlorofluorocarbons (such as CCl_2F_2) on the depletion of the ozone layer is well known. The use of substitutes, such as $CH_3CH_2F(g)$, for the chlorofluorocarbons, has largely corrected the problem. Calculate the volume occupied by 10.0 g of each of these compounds at STP:

a. $CCl_2F_2(g)$
b. $CH_3CH_2F(g)$

S9.2.28

(a) 1.85 L CCl_2F_2; (b) 4.66 L CH_3CH_2F

Q9.2.29

As 1 g of the radioactive element radium decays over 1 year, it produces 1.16×10^{18} alpha particles (helium nuclei). Each alpha particle becomes an atom of helium gas. What is the pressure in pascal of the helium gas produced if it occupies a volume of 125 mL at a temperature of 25 °C?

Q9.2.30

A balloon that is 100.21 L at 21 °C and 0.981 atm is released and just barely clears the top of Mount Crumpet in British Columbia. If the final volume of the balloon is 144.53 L at a temperature of 5.24 °C, what is the pressure experienced by the balloon as it clears Mount Crumpet?

S9.2.30

0.644 atm

Q9.2.31

If the temperature of a fixed amount of a gas is doubled at constant volume, what happens to the pressure?

Q9.2.32

If the volume of a fixed amount of a gas is tripled at constant temperature, what happens to the pressure?

S9.2.32

The pressure decreases by a factor of 3.

9.3: Stoichiometry of Gaseous Substances, Mixtures, and Reactions

Q9.3.1

What is the density of laughing gas, dinitrogen monoxide, N_2O, at a temperature of 325 K and a pressure of 113.0 kPa?

S9.3.1

1.) First convert kPa to atm

$$113.0\ kPa \times \frac{1\ atm}{101.325\ kPa} = 1.115\ atm$$

2.) The use the equation $d = \frac{PM}{RT}$ where d = density in g L^{-1} and M = molar mass in g mol^{-1}

$$d = \frac{(1.115\ atm)(44.02 \frac{g}{\cancel{mol}})}{(0.08206 \frac{\cancel{atm}\ L}{\cancel{mole}\ \cancel{°K}})(325\ \cancel{°K})} = 1.84\ \frac{g}{L}$$

Q9.3.2

Calculate the density of Freon 12, CF_2Cl_2, at 30.0 °C and 0.954 atm.

S9.3.2

4.64 g L^{-1}

Q9.3.3

Which is denser at the same temperature and pressure, dry air or air saturated with water vapor? Explain.

Q9.3.4

A cylinder of $O_2(g)$ used in breathing by emphysema patients has a volume of 3.00 L at a pressure of 10.0 atm. If the temperature of the cylinder is 28.0 °C, what mass of oxygen is in the cylinder?

S9.3.4

38.8 g

Q9.3.5

What is the molar mass of a gas if 0.0494 g of the gas occupies a volume of 0.100 L at a temperature 26 °C and a pressure of 307 torr?

S9.3.5

1.) convert torr to atm and °C to °K

$$307\ torr = 0.404 atm$$

$26°C = 300.°K$

2.) Use the equation $PV = nRT$ and solve for n

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

$$n = \frac{(0.404\ \cancel{atm})(0.100\ \cancel{L})}{(0.08206 \frac{\cancel{atm}\ \cancel{L}}{mol\ \cancel{°K}})(300.\ \cancel{°K})} = 0.00165\ moles$$

3.) Then divide grams by the number of moles to obtain the molar mass:

$$\frac{0.0494g}{0.00165\ moles} = 30.0 \frac{g}{mole}$$

Q9.3.6

What is the molar mass of a gas if 0.281 g of the gas occupies a volume of 125 mL at a temperature 126 °C and a pressure of 777 torr?

S9.3.6

72.0 g mol^{-1}

Q9.3.7

How could you show experimentally that the molecular formula of propene is C_3H_6, not CH_2?

Q9.3.8

The density of a certain gaseous fluoride of phosphorus is 3.93 g/L at STP. Calculate the molar mass of this fluoride and determine its molecular formula.

S9.3.8

88.1 g mol^{-1}; PF_3

Q9.3.9

Consider this question: What is the molecular formula of a compound that contains 39% C, 45% N, and 16% H if 0.157 g of the compound occupies 125 mL with a pressure of 99.5 kPa at 22 °C?

a. Outline the steps necessary to answer the question.
b. Answer the question.

Q9.3.10

A 36.0–L cylinder of a gas used for calibration of blood gas analyzers in medical laboratories contains 350 g CO_2, 805 g O_2, and 4,880 g N_2. At 25 degrees C, what is the pressure in the cylinder in atmospheres?

S9.3.10

141 atm

Q9.3.11

A cylinder of a gas mixture used for calibration of blood gas analyzers in medical laboratories contains 5.0% CO_2, 12.0% O_2, and the remainder N_2 at a total pressure of 146 atm. What is the partial pressure of each component of this gas? (The percentages given indicate the percent of the total pressure that is due to each component.)

Q9.3.12

A sample of gas isolated from unrefined petroleum contains 90.0% CH_4, 8.9% C_2H_6, and 1.1% C_3H_8 at a total pressure of 307.2 kPa. What is the partial pressure of each component of this gas? (The percentages given indicate the percent of the total pressure that is due to each component.)

S9.3.12

CH_4: 276 kPa; C_2H_6: 27 kPa; C_3H_8: 3.4 kPa

Q9.3.13

A mixture of 0.200 g of H_2, 1.00 g of N_2, and 0.820 g of Ar is stored in a closed container at STP. Find the volume of the container, assuming that the gases exhibit ideal behavior.

Q9.3.14

Most mixtures of hydrogen gas with oxygen gas are explosive. However, a mixture that contains less than 3.0 % O_2 is not. If enough O_2 is added to a cylinder of H_2 at 33.2 atm to bring the total pressure to 34.5 atm, is the mixture explosive?

S9.3.14

Yes

Q9.3.15

A commercial mercury vapor analyzer can detect, in air, concentrations of gaseous Hg atoms (which are poisonous) as low as 2×10^{-6} mg/L of air. At this concentration, what is the partial pressure of gaseous mercury if the atmospheric pressure is 733 torr at 26 °C?

Q9.3.16

A sample of carbon monoxide was collected over water at a total pressure of 756 torr and a temperature of 18 °C. What is the pressure of the carbon monoxide? (See Table for the vapor pressure of water.)

S9.3.16

740 torr

Q9.3.17

In an experiment in a general chemistry laboratory, a student collected a sample of a gas over water. The volume of the gas was 265 mL at a pressure of 753 torr and a temperature of 27 °C. The mass of the gas was 0.472 g. What was the molar mass of the gas?

Q9.3.18

Joseph Priestley first prepared pure oxygen by heating mercuric oxide, HgO:

$$2\,HgO(s) \longrightarrow 2\,Hg(l) + O_2(g)$$

a. Outline the steps necessary to answer the following question: What volume of O_2 at 23 °C and 0.975 atm is produced by the decomposition of 5.36 g of HgO?
b. Answer the question.

S9.3.18

(a) Determine the moles of HgO that decompose; using the chemical equation, determine the moles of O_2 produced by decomposition of this amount of HgO; and determine the volume of O_2 from the moles of O_2, temperature, and pressure. (b) 0.308 L

Q9.3.19

Cavendish prepared hydrogen in 1766 by the novel method of passing steam through a red-hot gun barrel:

$$4\,H_2O(g) + 3\,Fe(s) \longrightarrow Fe_3O_4(s) + 4\,H_2(g) \qquad (7.E.1)$$

a. Outline the steps necessary to answer the following question: What volume of H_2 at a pressure of 745 torr and a temperature of 20 °C can be prepared from the reaction of 15.O g of H_2O?
b. Answer the question.

Q9.3.20

The chlorofluorocarbon CCl_2F_2 can be recycled into a different compound by reaction with hydrogen to produce $CH_2F_2(g)$, a compound useful in chemical manufacturing:

$$CCl_2F_2(g) + 4\,H_2(g) \longrightarrow CH_2F_2(g) + 2\,HCl(g) \tag{7.E.2}$$

a. Outline the steps necessary to answer the following question: What volume of hydrogen at 225 atm and 35.5 °C would be required to react with 1 ton (1.000×10^3 kg) of CCl_2F_2?
b. Answer the question.

S9.3.20

a. Determine the molar mass of CCl_2F_2. From the balanced equation, calculate the moles of H_2 needed for the complete reaction. From the ideal gas law, convert moles of H_2 into volume.
b. 3.72×10^3 L

Q9.3.21

Automobile air bags are inflated with nitrogen gas, which is formed by the decomposition of solid sodium azide (NaN_3). The other product is sodium metal. Calculate the volume of nitrogen gas at 27 °C and 756 torr formed by the decomposition of 125 g of sodium azide.

Q9.3.22

Lime, CaO, is produced by heating calcium carbonate, $CaCO_3$; carbon dioxide is the other product.

a. Outline the steps necessary to answer the following question: What volume of carbon dioxide at 875° and 0.966 atm is produced by the decomposition of 1 ton (1.000×10^3 kg) of calcium carbonate?
b. Answer the question.

S9.3.22

(a) Balance the equation. Determine the grams of CO_2 produced and the number of moles. From the ideal gas law, determine the volume of gas. (b) 7.43×10^5 L

Q9.3.23

Before small batteries were available, carbide lamps were used for bicycle lights. Acetylene gas, C_2H_2, and solid calcium hydroxide were formed by the reaction of calcium carbide, CaC_2, with water. The ignition of the acetylene gas provided the light. Currently, the same lamps are used by some cavers, and calcium carbide is used to produce acetylene for carbide cannons.

a. Outline the steps necessary to answer the following question: What volume of C_2H_2 at 1.005 atm and 12.2 °C is formed by the reaction of 15.48 g of CaC_2 with water?
b. Answer the question.

Q9.3.24

Calculate the volume of oxygen required to burn 12.00 L of ethane gas, C_2H_6, to produce carbon dioxide and water, if the volumes of C_2H_6 and O_2 are measured under the same conditions of temperature and pressure.

S9.3.24

42.00 L

Q9.3.25

What volume of O_2 at STP is required to oxidize 8.0 L of NO at STP to NO_2? What volume of NO_2 is produced at STP?

Q9.3.26

Consider the following questions:

a. What is the total volume of the $CO_2(g)$ and $H_2O(g)$ at 600 °C and 0.888 atm produced by the combustion of 1.00 L of $C_2H_6(g)$ measured at STP?

b. What is the partial pressure of H_2O in the product gases?

S9.3.26

(a) 18.0 L; (b) 0.533 atm

Q9.3.27

Methanol, CH_3OH, is produced industrially by the following reaction:

$$\mathrm{CO}(g) + 2\,\mathrm{H_2}(g) \xrightarrow{\text{copper catalyst 300 °C, 300 atm}} \mathrm{CH_3OH}(g) \tag{7.E.3}$$

Q9.3.28

Assuming that the gases behave as ideal gases, find the ratio of the total volume of the reactants to the final volume.

Q9.3.29

What volume of oxygen at 423.0 K and a pressure of 127.4 kPa is produced by the decomposition of 129.7 g of BaO_2 to BaO and O_2?

S9.3.29

10.57 L O_2

Q9.3.30

A 2.50-L sample of a colorless gas at STP decomposed to give 2.50 L of N_2 and 1.25 L of O_2 at STP. What is the colorless gas?

Q9.3.31

Ethanol, C_2H_5OH, is produced industrially from ethylene, C_2H_4, by the following sequence of reactions:

$$3\,\mathrm{C_2H_4} + 2\,\mathrm{H_2SO_4} \longrightarrow \mathrm{C_2H_5HSO_4} + (\mathrm{C_2H_5})_2\mathrm{SO_4} \tag{7.E.4}$$

$$\mathrm{C_2H_5HSO_4} + (\mathrm{C_2H_5})_2\mathrm{SO_4} + 3\,\mathrm{H_2O} \longrightarrow 3\,\mathrm{C_2H_5OH} + 2\,\mathrm{H_2SO_4} \tag{7.E.5}$$

What volume of ethylene at STP is required to produce 1.000 metric ton (1000 kg) of ethanol if the overall yield of ethanol is 90.1%?

S9.3.31

5.40×10^5 L

Q9.3.32

One molecule of hemoglobin will combine with four molecules of oxygen. If 1.0 g of hemoglobin combines with 1.53 mL of oxygen at body temperature (37 °C) and a pressure of 743 torr, what is the molar mass of hemoglobin?

Q9.3.33

A sample of a compound of xenon and fluorine was confined in a bulb with a pressure of 18 torr. Hydrogen was added to the bulb until the pressure was 72 torr. Passage of an electric spark through the mixture produced Xe and HF. After the HF was removed by reaction with solid KOH, the final pressure of xenon and unreacted hydrogen in the bulb was 36 torr. What is the empirical formula of the xenon fluoride in the original sample? (Note: Xenon fluorides contain only one xenon atom per molecule.)

S9.3.33

XeF_2

Q9.3.34

One method of analyzing amino acids is the van Slyke method. The characteristic amino groups ($-NH_2$) in protein material are allowed to react with nitrous acid, HNO_2, to form N_2 gas. From the volume of the gas, the amount of amino acid can be determined. A 0.0604-g sample of a biological sample containing glycine, $CH_2(NH_2)COOH$, was analyzed by the van Slyke

method and yielded 3.70 mL of N_2 collected over water at a pressure of 735 torr and 29 °C. What was the percentage of glycine in the sample?

$$CH_2(NH_2)CO_2H + HNO_2 \longrightarrow CH_2(OH)CO_2H + H_2O + N_2$$

9.4: Effusion and Diffusion of Gases

Q9.4.1

A balloon filled with helium gas is found to take 6 hours to deflate to 50% of its original volume. How long will it take for an identical balloon filled with the same volume of hydrogen gas (instead of helium) to decrease its volume by 50%?

S9.4.1

4.2 hours

Q9.4.2

Explain why the numbers of molecules are not identical in the left- and right-hand bulbs shown in the center illustration of Figure.

Q9.4.3

Starting with the definition of rate of effusion and Graham's finding relating rate and molar mass, show how to derive the Graham's law equation, relating the relative rates of effusion for two gases to their molecular masses.

S9.4.3

Effusion can be defined as the process by which a gas escapes through a pinhole into a vacuum. Graham's law states that with a mixture of two gases A and B: $\left(\frac{\text{rate A}}{\text{rate B}}\right) = \left(\frac{\text{molar mass of B}}{\text{molar mass of A}}\right)^{1/2}$. Both A and B are in the same container at the same temperature, and therefore will have the same kinetic energy:

$$\text{KE}_\text{A} = \text{KE}_\text{BKE} = \frac{1}{2}mv^2 \text{ Therefore, } \frac{1}{2}m_\text{A}v_\text{A}^2 = \frac{1}{2}m_\text{B}v_\text{B}^2 \; \frac{v_\text{A}^2}{v_\text{B}^2} = \frac{m_\text{B}}{m_\text{A}} \left(\frac{v_\text{A}^2}{v_\text{B}^2}\right)^{1/2} = \left(\frac{m_\text{B}}{m_\text{A}}\right)^{1/2} \frac{v_\text{A}}{v_\text{B}} = \left(\frac{m_\text{B}}{m_\text{A}}\right)^{1/2}$$

Q9.4.4

Heavy water, D_2O (molar mass = 20.03 g mol^{-1}), can be separated from ordinary water, H_2O (molar mass = 18.01), as a result of the difference in the relative rates of diffusion of the molecules in the gas phase. Calculate the relative rates of diffusion of H_2O and D_2O.

Q9.4.5

Which of the following gases diffuse more slowly than oxygen? F_2, Ne, N_2O, C_2H_2, NO, Cl_2, H_2S

S9.4.5

F_2, N_2O, Cl_2, H_2S

Q9.4.6

During the discussion of gaseous diffusion for enriching uranium, it was claimed that $^{235}UF_6$ diffuses 0.4% faster than $^{238}UF_6$. Show the calculation that supports this value. The molar mass of $^{235}UF_6$ = 235.043930 + 6 × 18.998403 = 349.034348 g/mol, and the molar mass of $^{238}UF_6$ = 238.050788 + 6 × 18.998403 = 352.041206 g/mol.

Q9.4.7

Calculate the relative rate of diffusion of $^1H_2$ (molar mass 2.0 g/mol) compared to that of $^2H_2$ (molar mass 4.0 g/mol) and the relative rate of diffusion of O_2 (molar mass 32 g/mol) compared to that of O_3 (molar mass 48 g/mol).

S9.4.7

1.4; 1.2

Q9.4.8

A gas of unknown identity diffuses at a rate of 83.3 mL/s in a diffusion apparatus in which carbon dioxide diffuses at the rate of 102 mL/s. Calculate the molecular mass of the unknown gas.

Q9.4.9

When two cotton plugs, one moistened with ammonia and the other with hydrochloric acid, are simultaneously inserted into opposite ends of a glass tube that is 87.0 cm long, a white ring of NH_4Cl forms where gaseous NH_3 and gaseous HCl first come into contact. (Hint: Calculate the rates of diffusion for both NH_3 and HCl, and find out how much faster NH_3 diffuses than HCl.)

$$\mathrm{NH_3}(g) + \mathrm{HCl}(g) \longrightarrow \mathrm{NH_4Cl}(s) \tag{7.E.6}$$

Q9.4.10

At approximately what distance from the ammonia moistened plug does this occur?

S9.4.10

51.7 cm

9.5: The Kinetic-Molecular Theory

Q9.5.1

Using the postulates of the kinetic molecular theory, explain why a gas uniformly fills a container of any shape.

Q9.5.2

Can the speed of a given molecule in a gas double at constant temperature? Explain your answer.

S9.5.2

Yes. At any given instant, there are a range of values of molecular speeds in a sample of gas. Any single molecule can speed up or slow down as it collides with other molecules. The average velocity of all the molecules is constant at constant temperature.

Q9.5.3

Describe what happens to the average kinetic energy of ideal gas molecules when the conditions are changed as follows:

a. The pressure of the gas is increased by reducing the volume at constant temperature.
b. The pressure of the gas is increased by increasing the temperature at constant volume.
c. The average velocity of the molecules is increased by a factor of 2.

Q9.5.4

The distribution of molecular velocities in a sample of helium is shown in Figure. If the sample is cooled, will the distribution of velocities look more like that of H_2 or of H_2O? Explain your answer.

S9.5.4

H_2O. Cooling slows the velocities of the He atoms, causing them to behave as though they were heavier.

Q9.5.5

What is the ratio of the average kinetic energy of a SO_2 molecule to that of an O_2 molecule in a mixture of two gases? What is the ratio of the root mean square speeds, u_{rms}, of the two gases?

Q9.5.6

A 1-L sample of CO initially at STP is heated to 546 °C, and its volume is increased to 2 L.

a. What effect do these changes have on the number of collisions of the molecules of the gas per unit area of the container wall?
b. What is the effect on the average kinetic energy of the molecules?
c. What is the effect on the root mean square speed of the molecules?

S9.5.6

(a) The number of collisions per unit area of the container wall is constant. (b) The average kinetic energy doubles. (c) The root mean square speed increases to $\sqrt{2}$ times its initial value; u_{rms} is proportional to $\mathbf{KE_{avg}}$.

Q9.5.7

The root mean square speed of H_2 molecules at 25 °C is about 1.6 km/s. What is the root mean square speed of a N_2 molecule at 25 °C?

Q9.5.8

Answer the following questions:

a. Is the pressure of the gas in the hot air balloon shown at the opening of this chapter greater than, less than, or equal to that of the atmosphere outside the balloon?
b. Is the density of the gas in the hot air balloon shown at the opening of this chapter greater than, less than, or equal to that of the atmosphere outside the balloon?
c. At a pressure of 1 atm and a temperature of 20 °C, dry air has a density of 1.2256 g/L. What is the (average) molar mass of dry air?
d. The average temperature of the gas in a hot air balloon is 1.30×10^2 °F. Calculate its density, assuming the molar mass equals that of dry air.
e. The lifting capacity of a hot air balloon is equal to the difference in the mass of the cool air displaced by the balloon and the mass of the gas in the balloon. What is the difference in the mass of 1.00 L of the cool air in part (c) and the hot air in part (d)?
f. An average balloon has a diameter of 60 feet and a volume of 1.1×10^5 ft^3. What is the lifting power of such a balloon? If the weight of the balloon and its rigging is 500 pounds, what is its capacity for carrying passengers and cargo?
g. A balloon carries 40.0 gallons of liquid propane (density 0.5005 g/L). What volume of CO_2 and H_2O gas is produced by the combustion of this propane?
h. A balloon flight can last about 90 minutes. If all of the fuel is burned during this time, what is the approximate rate of heat loss (in kJ/min) from the hot air in the bag during the flight?

S9.5.1

(a) equal; (b) less than; (c) 29.48 g mol^{-1}; (d) 1.0966 g L^{-1}; (e) 0.129 g/L; (f) 4.01×10^5 g; net lifting capacity = 384 lb; (g) 270 L; (h) 39.1 kJ min^{-1}

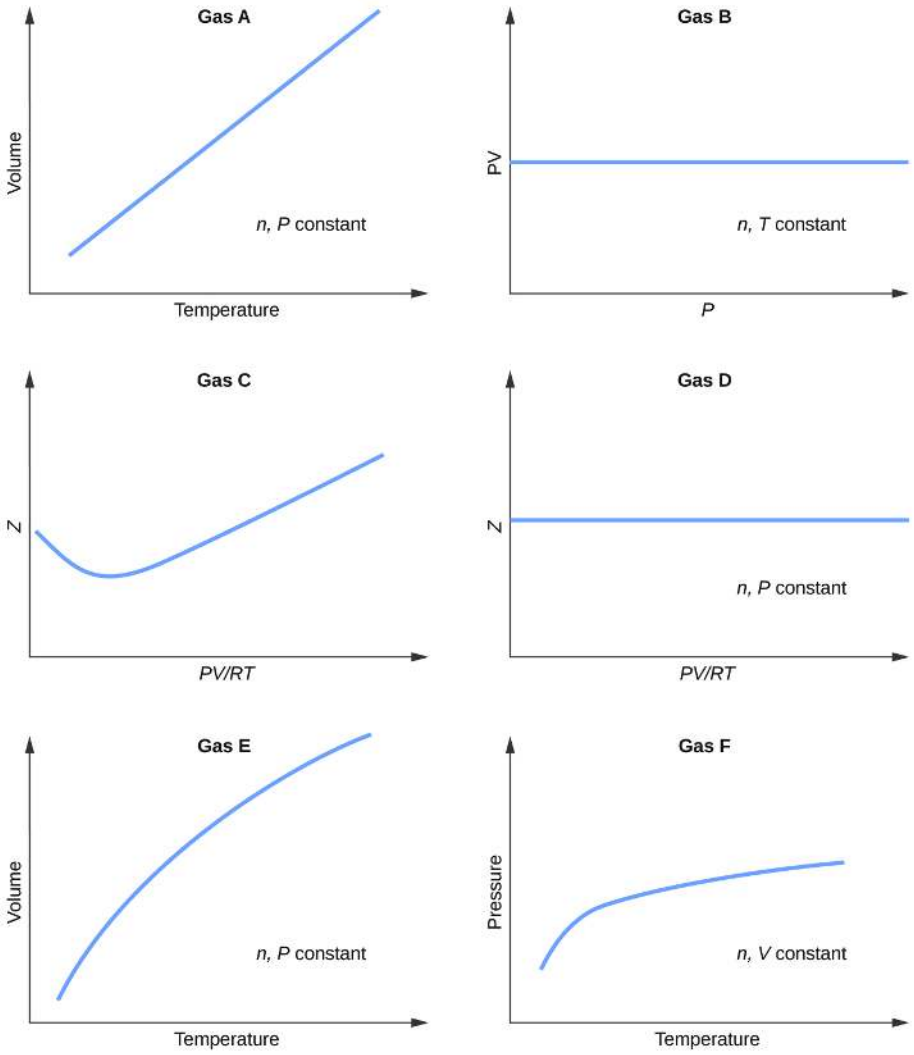
Q9.5.1

Show that the ratio of the rate of diffusion of Gas 1 to the rate of diffusion of Gas 2, $\frac{R_1}{R_2}$, is the same at 0 °C and 100 °C.

9.6: Non-Ideal Gas Behavior

Q9.6.1

Graphs showing the behavior of several different gases follow. Which of these gases exhibit behavior significantly different from that expected for ideal gases?



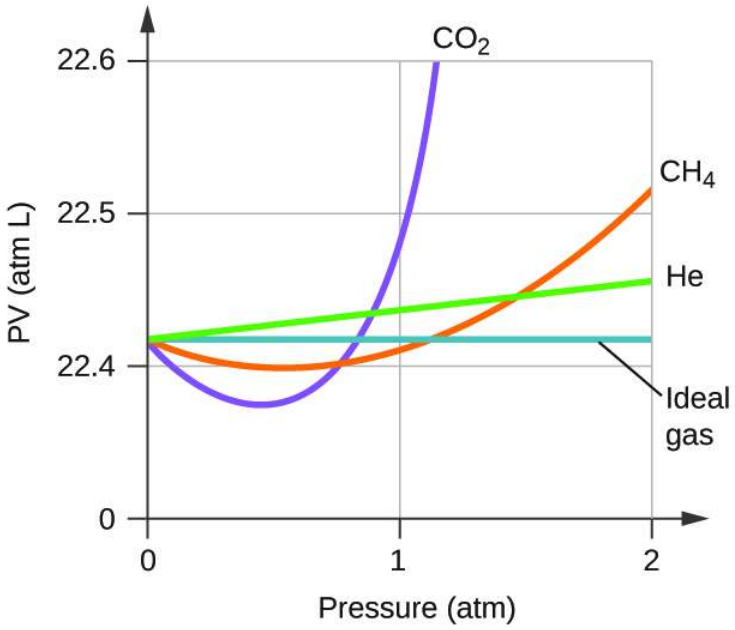
S9.6.1

Gases C, E, and F

Q9.6.3

Explain why the plot of PV for CO_2 differs from that of an ideal gas.

https://chem.libretexts.org/@go/page/216766



Q9.6.3

Under which of the following sets of conditions does a real gas behave most like an ideal gas, and for which conditions is a real gas expected to deviate from ideal behavior? Explain.

a. high pressure, small volume
b. high temperature, low pressure
c. low temperature, high pressure

S9.6.3

The gas behavior most like an ideal gas will occur under the conditions in (b). Molecules have high speeds and move through greater distances between collision; they also have shorter contact times and interactions are less likely. Deviations occur with the conditions described in (a) and (c). Under conditions of (a), some gases may liquefy. Under conditions of (c), most gases will liquefy.

Q9.6.4

Describe the factors responsible for the deviation of the behavior of real gases from that of an ideal gas.

Q9.6.5

For which of the following gases should the correction for the molecular volume be largest: CO, CO_2, H_2, He, NH_3, SF_6?

S9.6.6

SF_6

Q9.6.7

A 0.245-L flask contains 0.467 mol CO_2 at 159 °C. Calculate the pressure:

a. using the ideal gas law
b. using the van der Waals equation
c. Explain the reason for the difference.
d. Identify which correction (that for P or V) is dominant and why.

Q9.6.8

Answer the following questions:

a. If XX behaved as an ideal gas, what would its graph of Z vs. P look like?
b. For most of this chapter, we performed calculations treating gases as ideal. Was this justified?
c. What is the effect of the volume of gas molecules on Z? Under what conditions is this effect small? When is it large? Explain using an appropriate diagram.
d. What is the effect of intermolecular attractions on the value of Z? Under what conditions is this effect small? When is it large? Explain using an appropriate diagram.
e. In general, under what temperature conditions would you expect Z to have the largest deviations from the Z for an ideal gas?

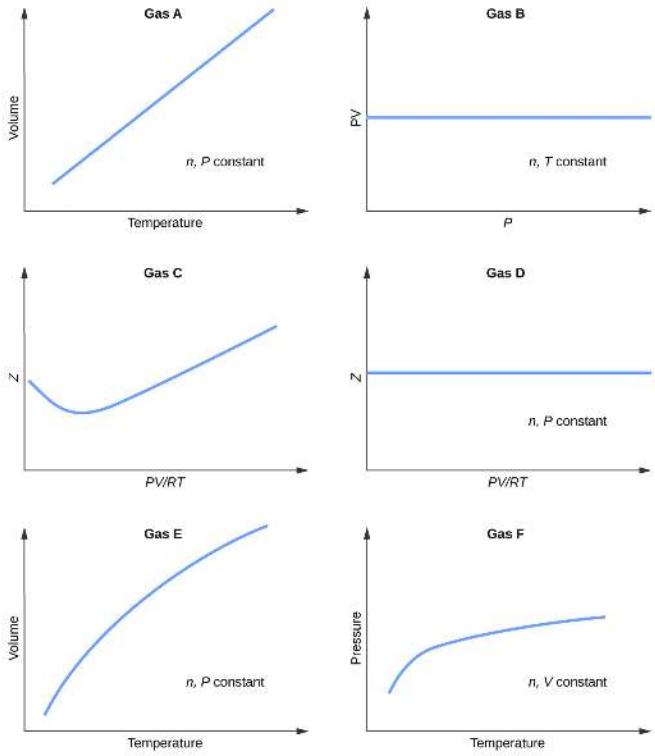
S9.6.8

(a) A straight horizontal line at 1.0; (b) When real gases are at low pressures and high temperatures they behave close enough to ideal gases that they are approximated as such, however, in some cases, we see that at a high pressure and temperature, the ideal gas approximation breaks down and is significantly different from the pressure calculated by the van der Waals equation (c) The greater the compressibility, the more the volume matters. At low pressures, the correction factor for intermolecular attractions is more significant, and the effect of the volume of the gas molecules on Z would be a small lowering compressibility. At higher pressures, the effect of the volume of the gas molecules themselves on Z would increase compressibility (see Figure) (d) Once again, at low pressures, the effect of intermolecular attractions on Z would be more important than the correction factor for the volume of the gas molecules themselves, though perhaps still small. At higher pressures and low temperatures, the effect of intermolecular attractions would be larger. See Figure. (e) low temperatures

9.6: Non-Ideal Gas Behavior

Exercises

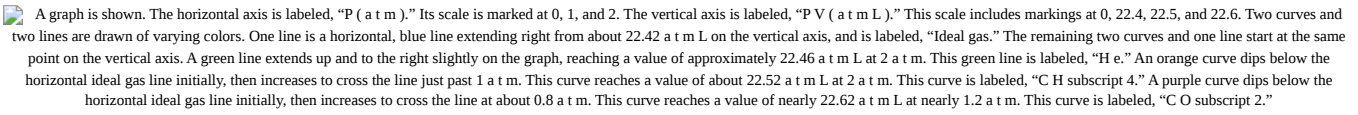
Graphs showing the behavior of several different gases follow. Which of these gases exhibit behavior significantly different from that expected for ideal gases?



Gases C, E, and F

https://chem.libretexts.org/@go/page/216766

Explain why the plot of *PV* for CO_2 differs from that of an ideal gas.



Under which of the following sets of conditions does a real gas behave most like an ideal gas, and for which conditions is a real gas expected to deviate from ideal behavior? Explain.

(a) high pressure, small volume

(b) high temperature, low pressure

(c) low temperature, high pressure

The gas behavior most like an ideal gas will occur under the conditions in (b). Molecules have high speeds and move through greater distances between collision; they also have shorter contact times and interactions are less likely. Deviations occur with the conditions described in (a) and (c). Under conditions of (a), some gases may liquefy. Under conditions of (c), most gases will liquefy.

Describe the factors responsible for the deviation of the behavior of real gases from that of an

ideal gas.

For which of the following gases should the correction for the molecular volume be largest:

CO, CO_2, H_2, He, NH_3, SF_6?

SF_6

A 0.245-L flask contains 0.467 mol CO_2 at 159 °C. Calculate the pressure:

(a) using the ideal gas law

(b) using the van der Waals equation

(c) Explain the reason for the difference.

(d) Identify which correction (that for P or V) is dominant and why.

Answer the following questions:

(a) If XX behaved as an ideal gas, what would its graph of Z vs. P look like?

(b) For most of this chapter, we performed calculations treating gases as ideal. Was this justified?

(c) What is the effect of the volume of gas molecules on Z? Under what conditions is this effect small? When is it large? Explain using an appropriate diagram.

(d) What is the effect of intermolecular attractions on the value of Z? Under what conditions is this effect small? When is it large? Explain using an appropriate diagram.

(e) In general, under what temperature conditions would you expect Z to have the largest deviations from the Z for an ideal gas?

(a) A straight horizontal line at 1.0; (b) When real gases are at low pressures and high temperatures they behave close enough to ideal gases that they are approximated as such, however, in some cases, we see that at a high pressure and temperature, the ideal gas approximation breaks down and is significantly different from the pressure calculated by the van der Waals equation (c) The greater the compressibility, the more the volume matters. At low pressures, the correction factor for intermolecular attractions is more significant, and the effect of the volume of the gas molecules on Z would be a small lowering compressibility. At higher pressures, the effect of the volume of the gas molecules themselves on Z would increase compressibility (see Figure) (d) Once again, at low pressures, the effect of intermolecular attractions on Z would be more important than the correction factor for the volume of the gas molecules themselves, though perhaps still small. At higher pressures and low temperatures, the effect of intermolecular attractions would be larger. See Figure. (e) low temperatures

This page titled 7.E: Gases (Exercises) is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

https://chem.libretexts.org/@go/page/216766

CHAPTER OVERVIEW

8: Thermochemistry

A general chemistry Libretexts Textmap organized around the textbook
General Chemistry -Atoms First
By OpenStax

I II III IV V VI VII VIII IX X XI XII XIII XIV XV XVI XVII XVIII XIX XX XXI ● **Homework**

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.

8.1: Energy Basics

8.2: Enthalpy

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 8: Thermochemistry is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

8.1: 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

Chemical changes and their accompanying changes in energy are important parts of our everyday world (Figure **8.1.1**). 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.



(a) (b) (c)

Figure **8.1.1**: 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.

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 **8.1.2**). A battery has potential energy because the chemicals within it can produce electricity that can do work.



(a) (b)

Figure **8.1.2**: (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).

Two pictures are shown and labeled a and b. Picture a shows a large waterfall with water falling from a high elevation at the top of the falls to a lower elevation. The second picture is a view looking down into the Hoover Dam. Water is shown behind the high wall of the dam on one side and at the base of the dam on the other.

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.

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 **8.1.3**). 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.

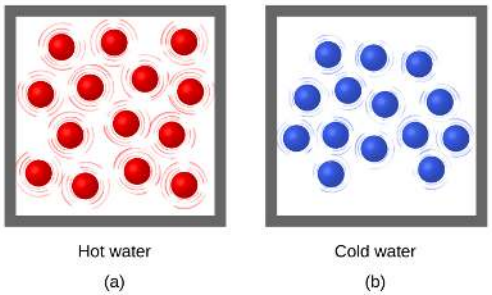
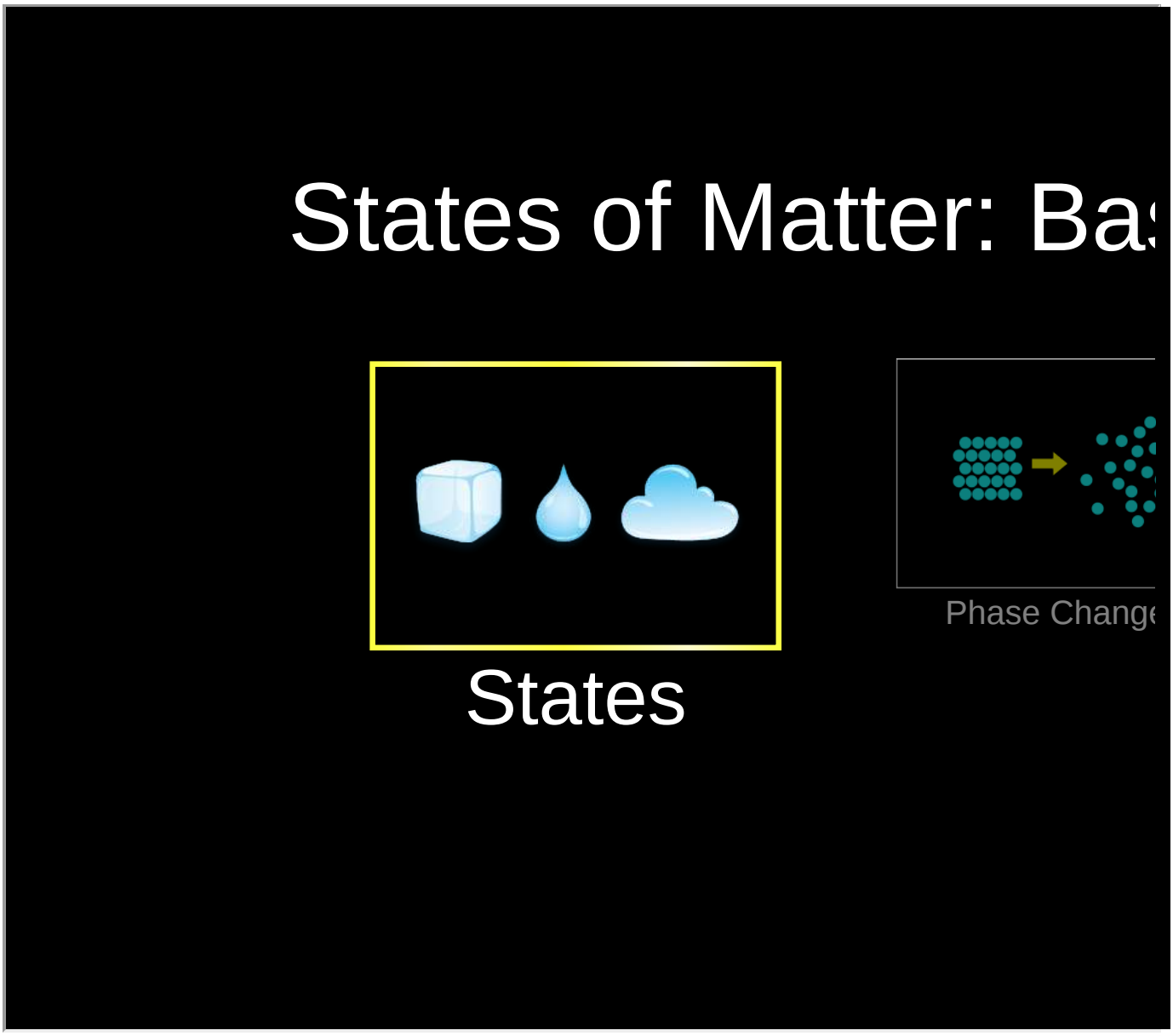


Figure **8.1.3**: (a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water.

Two molecular drawings are shown and labeled a and b. Drawing a is a box containing fourteen red spheres that are surrounded by lines indicating that the particles are moving rapidly. This drawing has a label that reads “Hot water.” Drawing b depicts another box of equal size that also contains fourteen spheres, but these are blue. They are all surrounded by smaller lines that depict some particle motion, but not as much as in drawing a. This drawing has a label that reads “Cold water.”



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)

$$C = \frac{q}{\Delta T} \tag{8.1.1}$$

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

$$C_{\text{small pan}} = \frac{18,140\ \text{J}}{50.0\ ^\circ\text{C}} = 363\ \text{J/°C} \tag{8.1.2}$$

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:

$$C_{\text{large pan}} = \frac{90,700\ \text{J}}{50.0\ ^\circ\text{C}} = 1814\ \text{J/°C} \tag{8.1.3}$$

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):

$$c = \frac{q}{\text{m}\Delta\text{T}} \tag{8.1.4}$$

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:

$$c_{\text{iron}} = \frac{18,140\ \text{J}}{(808\ \text{g})(50.0\ ^\circ\text{C})} = 0.449\ \text{J/g °C} \tag{8.1.5}$$

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:

$$c_{\text{iron}} = \frac{90,700\ \text{J}}{(4,040\ \text{g})(50.0\ ^\circ\text{C})} = 0.449\ \text{J/g °C} \tag{8.1.6}$$

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 **8.1.7**).



Figure **8.1.7**: 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).

The picture shows two black metal frying pans sitting on a flat surface. The left pan is about half the size of the right pan.

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 **8.1.1**.

Table **8.1.1**: 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
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
air		1.007
oxygen	$O_2(g)$	0.918
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
silicon	$Si(s)$	0.712

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:

$$q = (\text{specific heat}) \times (\text{mass of substance}) \times (\text{temperature change})$$
$$q = c \times m \times \Delta T$$
$$= c \times m \times (T_{\text{final}} - T_{\text{initial}})$$

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 8.1.1: 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:

$$\begin{aligned} q &= c \times m \times \Delta T \\ &= c \times m \times (T_{\text{final}} - T_{\text{initial}}) \\ &= (4.184\ \text{J/}\cancel{\text{g}}^{\circ}\text{C}) \times (800\ \cancel{\text{g}}) \times (85 - 21)^{\circ}\text{C} \\ &= (4.184\ \text{J/}\cancel{\text{g}}^{\circ}\cancel{\text{C}}) \times (800\ \cancel{\text{g}}) \times (64)^{\circ}\cancel{\text{C}} \\ &= 210,000\ \text{J} (= 210\ \text{kJ}) \end{aligned}$$

Because the temperature increased, the water absorbed heat and q is positive.

Exercise 8.1.1

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 8.1.2: Determining Other Quantities

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:

$$q = c \times m \times \Delta T$$
$$= c \times m \times (T_{\text{final}} - T_{\text{initial}})$$

Substituting the known values:

$$6,640 \text{ J} = c \times (348 \text{ g}) \times (43.6 - 22.4) \text{ °C}$$

Solving:

$$c = \frac{6,640 \text{ J}}{(348 \text{ g}) \times (21.2 \text{°C})} = 0.900 \text{ J/g °C}$$

Comparing this value with the values in Table 8.1.1, this value matches the specific heat of aluminum, which suggests that the unknown metal may be aluminum.

? Exercise 8.1.2

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

$c = 0.45 \text{ J/g °C}$; the metal is likely to be iron from checking Table 8.1.1.

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 8.1.8). 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.

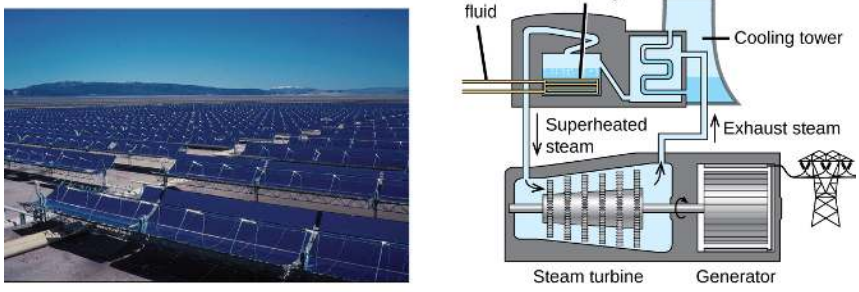


Figure 8.1.8: This solar thermal plant uses parabolic trough mirrors to concentrate sunlight. (credit a: modification of work by Bureau of Land Management)

This figure has two parts labeled a and b. Part a shows rows and rows of trough mirrors. Part b shows how a solar thermal plant works. Heat transfer fluid enters a tank via pipes. The tank contains water which is heated. As the heat is exchanged from the pipes to the water, the water becomes steam. The steam travels to a steam turbine. The steam turbine begins to turn which powers a generator. Exhaust steam exits the steam turbine and enters a cooling tower.

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 8.1.9). 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.



(a) (b)

Figure 8.1.9: (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)

Two pictures are shown and labeled a and b. Picture a shows a thermal plant with three tall metal towers. Picture b is an arial picture of the mirrors used at the plant. They are arranged in rows.

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.

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 8.1: Energy Basics is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

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

8.2: Enthalpy

Learning Objectives

- State the first law of thermodynamics
- Define enthalpy
- Identify endothermic and exothermic reactions from their enthalpy values

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 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.

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.

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).

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.

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.

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 ΔH 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:

$$\mathrm{H_2(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow H_2O(l)} \quad \Delta H = -286\ \mathrm{kJ} \tag{8.2.1}$$

   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).

Multiple \label

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.

$$\mathrm{H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow H_2O\,(g)} \quad \Delta H = -242\ k\,\mathrm{J} \tag{8.2.2}$$

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 8.2.1: 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 ?

$$\mathrm{HCl\,(aq) + NaOH\,(aq) \ \rightarrow NaCl\,(aq) + H_2O\,(l)} \tag{8.2.3}$$

Solution

For the reaction of 0.0500 mol acid (HCl), q = −2.9 kJ. This ratio

$$\frac{-2.9\ \mathrm{kJ}}{0.0500\ \mathrm{mol\ HCl}} \tag{8.2.4}$$

can be used as a conversion factor to find the heat produced when 1 mole of HCl reacts:

$$\Delta H = 1\ \cancel{\mathrm{mol\ HCl}} \times \frac{-2.9\ \mathrm{kJ}}{0.0500\ \cancel{\mathrm{mol\ HCl}}} = -58\ \mathrm{kJ} \tag{8.2.5}$$

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:

$$\mathrm{HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}} \quad \Delta H = -58\ \mathrm{kJ} \tag{8.2.6}$$

Exercise 8.2.1

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:

$$\mathrm{Zn_{(s)} + 2\,HCl_{(aq)} \longrightarrow ZnCl_{(aq)} + H_{2(g)}} \tag{8.2.7}$$

Answer

ΔH = −153 kJ

Be sure to take both stoichiometry and limiting reactants into account when determining the Δ*H* for a chemical reaction.

Example 8.2.2: Another Example of the Measurement of an Enthalpy Change

A gummy bear contains 2.67 g sucrose, $C_{12}H_{22}O_{11}$. When it reacts with 7.19 g potassium chlorate, $KClO_3$, 43.7 kJ of heat are produced. Determine the enthalpy change for the reaction

$$\mathrm{C_{12}H_{22}O_{11}(aq) + 8\,KClO_3(aq) \longrightarrow 12\,CO_2(g) + 11\,H_2O(l) + 8\,KCl(aq)} \tag{8.2.8}$$

Solution

We have $2.67\ \cancel{g} \times \dfrac{1\ \mathrm{mol}}{342.3\ \cancel{g}} = 0.00780\ \mathrm{mol\ C_{12}H_{22}O_{11}}$ available, and

$7.19\ \cancel{g} \times \dfrac{1\ \mathrm{mol}}{122.5\ \cancel{g}} = 0.0587\ \mathrm{mol\ KClO_3}$ available.

Since

$$0.0587\ \text{mol}\ KClO_3 \times \frac{1\ \text{mol}\ C_{12}H_{22}O_{11}}{8\ \text{mol}\ KClO_3} = 0.00734\ \text{mol}\ C_{12}H_{22}O_{11}$$

is needed, $C_{12}H_{22}O_{11}$ is the excess reactant and $KClO_3$ is the limiting reactant.

The reaction uses 8 mol $KClO_3$, and the conversion factor is $\frac{-43.7\ \text{kJ}}{0.0587\ \text{mol}\ KClO_3}$, so we have $\Delta H = 8\ \text{mol} \times \frac{-43.7\ \text{kJ}}{0.0587\ \text{mol}\ KClO_3} = -5960\ \text{kJ}$. The enthalpy change for this reaction is −5960 kJ, and the thermochemical equation is:

$$C_{12}H_{22}O_{11} + 8\,KClO_3 \longrightarrow 12\,CO_2 + 11\,H_2O + 8\,KCl \quad \Delta H = -5960\ kJ \tag{8.2.9}$$

Exercise 8.2.2

When 1.42 g of iron reacts with 1.80 g of chlorine, 3.22 g of $FeCl_{2(s)}$ and 8.60 kJ of heat is produced. What is the enthalpy change for the reaction when 1 mole of $FeCl_2\,(s)$ is produced?

Answer

ΔH = −338 kJ

Enthalpy changes are typically tabulated for reactions in which both the reactants and products are at the same conditions.

Contributors

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°_{298} 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. A negative value of an enthalpy change, Δ*H*, indicates an **exothermic reaction**; a positive value of Δ*H* indicates an **endothermic reaction**.

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

Contributors

- 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 8.2: Enthalpy is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

CHAPTER OVERVIEW

9: Liquids and Solids

A general chemistry Libretexts Textmap organized around the textbook
General Chemistry -Atoms First
By OpenStax

I *II* *III* *IV* *V* *VI* *VII* *VIII* *IX* *X* *XI* *XII* *XIII* *XIV* *XV* *XVI* *XVII* *XVIII* *XIX* *XX* *XXI* ● **Homework**

The great distances between atoms and molecules in a gaseous phase, and the corresponding absence of any significant interactions between them, allows for simple descriptions of many physical properties that are the same for all gases, regardless of their chemical identities. As described in the final module of the chapter on gases, this situation changes at high pressures and low temperatures—conditions that permit the atoms and molecules to interact to a much greater extent. In the liquid and solid states, these interactions are of considerable strength and play an important role in determining a number of physical properties that *do* depend on the chemical identity of the substance. In this chapter, the nature of these interactions and their effects on various physical properties of liquid and solid phases will be examined.

9.1: Intermolecular Forces

9.2: Properties of Liquids

9.3: Phase Transitions

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 9: Liquids and Solids is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

9.1: Intermolecular Forces

Learning Objectives

- Describe the types of intermolecular forces possible between atoms or molecules in condensed phases (dispersion forces, dipole-dipole attractions, and hydrogen bonding)
- Identify the types of intermolecular forces experienced by specific molecules based on their structures
- Explain the relation between the intermolecular forces present within a substance and the temperatures associated with changes in its physical state

As was the case for gaseous substances, the kinetic molecular theory may be used to explain the behavior of solids and liquids. In the following description, the term *particle* will be used to refer to an atom, molecule, or ion. Note that we will use the popular phrase "intermolecular attraction" to refer to attractive forces between the particles of a substance, regardless of whether these particles are molecules, atoms, or ions.

Consider these two aspects of the molecular-level environments in solid, liquid, and gaseous matter:

- Particles in a solid are tightly packed together and often arranged in a regular pattern; in a liquid, they are close together with no regular arrangement; in a gas, they are far apart with no regular arrangement.
- Particles in a solid vibrate about fixed positions and do not generally move in relation to one another; in a liquid, they move past each other but remain in essentially constant contact; in a gas, they move independently of one another except when they collide.

The differences in the properties of a solid, liquid, or gas reflect the strengths of the attractive forces between the atoms, molecules, or ions that make up each phase. The phase in which a substance exists depends on the relative extents of its intermolecular forces (IMFs) and the kinetic energies (KE) of its molecules. IMFs are the various forces of attraction that may exist between the atoms and molecules of a substance due to electrostatic phenomena, as will be detailed in this module. These forces serve to hold particles close together, whereas the particles' KE provides the energy required to overcome the attractive forces and thus increase the distance between particles. Figure 9.1.1 illustrates how changes in physical state may be induced by changing the temperature, hence, the average KE, of a given substance.

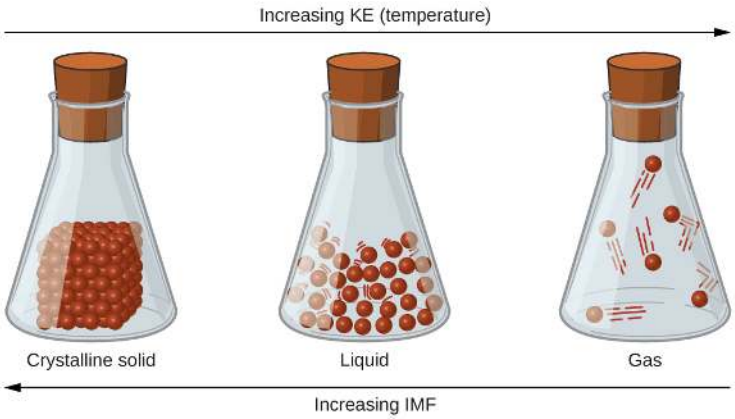


Figure 9.1.1: Transitions between solid, liquid, and gaseous states of a substance occur when conditions of temperature or pressure favor the associated changes in intermolecular forces. (Note: The space between particles in the gas phase is much greater than shown.)

Three sealed flasks are labeled, "Crystalline solid," "Liquid," and "Gas," from left to right. The first flask holds a cube composed of small spheres sitting on the bottom while the second flask shows a lot of small spheres in the bottom that are spaced a small distance apart from one another and have lines around them to indicate motion. The third flask shows a few spheres spread far from one another with larger lines to indicate motion. There is a right-facing arrow that spans the top of all three flasks. The arrow is labeled, "Increasing K E (temperature)." There is a left-facing arrow that spans the bottom of all three flasks. The arrow is labeled, "Increasing I M F."

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 **9.1.2**.



Figure **9.1.2**: Condensation forms when water vapor in the air is cooled enough to form liquid water, such as (a) on the outside of a cold beverage glass or (b) in the form of fog. (credit a: modification of work by Jenny Downing; credit b: modification of work by Cory Zanker)

Image a shows a brown colored beverage in a glass with condensation on the outside. Image b shows a body of water with fog hovering above the surface of the water.

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 **9.1.3**.



Figure **9.1.3**: Gaseous butane is compressed within the storage compartment of a disposable lighter, resulting in its condensation to the liquid state. (credit: modification of work by "Sam-Cat"/Flickr)

Finally, if the temperature of a liquid becomes sufficiently low, or the pressure on the liquid becomes sufficiently high, the molecules of the liquid no longer have enough KE to overcome the IMF between them, and a solid forms. A more thorough discussion of these and other changes of state, or phase transitions, is provided in a later module of this chapter.

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 **9.1.4** illustrates these different molecular forces. The strengths of these attractive forces vary widely, though usually the IMFs between small molecules are weak compared to the intramolecular forces that bond atoms together within a molecule. For example, to overcome the IMFs in one mole of liquid HCl and convert it into gaseous HCl requires only about 17 kilojoules. However, to break the covalent bonds between the hydrogen and chlorine atoms in one mole of HCl requires about 25 times more energy—430 kilojoules.

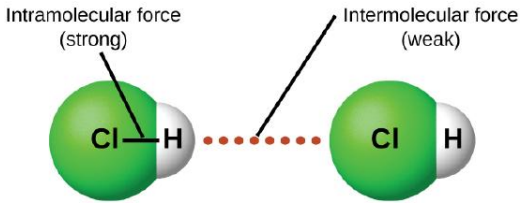


Figure **9.1.4**: Intramolecular forces keep a molecule intact. Intermolecular forces hold multiple molecules together and determine many of a substance's properties.

An image is shown in which two molecules composed of a green sphere labeled "C l" connected on the right to a white sphere labeled "H" are near one another with a dotted line labeled "Intermolecular force (weak)" drawn between them. A line connects the two spheres in each molecule and the line is labeled "Intramolecular force (strong)."

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 **9.1.5**.

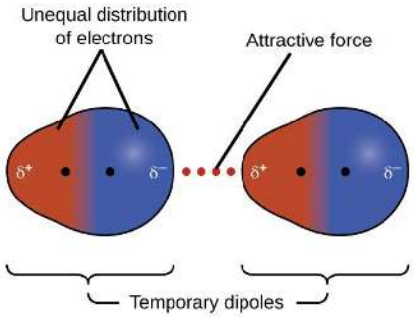


Figure **9.1.5**: Dispersion forces result from the formation of temporary dipoles, as illustrated here for two nonpolar diatomic molecules.

Two pairs of molecules are shown where each molecule has one larger blue side labeled "delta sign, negative sign" and a smaller red side labeled "delta sign, positive sign." Toward the middle of the both molecules, but still on each distinct side, is a black dot. Between the two images is a dotted line labeled, "Attractive force." In the first image, the red and blue sides are labeled, "Unequal distribution of electrons." Below both images are brackets. The brackets are labeled, "Temporary dipoles."

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 **9.1.1**.

Table **9.1.1**: Melting and Boiling Points of the Halogens

Halogen	Molar Mass	Atomic Radius	Melting Point	Boiling Point
fluorine, F_2	38 g/mol	72 pm	53 K	85 K
chlorine, Cl_2	71 g/mol	99 pm	172 K	238 K
bromine, Br_2	160 g/mol	114 pm	266 K	332 K
iodine, I_2	254 g/mol	133 pm	387 K	457 K
astatine, At_2	420 g/mol	150 pm	575 K	610 K

The increase in melting and boiling points with increasing atomic/molecular size may be rationalized by considering how the strength of dispersion forces is affected by the electronic structure of the atoms or molecules in the substance. In a larger atom, the valence electrons are, on average, farther from the nuclei than in a smaller atom. Thus, they are less tightly held and can more easily form the temporary dipoles that produce the attraction. The measure of how easy or difficult it is for another electrostatic charge (for example, a nearby ion or polar molecule) to distort a molecule's charge distribution (its electron cloud) is known as polarizability. A molecule that has a charge cloud that is easily distorted is said to be very polarizable and will have large dispersion forces; one with a charge cloud that is difficult to distort is not very polarizable and will have small dispersion forces.

Example **9.1.1**: London Forces and Their Effects

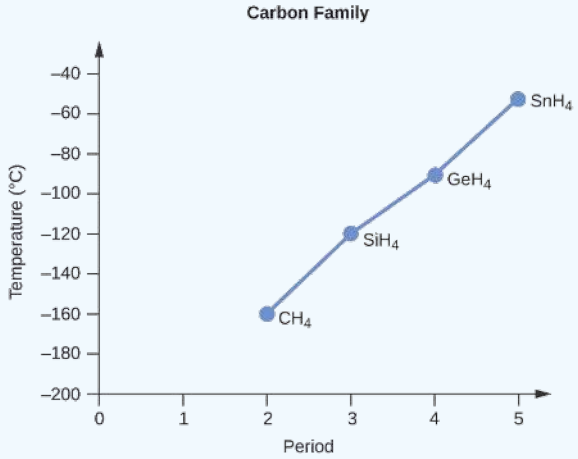
Order the following compounds of a group 14 element and hydrogen from lowest to highest boiling point: CH_4, SiH_4, GeH_4, and SnH_4. Explain your reasoning.

Solution

Applying the skills acquired in the chapter on chemical bonding and molecular geometry, all of these compounds are predicted to be nonpolar, so they may experience only dispersion forces: the smaller the molecule, the less polarizable and the weaker the dispersion forces; the larger the molecule, the larger the dispersion forces. The molar masses of CH_4, SiH_4, GeH_4, and SnH_4 are approximately 16 g/mol, 32 g/mol, 77 g/mol, and 123 g/mol, respectively. Therefore, CH_4 is expected to have the lowest boiling point and SnH_4 the highest boiling point. The ordering from lowest to highest boiling point is expected to be

$$CH_4 < SiH_4 < GeH_4 < SnH_4$$

A graph of the actual boiling points of these compounds versus the period of the group 14 elements shows this prediction to be correct:



A line graph, titled “Carbon Family,” is shown where the y-axis is labeled “Temperature, (degree sign C)” and has values of “negative 200” to “negative 40” from bottom to top in increments of 20. The x-axis is labeled “Period” and has values of “0” to “5” in increments of 1. The first point on the graph is labeled “C H subscript 4” and is at point “2, negative 160.” The second point on the graph is labeled “S i H subscript 4” and is at point “3, negative 120” while the third point on the graph is labeled “G e H subscript 4” and is at point “4, negative 100.” The fourth point on the graph is labeled “S n H subscript 4” and is at point “5, negative 60.”

? Exercise 9.1.1

Order the following hydrocarbons from lowest to highest boiling point: C_2H_6, C_3H_8, and C_4H_{10}.

Answer

All of these compounds are nonpolar and only have London dispersion forces: the larger the molecule, the larger the dispersion forces and the higher the boiling point. The ordering from lowest to highest boiling point is therefore

$$C_2H_6 < C_3H_8 < C_4H_{10}.$$

The shapes of molecules also affect the magnitudes of the dispersion forces between them. For example, boiling points for the isomers *n*-pentane, isopentane, and neopentane (shown in Figure **9.1.6**) are 36 °C, 27 °C, and 9.5 °C, respectively. Even though these compounds are composed of molecules with the same chemical formula, C_5H_{12}, the difference in boiling points suggests that dispersion forces in the liquid phase are different, being greatest for *n*-pentane and least for neopentane. The elongated shape of *n*-pentane provides a greater surface area available for contact between molecules, resulting in correspondingly stronger dispersion forces. The more compact shape of isopentane offers a smaller surface area available for intermolecular contact and, therefore, weaker dispersion forces. Neopentane molecules are the most compact of the three, offering the least available surface area for intermolecular contact and, hence, the weakest dispersion forces. This behavior is analogous to the connections that may be formed between strips of VELCRO brand fasteners: the greater the area of the strip’s contact, the stronger the connection.

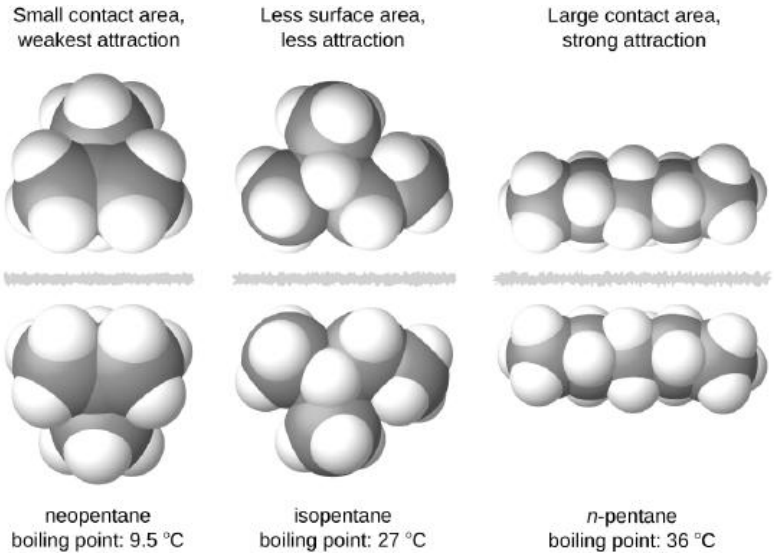


Figure **9.1.6**: The strength of the dispersion forces increases with the contact area between molecules, as demonstrated by the boiling points of these pentane isomers.

Three images of molecules are shown. The first shows a cluster of large, gray spheres each bonded together and to several smaller, white spheres. There is a gray, jagged line and then the mirror image of the first cluster of spheres is shown. Above these two clusters is the label, “Small contact area, weakest attraction,” and below is the label, “neopentane boiling point: 9.5 degrees C.” The second shows a chain of three gray spheres bonded by the middle sphere to a fourth gray sphere. Each gray sphere is bonded to several smaller, white spheres. There is a jagged, gray line and then the mirror image of the first chain appears. Above these two chains is the label, “Less surface area, less attraction,” and below is the label, “isopentane boiling point: 27 degrees C.” The third image shows a chain of five gray spheres bonded together and to several smaller, white spheres. There is a jagged gray line and then the mirror image of the first chain appears. Above these chains is the label, “Large contact area, strong attraction,” and below is the label, “n-pentane boiling point 36 degrees C.”

Applications: Geckos and Intermolecular Forces

Geckos have an amazing ability to adhere to most surfaces. They can quickly run up smooth walls and across ceilings that have no toe-holds, and they do this without having suction cups or a sticky substance on their toes. And while a gecko can lift its feet easily as it walks along a surface, if you attempt to pick it up, it sticks to the surface. How are geckos (as well as spiders and some other insects) able to do this? Although this phenomenon has been investigated for hundreds of years, scientists only recently uncovered the details of the process that allows geckos’ feet to behave this way.

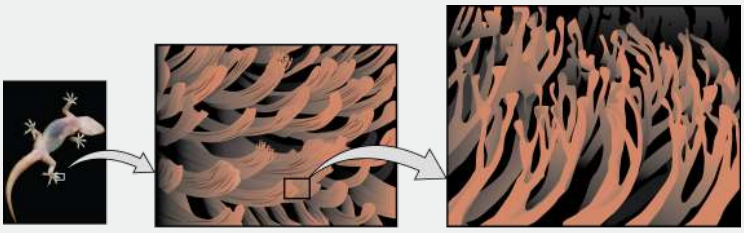


Figure **9.1.7**: Geckos’ toes contain large numbers of tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko’s millions of spatulae. By changing how the spatulae contact the surface, geckos can turn their stickiness “on” and “off.” (credit photo: modification of work by “JC*+A!”/Flickr)

Three figures are shown. The first is a photo of the bottom of a gecko’s foot. The second is bigger version which shows the setae. The third is a bigger version of the setae and shows the spatulae.

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 **9.1.7**, with a large total surface area for sticking to a surface. In 2000, Kellar Autumn, who leads a multi-institutional gecko research team, found that geckos adhered equally well to both polar silicon dioxide and nonpolar gallium arsenide. This proved that geckos stick to surfaces because of dispersion forces—weak intermolecular attractions arising from temporary,

synchronized charge distributions between adjacent molecules. Although dispersion forces are very weak, the total attraction over millions of spatulae is large enough to support many times the gecko's weight.

In 2014, two scientists developed a model to explain how geckos can rapidly transition from "sticky" to "non-sticky." Alex Greaney and Congcong Hu at Oregon State University described how geckos can achieve this by changing the angle between their spatulae and the surface. Geckos' feet, which are normally nonsticky, become sticky when a small shear force is applied. By curling and uncurling their toes, geckos can alternate between sticking and unsticking from a surface, and thus easily move across it. Further investigations may eventually lead to the development of better adhesives and other applications.



Watch this video to learn more about Kellar Autumn's research that determined that van der Waals forces are responsible for a gecko's ability to cling and climb.

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 9.1.8.

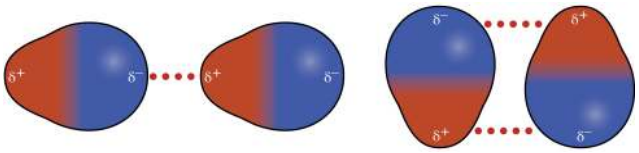


Figure 9.1.8: This image shows two arrangements of polar molecules, such as HCl, that allow an attraction between the partial negative end of one molecule and the partial positive end of another.

Two pairs of molecules are shown where each molecule has one larger blue side labeled "delta sign, negative sign" and a smaller red side labeled "delta sign, positive sign. In the first pair, the red sides of the two molecules both face to the left and the blue side to the right. A horizontal dotted line lies in between the two. In the second pair, the molecules face up and down, with the red and blue ends aligning. A horizontal dotted line lies between the red and blue ends facing upward and another lies between the red and blue ends facing downward.

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 9.1.2: Dipole-Dipole Forces and Their Effects

Predict which will have the higher boiling point: N_2 or CO. Explain your reasoning.

Solution

CO and N_2 are both diatomic molecules with masses of about 28 amu, so they experience similar London dispersion forces. Because CO is a polar molecule, it experiences dipole-dipole attractions. Because N_2 is nonpolar, its molecules cannot exhibit dipole-dipole attractions. The dipole-dipole attractions between CO molecules are comparably stronger than the dispersion forces between nonpolar N_2 molecules, so CO is expected to have the higher boiling point.

A common method for preparing oxygen is the decomposition

Exercise 9.1.2

Predict which will have the higher boiling point: **ICl** or **Br_2**. Explain your reasoning.

Answer

ICl. ICl and Br_2 have similar masses (~160 amu) and therefore experience similar London dispersion forces. ICl is polar and thus also exhibits dipole-dipole attractions; Br_2 is nonpolar and does not. The relatively stronger dipole-dipole attractions require more energy to overcome, so ICl will have the higher boiling point.

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 9.1.9 illustrates hydrogen bonding between water molecules.

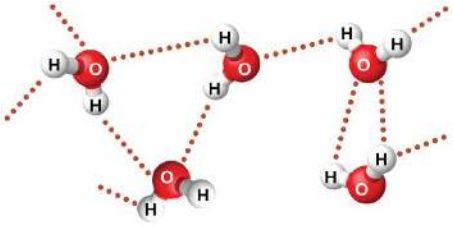


Figure 9.1.9: Water molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.

Five water molecules are shown near one another, but not touching. A dotted line lies between many of the hydrogen atoms on one molecule and the oxygen atom on another molecule.

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 **9.1.10**. As we progress down any of these groups, the polarities of the molecules decrease slightly, whereas the sizes of the molecules increase substantially. The effect of increasingly stronger dispersion forces dominates that of increasingly weaker dipole-dipole attractions, and the boiling points are observed to increase steadily. For the group 15, 16, and 17 hydrides, the boiling points for each class of compounds increase with increasing molecular mass for elements in periods 3, 4, and 5.

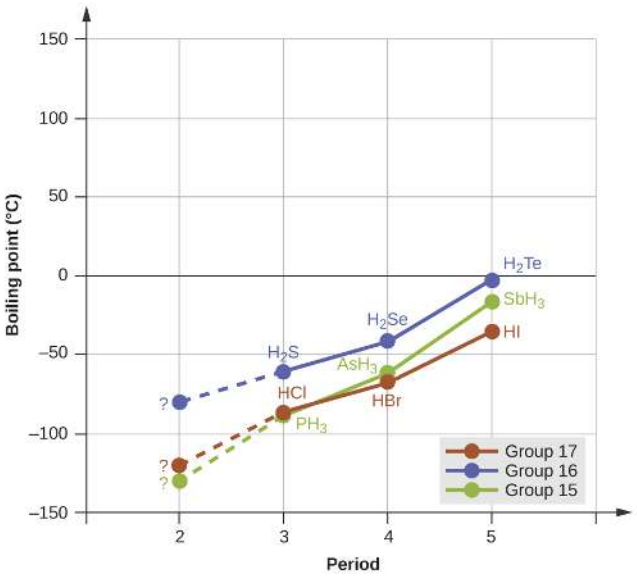


Figure **9.1.10**: In comparison to periods 3−5, the binary hydrides of period 2 elements in groups 17, 16 and 15 (F, O and N, respectively) exhibit anomalously high boiling points due to hydrogen bonding.

A line graph is shown where the y-axis is labeled “Boiling point (, degree sign, C)” and has values of “ negative 150” to “150” from bottom to top in increments of 50. The x-axis is labeled “Period” and has values of “0” to “5” in increments of 1. Three lines are shown on the graph and are labeled in the legend. The red line is labeled as “halogen family,” the blue is “oxygen family” and the green is “nitrogen family.” The first point on the red line is labeled “question mark” and is at point “2, negative 120”. The second point on the line is labeled “H C l” and is at point “3, negative 80” while the third point on the line is labeled “H B r” and is at point “4, negative 60”. The fourth point on the line is labeled “H I” and is at point “5, negative 40.” The first point on the green line is labeled “question mark” and is at point “2, negative 125.” The second point on the line is labeled “P H, subscript 3” and is at point “3, negative 80” while the third point on the line is labeled “A s H, subscript 3” and is at point “4, negative 55.” The fourth point on the line is labeled “S b H, subscript 3” and is at point “5, negative 10.” The first point on the blue line is labeled “question mark” and is at point “2, negative 80.” The second point on the line is labeled “H, subscript 2, S” and is at point “3, negative 55” while the third point on the line is labeled “H, subscript 2, S e” and is at point “4, negative 45.” The fourth point on the line is labeled “H, subscript 2, T e” and is at point “5, negative 3.”

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 **9.1.10**. The stark contrast between our naïve predictions and reality provides compelling evidence for the strength of hydrogen bonding.

✔ Example 9.1.3: Effect of Hydrogen Bonding on Boiling Points

Consider the compounds dimethylether (CH_3OCH_3), ethanol (CH_3CH_2OH), and propane ($CH_3CH_2CH_3$). Their boiling points, not necessarily in order, are −42.1 °C, −24.8 °C, and 78.4 °C. Match each compound with its boiling point. Explain your reasoning.

Solution

The VSEPR-predicted shapes of CH_3OCH_3, CH_3CH_2OH, and $CH_3CH_2CH_3$ are similar, as are their molar masses (46 g/mol, 46 g/mol, and 44 g/mol, respectively), so they will exhibit similar dispersion forces. Since $CH_3CH_2CH_3$ is nonpolar, it may

exhibit *only* dispersion forces. Because CH_3OCH_3 is polar, it will also experience dipole-dipole attractions. Finally, CH_3CH_2OH has an −OH group, and so it will experience the uniquely strong dipole-dipole attraction known as hydrogen bonding. So the ordering in terms of strength of IMFs, and thus boiling points, is $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CH_2OH$. The boiling point of propane is −42.1 °C, the boiling point of dimethylether is −24.8 °C, and the boiling point of ethanol is 78.5 °C.

? Exercise 9.1.3

Ethane (CH_3CH_3) has a melting point of −183 °C and a boiling point of −89 °C. Predict the melting and boiling points for methylamine (CH_3NH_2). Explain your reasoning.

Answer

The melting point and boiling point for methylamine are predicted to be significantly greater than those of ethane. CH_3CH_3 and CH_3NH_2 are similar in size and mass, but methylamine possesses an −NH group and therefore may exhibit hydrogen bonding. This greatly increases its IMFs, and therefore its melting and boiling points. It is difficult to predict values, but the known values are a melting point of −93 °C and a boiling point of −6 °C.

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 **9.1.10**.

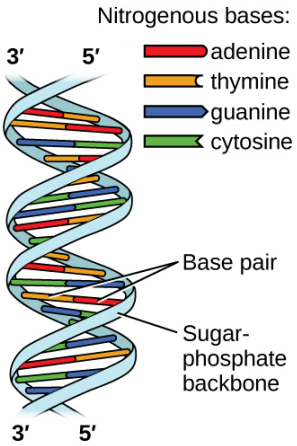


Figure 9.1.11: Two separate DNA molecules form a double-stranded helix in which the molecules are held together via hydrogen bonding. (credit: modification of work by Jerome Walker, Dennis Myts)

Two images are shown. The first lies on the left side of the page and shows a helical structure like a twisted ladder where the rungs of the ladder, labeled “Base pair” are red, yellow, green and blue paired bars. The red and yellow bars, which are always paired together, are labeled in the legend, which is titled “Nitrogenous bases” as “adenine” and “thymine,” respectively. The blue and green bars, which are always paired together, are labeled in the legend as “guanine” and “cytosine,” respectively. At the top of the helical structure, the left-hand side rail, or “Sugar, dash, phosphate backbone,” is labeled as “3, prime” while the right is labeled as “5, prime.” These labels are reversed at the bottom of the helix. To the right of the page is a large Lewis structure. The top left corner of this structure, labeled “5, prime,” shows a phosphorus atom single bonded to three oxygen atoms, one of which has a superscripted negative charge, and double bonded to a fourth oxygen atom. One of the single bonded oxygen atoms is single bonded to the left corner of a five-membered ring with an oxygen atom at its top point and which is single bonded to an oxygen atom on the bottom left. This oxygen atom is single bonded to a phosphorus atom that is single bonded to two other hydrogen atoms and double bonded to a fourth oxygen atom. The lower left of these oxygen atoms is single bonded to another oxygen atom that is single bonded to a five-membered ring with an oxygen in the upper bonding site. The bottom left of this ring has a hydroxyl group attached to it while the upper right carbon is single bonded to a nitrogen atom that is part of a five-membered ring bonded to a six-membered ring. Both of these rings have points of unsaturation and nitrogen atoms bonded into their structures. On the right side of the six-membered ring are two single bonded amine groups and a double bonded oxygen. Three separate dotted lines extend from these sites to corresponding sites on a second six-membered ring. This ring has points of unsaturation and a nitrogen atom in the bottom right bonding position that is single bonded to a five-membered ring on the right side of the image. This ring is single bonded to a carbon that is single bonded to an oxygen that is single bonded to a phosphorus. The phosphorus is single bonded to two other oxygen atoms and double bonded to a fourth oxygen atom. This group is labeled “5, prime.” The five-membered ring is also bonded on the top side to an oxygen that is bonded to a phosphorus single bonded to two other oxygen atoms and double bonded to a fourth oxygen atom. The upper left oxygen of this group is single bonded to a carbon that is single bonded to a five-membered ring with an oxygen in the bottom bonding position. This ring has a hydroxyl group on its upper right side that is labeled “3, prime” and is bonded on the left side to a nitrogen that is a member of a five-membered ring. This ring is bonded to a six-membered ring and both have points of unsaturation. This ring has a nitrogen on the left side, as well as an amine group, that have two dotted lines leading from them to an oxygen and amine group on a six membered ring. These dotted lines are labeled “Hydrogen bonds.” The six membered ring also has a double bonded oxygen on its lower side and a nitrogen atom on its left side that is single bonded to a five-membered ring. This ring connects to the two phosphate groups mentioned at the start of this to form a large circle. The name “guanine” is written below the lower left side of this image while the name “cytosine” is written on the lower right. The name “thymine” is written above the right side of the image and “adenine” is written on the top right. Three sections are indicated below the images where the left is labeled “Sugar, dash, phosphate backbone,” the middle is labeled “Bases” and the right is labeled “Sugar, dash, phosphate backbone.”

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 9.1.12

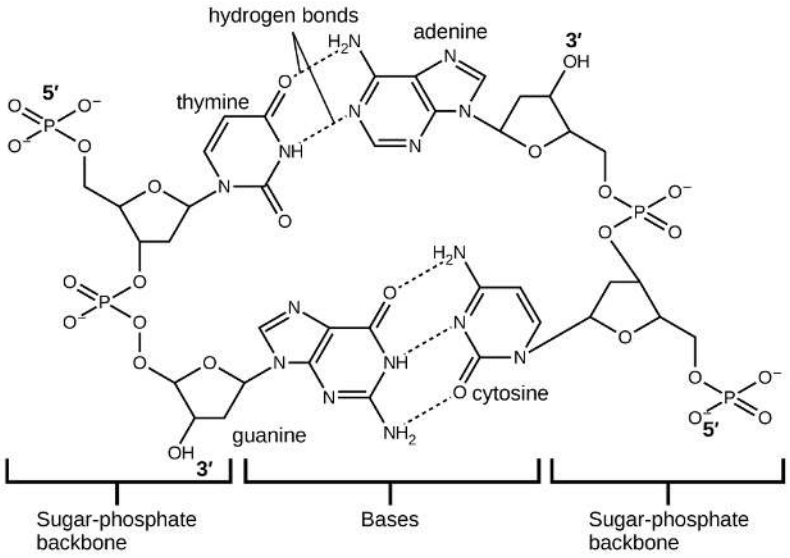


Figure 9.1.12: The geometries of the base molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called “complementary base pairs.”

A large Lewis structure is shown. The top left corner of this structure, labeled “5, prime,” shows a phosphorus atom single bonded to three oxygen atoms, one of which has a superscripted negative charge, and double bonded to a fourth oxygen atom. One of the single bonded oxygen atoms is single bonded to the left corner of a five-membered ring with an oxygen atom at its top point and which is single bonded to an oxygen atom on the bottom left. This oxygen atom is single bonded to a phosphorus atom that is single bonded to two other hydrogen atoms and double bonded to a fourth oxygen atom. The lower left of these oxygen atoms is single bonded to another oxygen atom that is single bonded to a five-membered ring with an oxygen in the upper bonding site. The bottom left of this ring has a hydroxyl group attached to it while the upper right carbon is single bonded to a nitrogen atom that is part of a five-membered ring bonded to a six-membered ring. Both of these rings have points of unsaturation and nitrogen atoms bonded into their structures. On the right side of the six-membered ring are two single bonded amine groups and a double bonded oxygen. Three separate dotted lines extend from these sites to corresponding sites on a second six-membered ring. This ring has points of unsaturation and a nitrogen atom in the bottom right bonding position that is single bonded to a five-membered ring on the right side of the image. This ring is single bonded to a carbon that is single bonded to an oxygen that is single bonded to a phosphorus. The phosphorus is single bonded to two other oxygen atoms and double bonded to a fourth oxygen atom. This group is labeled “5, prime.” The five-membered ring is also bonded on the top side to an oxygen that is bonded to a phosphorus single bonded to two other oxygen atoms and double bonded to a fourth oxygen atom. The upper left oxygen of this group is single bonded to a carbon that is single bonded to a five-membered ring with an oxygen in the bottom bonding position. This ring has a hydroxyl group on its upper right side that is labeled “3, prime” and is bonded on the left side to a nitrogen that is a member of a five-membered ring. This ring is bonded to a six-membered ring and both have points of unsaturation. This ring has a nitrogen on the left side, as well as an amine group, that have two dotted lines leading from them to an oxygen and amine group on a six membered ring. These dotted lines are labeled “Hydrogen bonds.” The six membered ring also has a double bonded oxygen on its lower side and a nitrogen atom on its left side that is single bonded to a five-membered ring. This ring connects to the two phosphate groups mentioned at the start of this to form a large circle. The name “guanine” is written below the lower left side of this image while the name “cytosine” is written on the lower right. The name “thymine” is written above the right side of the image and “adenine” is written on the top right. Three sections are indicated below the images where the left is labeled “Sugar, dash, phosphate backbone,” the middle is labeled “Bases” and the right is labeled “Sugar, dash, phosphate backbone.”

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.

Summary

The physical properties of condensed matter (liquids and solids) can be explained in terms of the kinetic molecular theory. In a liquid, intermolecular attractive forces hold the molecules in contact, although they still have sufficient kinetic energy to move past each other. Intermolecular attractive forces, collectively referred to as van der Waals forces, are responsible for the behavior of liquids and solids and are electrostatic in nature. Dipole-dipole attractions result from the electrostatic attraction of the partial negative end of one dipolar molecule for the partial positive end of another. The temporary dipole that results from the motion of the electrons in an atom can induce a dipole in an adjacent atom and give rise to the London dispersion force. London forces

increase with increasing molecular size. Hydrogen bonds are a special type of dipole-dipole attraction that results when hydrogen is bonded to one of the three most electronegative elements: F, O, or N.

Glossary

dipole-dipole attraction
intermolecular attraction between two permanent dipoles

dispersion force
(also, London dispersion force) attraction between two rapidly fluctuating, temporary dipoles; significant only when particles are very close together

hydrogen bonding
occurs when exceptionally strong dipoles attract; bonding that exists when hydrogen is bonded to one of the three most electronegative elements: F, O, or N

induced dipole
temporary dipole formed when the electrons of an atom or molecule are distorted by the instantaneous dipole of a neighboring atom or molecule

instantaneous dipole
temporary dipole that occurs for a brief moment in time when the electrons of an atom or molecule are distributed asymmetrically

intermolecular force
noncovalent attractive force between atoms, molecules, and/or ions

polarizability
measure of the ability of a charge to distort a molecule's charge distribution (electron cloud)

van der Waals force
attractive or repulsive force between molecules, including dipole-dipole, dipole-induced dipole, and London dispersion forces; does not include forces due to covalent or ionic bonding, or the attraction between ions and molecules

---

This page titled 9.1: Intermolecular Forces is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

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

9.2: Properties of Liquids

Learning Objectives

- Distinguish between adhesive and cohesive forces
- Define viscosity, surface tension, and capillary rise
- Describe the roles of intermolecular attractive forces in each of these properties/phenomena

When you pour a glass of water, or fill a car with gasoline, you observe that water and gasoline flow freely. But when you pour syrup on pancakes or add oil to a car engine, you note that syrup and motor oil do not flow as readily. The viscosity of a liquid is a measure of its resistance to flow. Water, gasoline, and other liquids that flow freely have a low viscosity. Honey, syrup, motor oil, and other liquids that do not flow freely, like those shown in Figure **9.2.1**, have higher viscosities. We can measure viscosity by measuring the rate at which a metal ball falls through a liquid (the ball falls more slowly through a more viscous liquid) or by measuring the rate at which a liquid flows through a narrow tube (more viscous liquids flow more slowly).



Figure **9.2.1**: (a) Honey and (b) motor oil are examples of liquids with high viscosities; they flow slowly. (credit a: modification of work by Scott Bauer; credit b: modification of work by David Nagy)

Two photographs are shown and labeled “a” and “b.” Photo a shows a jar of honey with a dipper drizzling it onto a biscuit. More biscuits are shown in a basket in the background. Photo b shows the engine of a car and a person adding motor oil to the engine.

The IMFs between the molecules of a liquid, the size and shape of the molecules, and the temperature determine how easily a liquid flows. As Table **9.2.1** shows, the more structurally complex are the molecules in a liquid and the stronger the IMFs between them, the more difficult it is for them to move past each other and the greater is the viscosity of the liquid. As the temperature increases, the molecules move more rapidly and their kinetic energies are better able to overcome the forces that hold them together; thus, the viscosity of the liquid decreases.

Table **9.2.1**: Viscosities of Common Substances at 25 °C

Substance	Formula	Viscosity (mPa·s)
water	H_2O	0.890
mercury	Hg	1.526
ethanol	C_2H_5OH	1.074
octane	C_8H_{18}	0.508
ethylene glycol	$CH_2(OH)CH_2(OH)$	16.1
honey	variable	~2,000–10,000
motor oil	variable	~50–500

The various IMFs between identical molecules of a substance are examples of cohesive forces. The molecules within a liquid are surrounded by other molecules and are attracted equally in all directions by the cohesive forces within the liquid. However, the molecules on the surface of a liquid are attracted only by about one-half as many molecules. Because of the unbalanced molecular

attractions on the surface molecules, liquids contract to form a shape that minimizes the number of molecules on the surface—that is, the shape with the minimum surface area. A small drop of liquid tends to assume a spherical shape, as shown in Figure **9.2.2**, because in a sphere, the ratio of surface area to volume is at a minimum. Larger drops are more greatly affected by gravity, air resistance, surface interactions, and so on, and as a result, are less spherical.

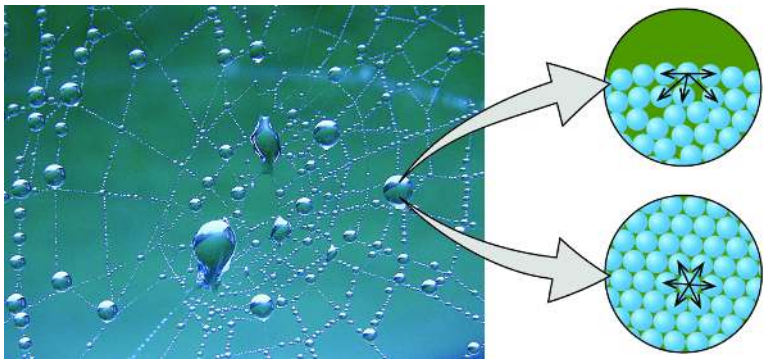


Figure **9.2.2**: Attractive forces result in a spherical water drop that minimizes surface area; cohesive forces hold the sphere together; adhesive forces keep the drop attached to the web. (credit photo: modification of work by "OliBac"/Flickr)

A photo of a spider's web with droplets of water attached to it is shown. Two images are shown the right of the photo and arrows lead from the photo to the images. The upper image shows twenty eight blue spheres stacked one atop the other in the bottom of a circular background. Five arrows are drawn pointing to the sides and downward from the sphere in the top middle of the drawing. The lower image shows another circular background of the same size as the first, but this time the blue spheres fill the image and are packed closely together. A sphere in the middle has six arrows pointing in all directions away from it.

Surface tension is defined as the energy required to increase the surface area of a liquid, or the force required to increase the length of a liquid surface by a given amount. This property results from the cohesive forces between molecules at the surface of a liquid, and it causes the surface of a liquid to behave like a stretched rubber membrane. Surface tensions of several liquids are presented in Table **9.2.2**.

Table **9.2.2**: Surface Tensions of Common Substances at 25 °C

Substance	Formula	Surface Tension (mN/m)
water	H_2O	71.99
mercury	Hg	458.48
ethanol	C_2H_5OH	21.97
octane	C_8H_{18}	21.14
ethylene glycol	$CH_2(OH)CH_2(OH)$	47.99

Among common liquids, water exhibits a distinctly high surface tension due to strong hydrogen bonding between its molecules. As a result of this high surface tension, the surface of water represents a relatively "tough skin" that can withstand considerable force without breaking. A steel needle carefully placed on water will float. Some insects, like the one shown in Figure **9.2.3**, even though they are denser than water, move on its surface because they are supported by the surface tension.

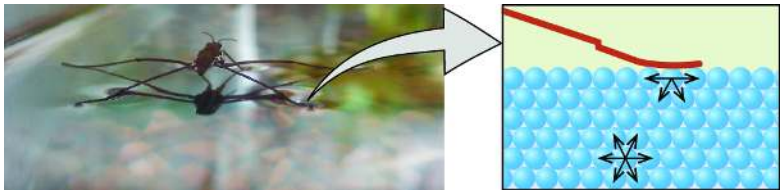


Figure **9.2.3**: Surface tension (right) prevents this insect, a "water strider," from sinking into the water.

A photo and a diagram as shown and a right-facing arrow leads from the photo to the image. The photo shows an insect standing on the surface of a sample of water. The image shows a square background that is two thirds covered in blue spheres that are closely packet together. A brown line starts at the upper left corner of the background and rests on top of the first row of spheres. The sphere directly under this low point of the line has four arrows drawn on it that face to both sides and downward. A sphere in the bottom center of the image has six arrows drawn on it that all face outward in different directions.

The IMFs of attraction between two *different* molecules are called adhesive forces. Consider what happens when water comes into contact with some surface. If the adhesive forces between water molecules and the molecules of the surface are weak compared to the cohesive forces between the water molecules, the water does not "wet" the surface. For example, water does not wet waxed surfaces or many plastics such as polyethylene. Water forms drops on these surfaces because the cohesive forces within the drops are greater than the adhesive forces between the water and the plastic. Water spreads out on glass because the adhesive force between water and glass is greater than the cohesive forces within the water. When water is confined in a glass tube, its meniscus (surface) has a concave shape because the water wets the glass and creeps up the side of the tube. On the other hand, the cohesive forces between mercury atoms are much greater than the adhesive forces between mercury and glass. Mercury therefore does not wet glass, and it forms a convex meniscus when confined in a tube because the cohesive forces within the mercury tend to draw it into a drop (Figure **9.2.4**).

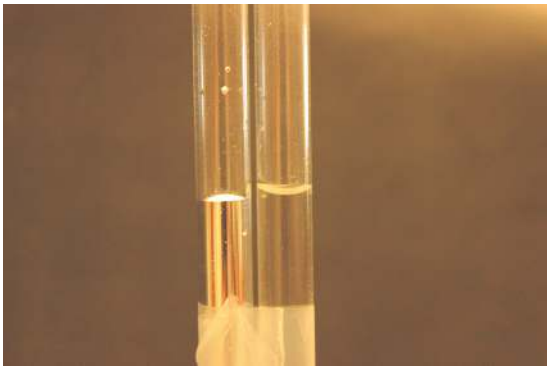


Figure **9.2.4**: Differences in the relative strengths of cohesive and adhesive forces result in different meniscus shapes for mercury (left) and water (right) in glass tubes. (credit: Mark Ott)

This figure shows two test tubes. The test tube on the left contains mercury with a meniscus that rounds up. The test tube on the right contains water with a meniscus that rounds down.

If you place one end of a paper towel in spilled wine, as shown in Figure **9.2.5**, the liquid wicks up the paper towel. A similar process occurs in a cloth towel when you use it to dry off after a shower. These are examples of capillary action—when a liquid flows within a porous material due to the attraction of the liquid molecules to the surface of the material and to other liquid molecules. The adhesive forces between the liquid and the porous material, combined with the cohesive forces within the liquid, may be strong enough to move the liquid upward against gravity.

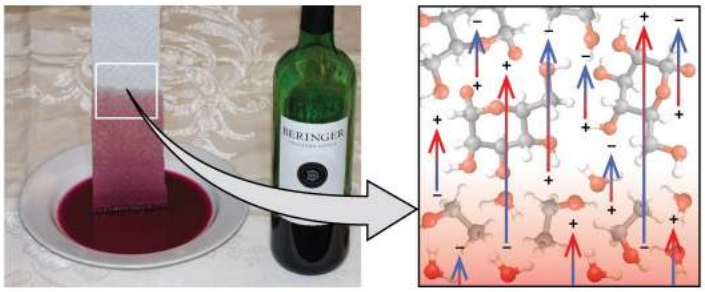


Figure **9.2.5**: Wine wicks up a paper towel (left) because of the strong attractions of water (and ethanol) molecules to the −OH groups on the towel's cellulose fibers and the strong attractions of water molecules to other water (and ethanol) molecules (right). (credit photo: modification of work by Mark Blaser)

A photo and a diagram are shown. In the photo, a paper towel is dipped into a bowl full of a red liquid sitting on a countertop. The red liquid is traveling up the lower part of the paper towel, and this section of the photo has a square drawn around it. A right-facing arrow leads from this square to the image. The image is square and has a background of two types of molecules, mixed together. The first type of molecule is composed of two bonded black spheres, one of which is single bonded to three white spheres and one of which is single bonded to two white spheres and a red sphere that is itself bonded to a white sphere. The other type of molecule is composed of six black spheres bonded together in a row and bonded to other red and white spheres. Six upward-facing arrows are drawn on top of this background. They have positive signs on their lower ends and negative signs on their heads. Four upward-facing arrows are drawn with their signs reversed.

Towels soak up liquids like water because the fibers of a towel are made of molecules that are attracted to water molecules. Most cloth towels are made of cotton, and paper towels are generally made from paper pulp. Both consist of long molecules of cellulose

that contain many −OH groups. Water molecules are attracted to these −OH groups and form hydrogen bonds with them, which draws the H_2O molecules up the cellulose molecules. The water molecules are also attracted to each other, so large amounts of water are drawn up the cellulose fibers.

Capillary action can also occur when one end of a small diameter tube is immersed in a liquid, as illustrated in Figure **9.2.6**. If the liquid molecules are strongly attracted to the tube molecules, the liquid creeps up the inside of the tube until the weight of the liquid and the adhesive forces are in balance. The smaller the diameter of the tube is, the higher the liquid climbs. It is partly by capillary action occurring in plant cells called xylem that water and dissolved nutrients are brought from the soil up through the roots and into a plant. Capillary action is the basis for thin layer chromatography, a laboratory technique commonly used to separate small quantities of mixtures. You depend on a constant supply of tears to keep your eyes lubricated and on capillary action to pump tear fluid away.

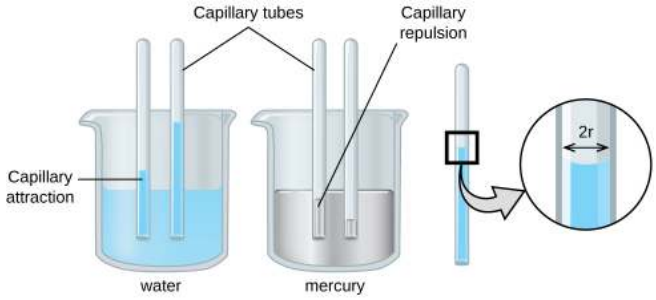


Figure **9.2.6**: Depending upon the relative strengths of adhesive and cohesive forces, a liquid may rise (such as water) or fall (such as mercury) in a glass capillary tube. The extent of the rise (or fall) is directly proportional to the surface tension of the liquid and inversely proportional to the density of the liquid and the radius of the tube.

An image of two beakers and a tube is shown. The first beaker, drawn on the left and labeled “Water,” is drawn half-full of a blue liquid. Two tubes are placed vertically in the beaker and inserted into the liquid. The liquid is shown higher in the tubes than in the beaker and is labeled “Capillary attraction.” The second beaker, drawn in the middle and labeled “Mercury,” is drawn half-full of a gray liquid. Two tubes are placed vertically in the beaker and inserted into the liquid. The liquid is shown lower in the tubes than in the beaker and is labeled “Capillary repulsion.” Lines point to the vertical tubes and label them “Capillary tubes.” A separate drawing of one of the vertical tubes from the first beaker is shown on the right. A right-facing arrow leads from the liquid in the tube to a square call-out box that shows a close-up view of the liquid’s surface. The distance across the tube is labeled “2 r” in this image.

The height to which a liquid will rise in a capillary tube is determined by several factors as shown in the following equation:

$$h = \frac{2T\cos\theta}{r\rho g} \tag{9.2.1}$$

where

- h is the height of the liquid inside the capillary tube relative to the surface of the liquid outside the tube,
- T is the surface tension of the liquid,
- θ is the contact angle between the liquid and the tube,
- r is the radius of the tube, ρ is the density of the liquid, and
- g is the acceleration due to gravity, 9.8 m/s^2.

When the tube is made of a material to which the liquid molecules are strongly attracted, they will spread out completely on the surface, which corresponds to a contact angle of 0°. This is the situation for water rising in a glass tube.

Example 9.2.1: Capillary Rise

At 25 °C, how high will water rise in a glass capillary tube with an inner diameter of 0.25 mm?

For water, T = 71.99 mN/m and ρ = 1.0 g/cm^3.

Solution

The liquid will rise to a height h given by Equation 9.2.1 :

$$h = \frac{2T\cos\theta}{r\rho g}$$

The Newton is defined as a kg m/s^2, and so the provided surface tension is equivalent to 0.07199 kg/s^2. The provided density must be converted into units that will cancel appropriately: ρ = 1000 kg/m^3. The diameter of the tube in meters is 0.00025 m, so the radius is 0.000125 m. For a glass tube immersed in water, the contact angle is θ = 0°, so cos θ = 1. Finally, acceleration due to gravity on the earth is g = 9.8 m/s^2. Substituting these values into the equation, and cancelling units, we have:

$$h = \frac{2(0.07199\ \text{kg/s}^2)}{(0.000125\ \text{m})(1000\ \text{kg/m}^3)(9.8\ \text{m/s}^2)} = 0.12\ \text{m} = 12\ \text{cm}$$

? Exercise 9.2.1

Water rises in a glass capillary tube to a height of 8.4 cm. What is the diameter of the capillary tube?

Answer

diameter = 0.36 mm

Applications: Capillary Action is Used to Draw Blood

Many medical tests require drawing a small amount of blood, for example to determine the amount of glucose in someone with diabetes or the hematocrit level in an athlete. This procedure can be easily done because of capillary action, the ability of a liquid to flow up a small tube against gravity, as shown in Figure 9.2.7. When your finger is pricked, a drop of blood forms and holds together due to surface tension—the unbalanced intermolecular attractions at the surface of the drop. Then, when the open end of a narrow-diameter glass tube touches the drop of blood, the adhesive forces between the molecules in the blood and those at the glass surface draw the blood up the tube. How far the blood goes up the tube depends on the diameter of the tube (and the type of fluid). A small tube has a relatively large surface area for a given volume of blood, which results in larger (relative) attractive forces, allowing the blood to be drawn farther up the tube. The liquid itself is held together by its own cohesive forces. When the weight of the liquid in the tube generates a downward force equal to the upward force associated with capillary action, the liquid stops rising.



Figure 9.2.7:: Blood is collected for medical analysis by capillary action, which draws blood into a small diameter glass tube. (credit: modification of work by Centers for Disease Control and Prevention)

A photograph shows a person’s hand being held by a person wearing medical gloves. A thin glass tube is pressed against the persons finger and blood is moving up the tube.

Key Concepts and Summary

The intermolecular forces between molecules in the liquid state vary depending upon their chemical identities and result in corresponding variations in various physical properties. Cohesive forces between like molecules are responsible for a liquid’s viscosity (resistance to flow) and surface tension (elasticity of a liquid surface). Adhesive forces between the molecules of a liquid and different molecules composing a surface in contact with the liquid are responsible for phenomena such as surface wetting and capillary rise.

Key Equations

- $h = \frac{2T\cos\theta}{r\rho g}$

Glossary

adhesive force
force of attraction between molecules of different chemical identities

capillary action
flow of liquid within a porous material due to the attraction of the liquid molecules to the surface of the material and to other liquid molecules

cohesive force
force of attraction between identical molecules

surface tension
energy required to increase the area, or length, of a liquid surface by a given amount

viscosity
measure of a liquid’s resistance to flow

This page titled 9.2: Properties of Liquids is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

- **10.3: Properties of Liquids** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

9.3: Phase Transitions

Learning Objectives

- Define phase transitions and phase transition temperatures
- Explain the relation between phase transition temperatures and intermolecular attractive forces
- Describe the processes represented by typical heating and cooling curves, and compute heat flows and enthalpy changes accompanying these processes

We witness and utilize changes of physical state, or phase transitions, in a great number of ways. As one example of global significance, consider the evaporation, condensation, freezing, and melting of water. These changes of state are essential aspects of our earth's water cycle as well as many other natural phenomena and technological processes of central importance to our lives. In this module, the essential aspects of phase transitions are explored.

Vaporization and Condensation

When a liquid vaporizes in a closed container, gas molecules cannot escape. As these gas phase molecules move randomly about, they will occasionally collide with the surface of the condensed phase, and in some cases, these collisions will result in the molecules re-entering the condensed phase. The change from the gas phase to the liquid is called condensation. When the rate of condensation becomes equal to the rate of vaporization, neither the amount of the liquid nor the amount of the vapor in the container changes. The vapor in the container is then said to be *in equilibrium* with the liquid. Keep in mind that this is not a static situation, as molecules are continually exchanged between the condensed and gaseous phases. Such is an example of a dynamic equilibrium, the status of a system in which reciprocal processes (for example, vaporization and condensation) occur at equal rates. The pressure exerted by the vapor in equilibrium with a liquid in a closed container at a given temperature is called the liquid's vapor pressure (or equilibrium vapor pressure). The area of the surface of the liquid in contact with a vapor and the size of the vessel have no effect on the vapor pressure, although they do affect the time required for the equilibrium to be reached. We can measure the vapor pressure of a liquid by placing a sample in a closed container, like that illustrated in Figure **9.3.1**, and using a manometer to measure the increase in pressure that is due to the vapor in equilibrium with the condensed phase.

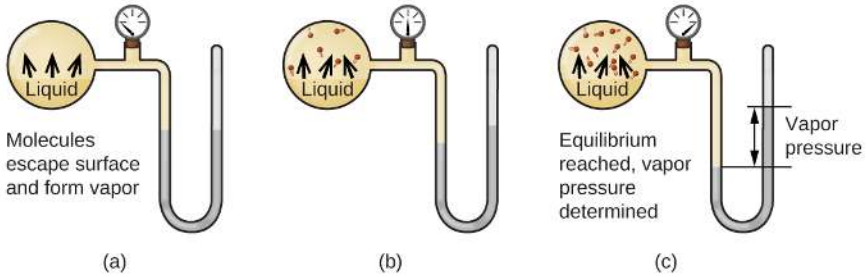


Figure **9.3.1**: In a closed container, dynamic equilibrium is reached when (a) the rate of molecules escaping from the liquid to become the gas (b) increases and eventually (c) equals the rate of gas molecules entering the liquid. When this equilibrium is reached, the vapor pressure of the gas is constant, although the vaporization and condensation processes continue.

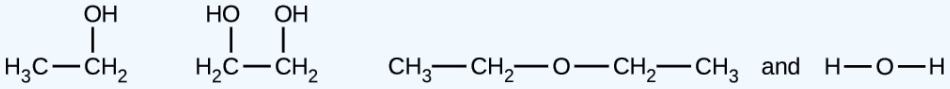
Three images are shown and labeled "a," "b," and "c." Each image shows a round bulb connected on the right to a tube that is horizontal, then is bent vertically, curves, and then is vertical again to make a u-shape. A valve is located in the horizontal portion of the tube. Image a depicts a liquid in the bulb, labeled, "Liquid," and upward-facing arrows leading away from the surface of the liquid. The phrase, "Molecules escape surface and form vapor" is written below the bulb, and a gray liquid in the u-shaped portion of the tube is shown at equal heights on the right and left sides. Image b depicts a liquid in the bulb, labeled, "Liquid," and upward-facing arrows leading away from the surface of the liquid to molecules drawn in the upper portion of the bulb. A gray liquid in the u-shaped portion of the tube is shown slightly higher on the right side than on the left side. Image c depicts a liquid in the bulb, labeled, "Liquid," and upward-facing arrows leading away from the surface of the liquid to molecules drawn in the upper portion of the bulb. There are more molecules present in c than in b. The phrase "Equilibrium reached, vapor pressure determined," is written below the bulb and a gray liquid in the u-shaped portion of the tube is shown higher on the right side. A horizontal line is drawn level with each of these liquid levels and the distance between the lines is labeled with a double-headed arrow. This section is labeled with the phrase, "Vapor pressure."

The chemical identities of the molecules in a liquid determine the types (and strengths) of intermolecular attractions possible; consequently, different substances will exhibit different equilibrium vapor pressures. Relatively strong intermolecular attractive

forces will serve to impede vaporization as well as favoring “recapture” of gas-phase molecules when they collide with the liquid surface, resulting in a relatively low vapor pressure. Weak intermolecular attractions present less of a barrier to vaporization, and a reduced likelihood of gas recapture, yielding relatively high vapor pressures. The following example illustrates this dependence of vapor pressure on intermolecular attractive forces.

Example 9.3.1: Explaining Vapor Pressure in Terms of IMFs

Given the shown structural formulas for these four compounds, explain their relative vapor pressures in terms of types and extents of IMFs:



ethanol ethylene glycol diethyl ether water

Solution

Diethyl ether has a very small dipole and most of its intermolecular attractions are London forces. Although this molecule is the largest of the four under consideration, its IMFs are the weakest and, as a result, its molecules most readily escape from the liquid. It also has the highest vapor pressure. Due to its smaller size, ethanol exhibits weaker dispersion forces than diethyl ether. However, ethanol is capable of hydrogen bonding and, therefore, exhibits stronger overall IMFs, which means that fewer molecules escape from the liquid at any given temperature, and so ethanol has a lower vapor pressure than diethyl ether. Water is much smaller than either of the previous substances and exhibits weaker dispersion forces, but its extensive hydrogen bonding provides stronger intermolecular attractions, fewer molecules escaping the liquid, and a lower vapor pressure than for either diethyl ether or ethanol. Ethylene glycol has two −OH groups, so, like water, it exhibits extensive hydrogen bonding. It is much larger than water and thus experiences larger London forces. Its overall IMFs are the largest of these four substances, which means its vaporization rate will be the slowest and, consequently, its vapor pressure the lowest.

Exercise 9.3.1

At 20 °C, the vapor pressures of several alcohols are given in this table. Explain these vapor pressures in terms of types and extents of IMFs for these alcohols:

At 20 °C, the vapor pressures of several alcohols

Compound	methanol CH_3OH	ethanol C_2H_5OH	propanol C_3H_7OH	butanol C_4H_9OH
Vapor Pressure at 20 °C	11.9 kPa	5.95 kPa	2.67 kPa	0.56 kPa

Answer

All these compounds exhibit hydrogen bonding; these strong IMFs are difficult for the molecules to overcome, so the vapor pressures are relatively low. As the size of molecule increases from methanol to butanol, dispersion forces increase, which means that the vapor pressures decrease as observed:

$$P_{methanol} > P_{ethanol} > P_{propanol} > P_{butanol}$$

As temperature increases, the vapor pressure of a liquid also increases due to the increased average KE of its molecules. Recall that at any given temperature, the molecules of a substance experience a range of kinetic energies, with a certain fraction of molecules having a sufficient energy to overcome IMF and escape the liquid (vaporize). At a higher temperature, a greater fraction of molecules have enough energy to escape from the liquid, as shown in Figure 9.3.2. The escape of more molecules per unit of time and the greater average speed of the molecules that escape both contribute to the higher vapor pressure.

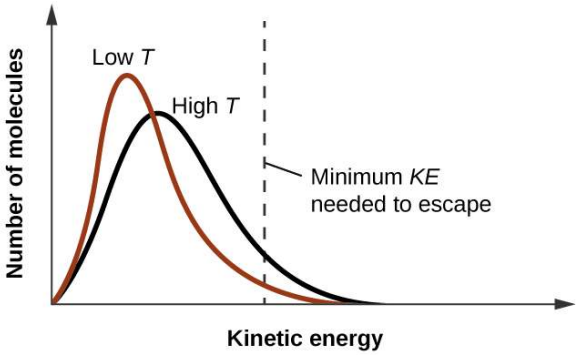


Figure 9.3.2: Temperature affects the distribution of kinetic energies for the molecules in a liquid. At the higher temperature, more molecules have the necessary kinetic energy, KE, to escape from the liquid into the gas phase.

A graph is shown where the y-axis is labeled “Number of molecules” and the x-axis is labeled “Kinetic Energy.” Two lines are graphed and a vertical dotted line, labeled “Minimum K E needed to escape,” is drawn halfway across the x-axis. The first line move sharply upward and has a high peak near the left side of the x-axis. It drops just as steeply and ends about 60 percent of the way across the x-axis. This line is labeled “Low T.” A second line, labeled “High T,” begins at the same point as the first, but does not go to such a high point, is wider, and ends slightly further to the right on the x-axis.

Boiling Points

When the vapor pressure increases enough to equal the external atmospheric pressure, the liquid reaches its boiling point. The boiling point of a liquid is the temperature at which its equilibrium vapor pressure is equal to the pressure exerted on the liquid by its gaseous surroundings. For liquids in open containers, this pressure is that due to the earth’s atmosphere. The normal boiling point of a liquid is defined as its boiling point when surrounding pressure is equal to 1 atm (101.3 kPa). Figure 9.3.3 shows the variation in vapor pressure with temperature for several different substances. Considering the definition of boiling point, these curves may be seen as depicting the dependence of a liquid’s boiling point on surrounding pressure.

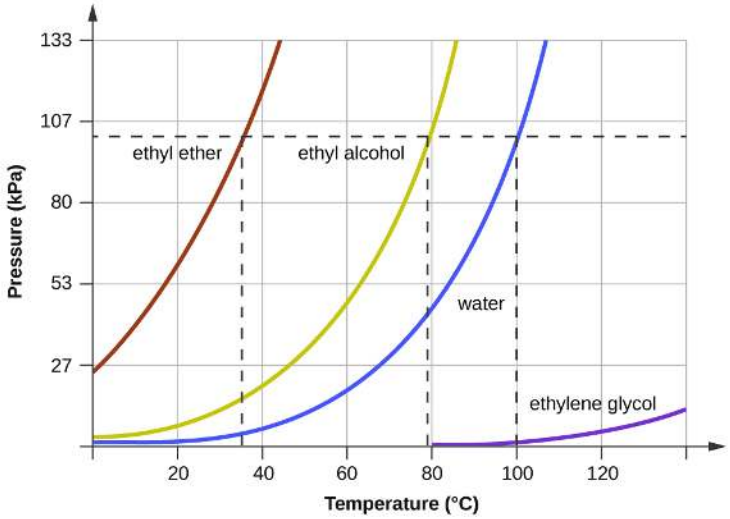


Figure 9.3.3: The boiling points of liquids are the temperatures at which their equilibrium vapor pressures equal the pressure of the surrounding atmosphere. Normal boiling points are those corresponding to a pressure of 1 atm (101.3 kPa.)

A graph is shown where the x-axis is labeled “Temperature (degree sign, C)” and has values of 200 to 1000 in increments of 200 and the y-axis is labeled “Pressure (k P a)” and has values of 20 to 120 in increments of 20. A horizontal dotted line extends across the graph at point 780 on the y-axis while three vertical dotted lines extend from points 35, 78, and 100 to meet the horizontal dotted line. Four lines are graphed. The first line, labeled “ethyl ether,” begins at the point “0 , 200” and extends in a slight curve to point “45, 1000” while the second line, labeled “ethanol”, extends from point “0, 20” to point “88, 1000” in a more extreme curve. The third line, labeled “water,” begins at the point “0, 0” and extends in a curve to point “108, 1000” while the fourth line, labeled “ethylene glycol,” extends from point “80, 0” to point “140, 100” in a very shallow curve.

Example 9.3.2: A Boiling Point at Reduced Pressure

A typical atmospheric pressure in Leadville, Colorado (elevation 10,200 feet) is 68 kPa. Use the graph in Figure **9.3.3** to determine the boiling point of water at this elevation.

Solution

The graph of the vapor pressure of water versus temperature in Figure **9.3.3** indicates that the vapor pressure of water is 68 kPa at about 90 °C. Thus, at about 90 °C, the vapor pressure of water will equal the atmospheric pressure in Leadville, and water will boil.

Exercise 9.3.2

The boiling point of ethyl ether was measured to be 10 °C at a base camp on the slopes of Mount Everest. Use Figure **9.3.3** to determine the approximate atmospheric pressure at the camp.

Answer

Approximately 40 kPa (0.4 atm)

The quantitative relation between a substance's vapor pressure and its temperature is described by the Clausius-Clapeyron equation:

$$P = Ae^{-\Delta H_{vap}/RT} \tag{9.3.1}$$

where

- ΔH_{vap} is the enthalpy of vaporization for the liquid,
- R is the gas constant, and
- $\ln A$ is a constant whose value depends on the chemical identity of the substance.

Equation 9.3.1 is often rearranged into logarithmic form to yield the linear equation:

$$\ln P = -\frac{\Delta H_{vap}}{RT} + \ln A \tag{9.3.2}$$

This linear equation may be expressed in a two-point format that is convenient for use in various computations, as demonstrated in the examples and exercises that follow. If at temperature T_1, the vapor pressure is P_1, and at temperature T_2, the vapor pressure is T_2, the corresponding linear equations are:

$$\ln P_1 = -\frac{\Delta H_{vap}}{RT_1} + \ln A$$

and

$$\ln P_2 = -\frac{\Delta H_{vap}}{RT_2} + \ln A \tag{9.3.3}$$

Since the constant, ln A, is the same, these two equations may be rearranged to isolate $\ln A$ and then set them equal to one another:

$$\ln P_1 + \frac{\Delta H_{vap}}{RT_1} = \ln P_2 + \frac{\Delta H_{vap}}{RT_2}$$

which can be combined into:

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{9.3.4}$$

Example 9.3.3: Estimating Enthalpy of Vaporization

Isooctane (2,2,4-trimethylpentane) has an octane rating of 100. It is used as one of the standards for the octane-rating system for gasoline. At 34.0 °C, the vapor pressure of isooctane is 10.0 kPa, and at 98.8 °C, its vapor pressure is 100.0 kPa. Use this information to estimate the enthalpy of vaporization for isooctane.

Solution

The enthalpy of vaporization, ΔH_{vap}, can be determined by using the Clausius-Clapeyron equation (Equation 9.3.4):

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Since we have two vapor pressure-temperature values

- $T_1 = 34.0°C = 307.2\,K$
- $P_1 = 10.0\,kPa$ and
- $T_2 = 98.8°C = 372.0\,K$
- $P_2 = 100\,kPa$

we can substitute them into this equation and solve for ΔH_{vap}. Rearranging the Clausius-Clapeyron equation and solving for ΔH_{vap} yields:

$$\begin{aligned}\Delta H_{\text{vap}} &= \frac{R \cdot \ln\left(\frac{P_2}{P_1}\right)}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \\ &= \frac{(8.3145\,J/mol \cdot K) \cdot \ln\left(\frac{100\,kPa}{10.0\,kPa}\right)}{\left(\frac{1}{307.2\,K} - \frac{1}{372.0\,K}\right)} \\ &= 33,800\,J/mol = 33.8\,kJ/mol\end{aligned}$$

Note that the pressure can be in any units, so long as they agree for both P values, but the temperature must be in kelvin for the Clausius-Clapeyron equation to be valid.

Exercise 9.3.3

At 20.0 °C, the vapor pressure of ethanol is 5.95 kPa, and at 63.5 °C, its vapor pressure is 53.3 kPa. Use this information to estimate the enthalpy of vaporization for ethanol.

Answer

47,782 J/mol = 47.8 kJ/mol

Example 9.3.4: Estimating Temperature (or Vapor Pressure)

For benzene (C_6H_6), the normal boiling point is 80.1 °C and the enthalpy of vaporization is 30.8 kJ/mol. What is the boiling point of benzene in Denver, where atmospheric pressure = 83.4 kPa?

Solution

If the temperature and vapor pressure are known at one point, along with the enthalpy of vaporization, ΔH_{vap}, then the temperature that corresponds to a different vapor pressure (or the vapor pressure that corresponds to a different temperature) can be determined by using the Clausius-Clapeyron equation (Equation 9.3.1) :

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Since the normal boiling point is the temperature at which the vapor pressure equals atmospheric pressure at sea level, we know one vapor pressure-temperature value (T_1 = 80.1 °C = 353.3 K, P_1 = 101.3 kPa, ΔH_{vap} = 30.8 kJ/mol) and want to find the temperature (T_2) that corresponds to vapor pressure P_2 = 83.4 kPa. We can substitute these values into the Clausius-Clapeyron equation and then solve for T_2. Rearranging the Clausius-Clapeyron equation and solving for T_2 yields:

$$T_2 = \left(\frac{-R \cdot \ln\left(\frac{P_2}{P_1}\right)}{\Delta H_{vap}} + \frac{1}{T_1} \right)^{-1}$$

$$= \left(\frac{-(8.3145\ \text{J/mol·K}) \cdot \ln\left(\frac{83.4\ \text{kPa}}{101.3\ \text{kPa}}\right)}{30{,}800\ \text{J/mol}} + \frac{1}{353.3\ \text{K}} \right)^{-1}$$

$$= 346.9\ \text{K or } 73.8°\text{C}$$

Exercise 9.3.4

For acetone $(CH_3)_2CO$, the normal boiling point is 56.5 °C and the enthalpy of vaporization is 31.3 kJ/mol. What is the vapor pressure of acetone at 25.0 °C?

Answer

30.1 kPa

Enthalpy of Vaporization

Vaporization is an endothermic process. The cooling effect can be evident when you leave a swimming pool or a shower. When the water on your skin 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}. For example, the vaporization of water at standard temperature is represented by:

$$H_2O(l) \longrightarrow H_2O(g) \quad \Delta H_{vap} = 44.01\ \text{kJ/mol}$$

As described in the chapter on thermochemistry, the reverse of an endothermic process is exothermic. And so, the condensation of a gas releases heat:

$$H_2O(g) \longrightarrow H_2O(l) \quad \Delta H_{con} = -\Delta H_{vap} = -44.01\ \text{kJ/mol}$$

Example 9.3.5: Using Enthalpy of Vaporization

One way our body is cooled is by evaporation of the water in sweat (Figure 9.3.4). 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); $\Delta H_{vap} = 43.46\ kJ/mol$ at 37 °C.



Figure 9.3.4: 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:

$$1.5 \cancel{L} \times \frac{1000 \cancel{g}}{1 \cancel{L}} \times \frac{1 \cancel{\text{mol}}}{18 \cancel{g}} \times \frac{43.46 \text{ kJ}}{1 \cancel{\text{mol}}} = 3.6 \times 10^3 \text{ kJ}$$

Thus, 3600 kJ of heat are removed by the evaporation of 1.5 L of water.

? Exercise 9.3.5: 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

Melting and Freezing

When we heat a crystalline solid, we increase the average energy of its atoms, molecules, or ions and the solid gets hotter. At some point, the added energy becomes large enough to partially overcome the forces holding the molecules or ions of the solid in their fixed positions, and the solid begins the process of transitioning to the liquid state, or melting. At this point, the temperature of the solid stops rising, despite the continual input of heat, and it remains constant until all of the solid is melted. Only after all of the solid has melted will continued heating increase the temperature of the liquid (Figure 9.3.5.



Figure 9.3.5: (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).

This figure shows four photos each labeled, “a,” “b,” “c,” and, “d.” Each photo shows a beaker with ice and a digital thermometer. The first photo shows ice cubes in the beaker, and the thermometer reads negative 12.0 degrees C. The second photo shows slightly melted ice, and the thermometer reads 0.0 degrees C. The third photo shows more water than ice in the beaker. The thermometer reads 0.0 degrees C. The fourth photo shows the ice completely melted, and the thermometer reads 22.2 degrees C.

If we stop heating during melting and place the mixture of solid and liquid in a perfectly insulated container so no heat can enter or escape, the solid and liquid phases remain in equilibrium. This is almost the situation with a mixture of ice and water in a very good thermos bottle; 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 reciprocal processes of melting and freezing occur at equal rates, and the quantities of solid and liquid therefore remain constant. The temperature at which the solid and liquid phases of a given substance are in equilibrium is called the melting point of the solid or the freezing point of the liquid. Use of one term or the other is normally dictated by the direction of the phase transition being considered, for example, solid to liquid (melting) or liquid to solid (freezing).

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.

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, ΔHfus of the substance. The enthalpy of fusion of ice is 6.0 kJ/mol at 0 °C. Fusion (melting) is an endothermic process:

$$\mathrm{H_2O_{(s)} \rightarrow H_2O_{(l)} \quad \Delta H_{fus} = 6.01\ kJ/mol} \tag{9.3.5}$$

The reciprocal process, freezing, is an exothermic process whose enthalpy change is −6.0 kJ/mol at 0 °C:

$$\mathrm{H_2O_{(l)} \rightarrow H_2O_{(s)} \quad \Delta H_{frz} = -\Delta H_{fus} = -6.01\ kJ/mol} \tag{9.3.6}$$

Sublimation and Deposition

Some solids can transition directly into the gaseous state, bypassing the liquid state, via a process known as sublimation. At room temperature and standard pressure, a piece of dry ice (solid CO_2) sublimes, appearing to gradually disappear without ever forming any liquid. Snow and ice sublime at temperatures below the melting point of water, a slow process that may be accelerated by winds and the reduced atmospheric pressures at high altitudes. When solid iodine is warmed, the solid sublimes and a vivid purple vapor forms (Figure **9.3.6**). The reverse of sublimation is called deposition, a process in which gaseous substances condense directly into the solid state, bypassing the liquid state. The formation of frost is an example of deposition.



Figure **9.3.6**: Sublimation of solid iodine in the bottom of the tube produces a purple gas that subsequently deposits as solid iodine on the colder part of the tube above. (credit: modification of work by Mark Ott)

This figure shows a test tube. In the bottom is a dark substance which breaks up into a purple gas at the top.

Like vaporization, the process of sublimation requires an input of energy to overcome intermolecular attractions. The enthalpy of sublimation, ΔHsub, is the energy required to convert one mole of a substance from the solid to the gaseous state. For example, the sublimation of carbon dioxide is represented by:

$$\mathrm{CO_2(s) \longrightarrow CO_2(g) \quad \Delta H_{sub} = 26.1\ kJ/mol}$$

Likewise, the enthalpy change for the reverse process of deposition is equal in magnitude but opposite in sign to that for sublimation:

$$\mathrm{CO_2(g) \longrightarrow CO_2(s) \quad \Delta H_{dep} = -\Delta H_{sub} = -26.1\ kJ/mol}$$

Consider the extent to which intermolecular attractions must be overcome to achieve a given phase transition. Converting a solid into a liquid requires that these attractions be only partially overcome; transition to the gaseous state requires that they be completely overcome. As a result, the enthalpy of fusion for a substance is less than its enthalpy of vaporization. This same logic

can be used to derive an approximate relation between the enthalpies of all phase changes for a given substance. Though not an entirely accurate description, sublimation may be conveniently modeled as a sequential two-step process of melting followed by vaporization in order to apply Hess's Law.

$$\begin{array}{rl} \text{solid} \longrightarrow \text{liquid} & \Delta H_{\text{fus}} \\ \underline{\text{liquid} \longrightarrow \text{gas}} & \underline{\Delta H_{\text{vap}}} \\ \text{solid} \longrightarrow \text{gas} & \Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}} \end{array}$$

Viewed in this manner, the enthalpy of sublimation for a substance may be estimated as the sum of its enthalpies of fusion and vaporization, as illustrated in Figure **9.3.7**. For example:

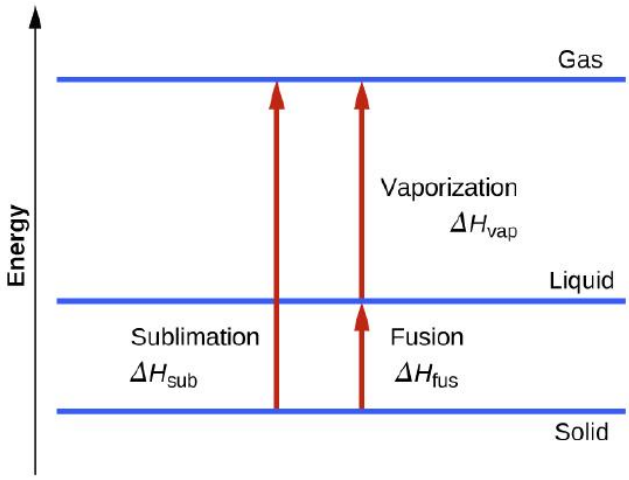


Figure **9.3.7**: For a given substance, the sum of its enthalpy of fusion and enthalpy of vaporization is approximately equal to its enthalpy of sublimation.

A diagram is shown with a vertical line drawn on the left side and labeled "Energy" and three horizontal lines drawn near the bottom, lower third and top of the diagram. These three lines are labeled, from bottom to top, "Solid," "Liquid" and "Gas." Near the middle of the diagram, a vertical, upward-facing arrow is drawn from the solid line to the gas line and labeled "Sublimation, delta sign, H, subscript sub." To the right of this arrow is a second vertical, upward-facing arrow that is drawn from the solid line to the liquid line and labeled "Fusion, delta sign, H, subscript fus." Above the second arrow is a third arrow drawn from the liquid line to the gas line and labeled, "Vaporization, delta sign, H, subscript vap."

Heating and Cooling Curves

In the chapter on thermochemistry, the relation between the amount of heat absorbed or related by a substance, q, and its accompanying temperature change, ΔT, was introduced:

$$q = mc\Delta T$$

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. When a substance being heated or cooled reaches a temperature corresponding to one of its phase transitions, further gain or loss of heat is a result of diminishing or enhancing intermolecular attractions, instead of increasing or decreasing molecular kinetic energies. While a substance is undergoing a change in state, its temperature remains constant. Figure **9.3.8** shows a typical heating curve.

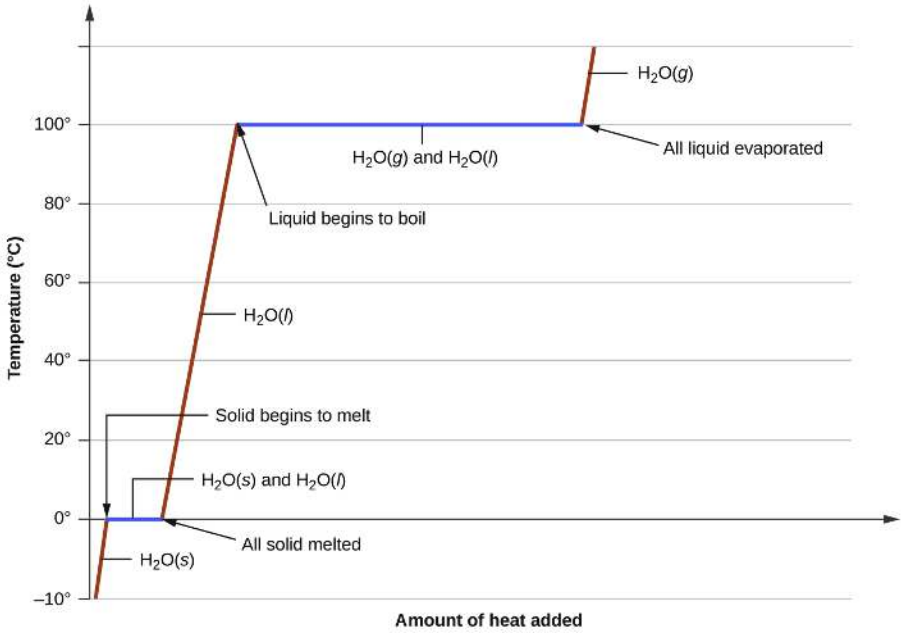


Figure **9.3.8**: A typical heating curve for a substance depicts changes in temperature that result as the substance absorbs increasing amounts of heat. Plateaus in the curve (regions of constant temperature) are exhibited when the substance undergoes phase transitions.

A graph is shown where the x-axis is labeled “Amount of heat added” and the y-axis is labeled “Temperature (degree sign C)” and has values of negative 10 to 100 in increments of 20. A right-facing horizontal arrow extends from point “0, 0” to the right side of the graph. A line graph begins at the lower left of the graph and moves to point “0” on the y-axis. This segment of the line is labeled “H, subscript 2, O (s).” The line then flattens and travels horizontally for a small distance. This segment is labeled “Solid begins to melt” on its left side and “All solid melted” on its right side. The line then goes steeply upward in a linear fashion until it hits point “100” on the y-axis. This segment of the line is labeled “H, subscript 2, O,(l).” The line then flattens and travels horizontally for a moderate distance. This segment is labeled “Liquid begins to boil” on its left side and “All liquid evaporated” on its right side. The line then rises to a point above “100” on the y-axis. This segment of the line is labeled “H, subscript 2, O (g).”

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: For example, temperature remains constant while the change of state is in progress.

✔ Example **9.3.6**: 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:

$$q_{\text{total}} = (m \cdot c \cdot \Delta T)_{\text{ice}} + n \cdot \Delta H_{\text{fus}} + (m \cdot c \cdot \Delta T)_{\text{water}} + n \cdot \Delta H_{\text{vap}} + (m \cdot c \cdot \Delta T)_{\text{steam}}$$

$$= (135\ \text{g} \cdot 2.09\ \text{J/g·°C} \cdot 15\text{°C}) + \left(135 \cdot \frac{1\ \text{mol}}{18.02\ \text{g}} \cdot 6.01\ \text{kJ/mol}\right)$$

$$+(135\ \text{g} \cdot 4.18\ \text{J/g·°C} \cdot 100\text{°C}) + \left(135\ \text{g} \cdot \frac{1\ \text{mol}}{18.02\ \text{g}} \cdot 40.67\ \text{kJ/mol}\right)$$

$$+(135\ \text{g} \cdot 1.84\ \text{J/g·°C} \cdot 20\text{°C})$$

$$= 4230\ \text{J} + 45.0\ \text{kJ} + 56,500\ \text{J} + 305\ \text{kJ} + 4970\ \text{J}$$

Converting the quantities in J to kJ permits them to be summed, yielding 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 9.3.6

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

Summary

Phase transitions are processes that convert matter from one physical state into another. There are six phase transitions between the three phases of matter. Melting, vaporization, and sublimation are all endothermic processes, requiring an input of heat to overcome intermolecular attractions. The reciprocal transitions of freezing, condensation, and deposition are all exothermic processes, involving heat as intermolecular attractive forces are established or strengthened. The temperatures at which phase transitions occur are determined by the relative strengths of intermolecular attractions and are, therefore, dependent on the chemical identity of the substance.

Key Equations

- $P = Ae^{-\Delta H_{\text{vap}}/RT}$
- $\ln P = -\dfrac{\Delta H_{\text{vap}}}{RT} + \ln A$
- $\ln\left(\dfrac{P_2}{P_1}\right) = \dfrac{\Delta H_{\text{vap}}}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$

Glossary

boiling point
temperature at which the vapor pressure of a liquid equals the pressure of the gas above it

Clausius-Clapeyron equation
mathematical relationship between the temperature, vapor pressure, and enthalpy of vaporization for a substance

condensation
change from a gaseous to a liquid state

deposition
change from a gaseous state directly to a solid state

dynamic equilibrium
state of a system in which reciprocal processes are occurring at equal rates

freezing
change from a liquid state to a solid state

freezing point

temperature at which the solid and liquid phases of a substance are in equilibrium; see also *melting point*

melting

change from a solid state to a liquid state

melting point

temperature at which the solid and liquid phases of a substance are in equilibrium; see also *freezing point*

normal boiling point

temperature at which a liquid’s vapor pressure equals 1 atm (760 torr)

sublimation

change from solid state directly to gaseous state

vapor pressure

(also, equilibrium vapor pressure) pressure exerted by a vapor in equilibrium with a solid or a liquid at a given temperature

vaporization

change from liquid state to gaseous state

This page titled 9.3: Phase Transitions is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

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

CHAPTER OVERVIEW

10: Solutions and Colloids

A general chemistry Libretexts Textmap organized around the textbook
General Chemistry -Atoms First
By OpenStax

I II III IV V VI VII VIII IX X XI XII XIII XIV XV XVI XVII XVIII XIX XX XXI ● **Homework**

In this chapter, we will consider the nature of solutions, and examine factors that determine whether a solution will form and what properties it may have. In addition, we will discuss colloids—systems that resemble solutions but consist of dispersions of particles somewhat larger than ordinary molecules or ions.

10.1: The Dissolution Process
10.2: Molarity
10.3: Other Units for Solution Concentrations
10.4: Solubility
10.5: Colligative Properties
10.6: Colloids

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 10: Solutions and Colloids is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

10.1: The Dissolution Process

Learning Objectives

- Describe the basic properties of solutions and how they form.
- Predict whether a given mixture will yield a solution based on molecular properties of its components.
- Explain why some solutions either produce or absorb heat when they form.

An earlier chapter of this text introduced *solutions*, defined as homogeneous mixtures of two or more substances. Often, one component of a solution is present at a significantly greater concentration, in which case it is called the solvent. The other components of the solution present in relatively lesser concentrations are called solutes. Sugar is a covalent solid composed of sucrose molecules, $\mathrm{C_{12}H_{22}O_{11}}$. When this compound dissolves in water, its molecules become uniformly distributed among the molecules of water:

$$\mathrm{C_{12}H_{22}O_{11}\,(s) \longrightarrow C_{12}H_{22}O_{11}\,(aq)} \tag{10.1.1}$$

The subscript "aq" in the equation signifies that the sucrose molecules are solutes and are therefore *individually dispersed* throughout the *aqueous solution* (water is the solvent). Although sucrose molecules are heavier than water molecules, they remain dispersed throughout the solution; gravity does not cause them to "settle out" over time.

Potassium dichromate, $\mathrm{K_2Cr_2O_7}$, is an ionic compound composed of colorless potassium ions, $\mathrm{K^+}$, and orange dichromate ions, $\mathrm{Cr_2O_7^{2-}}$. When a small amount of solid potassium dichromate is added to water, the compound dissolves and dissociates to yield potassium ions and dichromate ions uniformly distributed throughout the mixture (Figure 10.1.1), as indicated in this equation:

$$\mathrm{K_2Cr_2O_7\,(s) \longrightarrow 2\,K^+\,(aq) + Cr_2O_7^{2-}\,(aq)} \tag{10.1.2}$$

As with the mixture of sugar and water, this mixture is also an aqueous solution. Its solutes, potassium and dichromate ions, remain individually dispersed among the solvent (water) molecules.



Figure 10.1.1: When potassium dichromate ($\mathrm{K_2Cr_2O_7}$) is mixed with water, it forms a homogeneous orange solution. (credit: modification of work by Mark Ott).

The first photo shows a small mound of an orange crystalline solid. There is a right-facing arrow. The second photo shows a translucent, colorless liquid in a clear container. There is a right-facing arrow. The third photo shows a translucent orange liquid in a clear, covered container.

Water is used so often as a solvent that the word solution has come to imply an aqueous solution to many people. However, almost any gas, liquid, or solid can act as a solvent. Many alloys are solid solutions of one metal dissolved in another; for example, US five-cent coins contain nickel dissolved in copper. Air is a gaseous solution, a homogeneous mixture of nitrogen, oxygen, and several other gases. Oxygen (a gas), alcohol (a liquid), and sugar (a solid) all dissolve in water (a liquid) to form liquid solutions. Table 10.1.1 gives examples of several different solutions and the phases of the solutes and solvents.

Table 10.1.1: Different Types of Solutions

Solution	Solute	Solvent
air	$O_2(g)$	$N_2(g)$
soft drinks	$CO_2(g)$	$H_2O(l)$
hydrogen in palladium	$H_2(g)$	$Pd(s)$
rubbing alcohol	$H_2O(l)$	$C_3H_8O(l)$ (2-propanol)
saltwater	$NaCl(s)$	$H_2O(l)$
brass	$Zn(s)$	$Cu(s)$

Solutions exhibit these defining traits:

- They are homogeneous; that is, after a solution is mixed, it has the same composition at all points throughout (its composition is uniform).
- The physical state of a solution—solid, liquid, or gas—is typically the same as that of the solvent, as demonstrated by the examples in Table **10.1.1**.
- The components of a solution are dispersed on a molecular scale; that is, they consist of a mixture of separated molecules, atoms, and/or ions.
- The dissolved solute in a solution will not settle out or separate from the solvent.
- The composition of a solution, or the concentrations of its components, can be varied continuously, within limits.

The Formation of Solutions

The formation of a solution is an example of a spontaneous process, a process that occurs under specified conditions without the requirement of energy from some external source. Sometimes we stir a mixture to speed up the dissolution process, but this is not necessary; a homogeneous solution would form if we waited long enough. The topic of spontaneity is critically important to the study of chemical thermodynamics and is treated more thoroughly in a later chapter of this text. For purposes of this chapter's discussion, it will suffice to consider two criteria that *favor*, but do not guarantee, the spontaneous formation of a solution:

1. a decrease in the internal energy of the system (an exothermic change, as discussed in the previous chapter on thermochemistry)
2. an increase in the disorder in the system (which indicates an increase in the *entropy* of the system, as you will learn about in the later chapter on thermodynamics)

In the process of dissolution, an internal energy change often, but not always, occurs as heat is absorbed or evolved. An increase in disorder always results when a solution forms.

When the strengths of the intermolecular forces of attraction between solute and solvent species in a solution are no different than those present in the separated components, the solution is formed with no accompanying energy change. Such a solution is called an ideal solution. A mixture of ideal gases (or gases such as helium and argon, which closely approach ideal behavior) is an example of an ideal solution, since the entities comprising these gases experience no significant intermolecular attractions.

When containers of helium and argon are connected, the gases spontaneously mix due to diffusion and form a solution (Figure **10.1.2**). The formation of this solution clearly involves an increase in disorder, since the helium and argon atoms occupy a volume twice as large as that which each occupied before mixing.

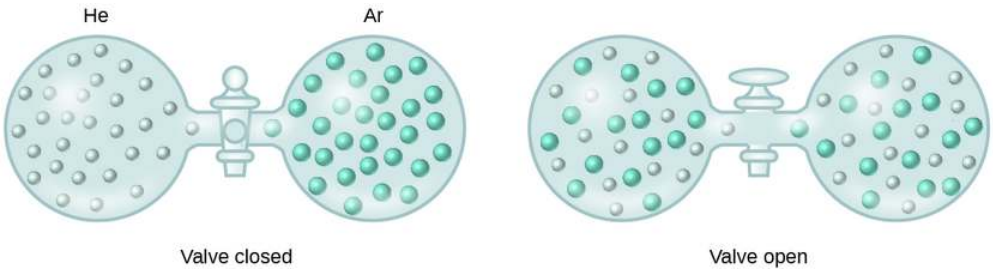


Figure **10.1.2**: Samples of helium and argon spontaneously mix to give a solution in which the disorder of the atoms of the two gases is increased.

Two figures are shown. The first contains two spherical containers joined by a closed stopcock. The container to the left is labeled H e. It holds about thirty evenly dispersed, small, light blue spheres. The container on the right is labeled A r and contains about thirty slightly larger blue-green spheres. The second, similar figure has an open stopcock between the two spherical containers. The light blue and green spheres are evenly dispersed and present in both containers.

Ideal solutions may also form when structurally similar liquids are mixed. For example, mixtures of the alcohols methanol (CH_3OH) and ethanol (C_2H_5OH) form ideal solutions, as do mixtures of the hydrocarbons pentane, $\mathbf{C_5H_{12}}$, and hexane, $\mathbf{C_6H_{14}}$. Placing methanol and ethanol, or pentane and hexane, in the bulbs shown in Figure **10.1.2** will result in the same diffusion and subsequent mixing of these liquids as is observed for the He and Ar gases (although at a much slower rate), yielding solutions with no significant change in energy. Unlike a mixture of gases, however, the components of these liquid-liquid solutions do, indeed, experience intermolecular attractive forces. But since the molecules of the two substances being mixed are structurally very similar, the intermolecular attractive forces between like and unlike molecules are essentially the same, and the dissolution process, therefore, does not entail any appreciable increase or decrease in energy. These examples illustrate how diffusion alone can provide the driving force required to cause the spontaneous formation of a solution. In some cases, however, the relative magnitudes of intermolecular forces of attraction between solute and solvent species may prevent dissolution.

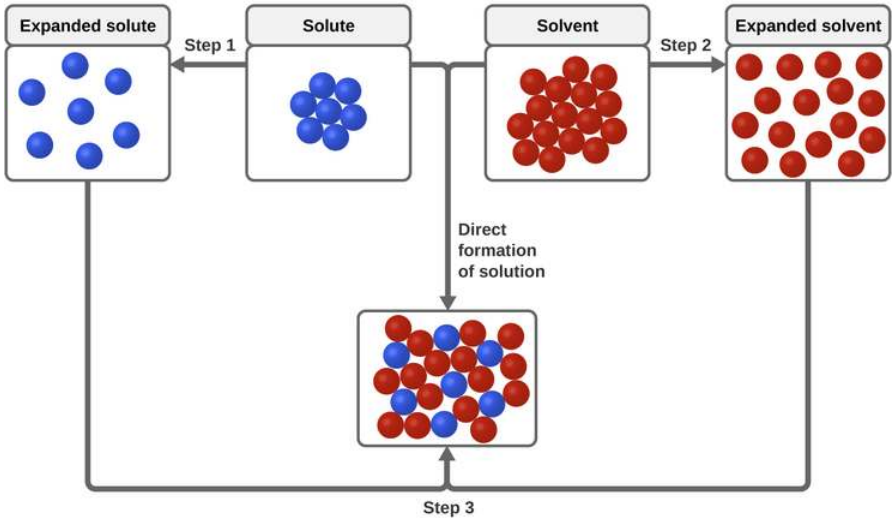


Figure **10.1.3**: This schematic representation of dissolution shows a stepwise process involving the endothermic separation of solute and solvent species (Steps 1 and 2) and exothermic solvation (Step 3).

The top, central region of the figure shows solute particles as seven blue spheres and solvent particles as 16 red spheres in separate, labeled boxes. The particles in these boxes are touching. An arrow labeled “Step 1” points left of the solute box, and shows the blue spheres no longer touching in another box labeled “expanded solute.” An arrow labeled “Step 2” points right from the solvent box and shows the red spheres no longer touching in another box labeled “expanded solvent.” Arrows proceed from the bottom of the expanded solute and expanded solvent boxes and join at the bottom of the figure where a step 3 label is shown. The joined arrows point to a box just above in which the red and blue spheres are mixed together and touching. The solute and solvent boxes are joined by another arrow labeled “direct formation of solution” which points downward at the center of the figure. This arrow also points to the box containing mixed red and blue spheres near the bottom of the figure.

Three types of intermolecular attractive forces are relevant to the dissolution process: solute-solute, solvent-solvent, and solute-solvent. As illustrated in Figure **10.1.3**, the formation of a solution may be viewed as a stepwise process in which energy is consumed to overcome solute-solute and solvent-solvent attractions (endothermic processes) and released when solute-solvent attractions are established (an exothermic process referred to as solvation). The relative magnitudes of the energy changes

associated with these stepwise processes determine whether the dissolution process overall will release or absorb energy. In some cases, solutions do not form because the energy required to separate solute and solvent species is so much greater than the energy released by solvation.



Figure **10.1.4**: A mixture of nonpolar cooking oil and polar water does not yield a solution. (credit: Gautam Dogra).

For example, cooking oils and water will not mix to any appreciable extent to yield solutions (Figure **10.1.4**). Hydrogen bonding is the dominant intermolecular attractive force present in liquid water; the nonpolar hydrocarbon molecules of cooking oils are not capable of hydrogen bonding, instead being held together by dispersion forces. Forming an oil-water solution would require overcoming the very strong hydrogen bonding in water, as well as the significantly strong dispersion forces between the relatively large oil molecules. And, since the polar water molecules and nonpolar oil molecules would not experience very strong intermolecular attraction, very little energy would be released by solvation.

On the other hand, a mixture of ethanol and water will mix in any proportions to yield a solution. In this case, both substances are capable of hydrogen bonding, and so the solvation process is sufficiently exothermic to compensate for the endothermic separations of solute and solvent molecules.



Figure **10.1.5**: An instant cold pack gets cold when certain salts, such as ammonium nitrate, dissolve in water—an endothermic process.

This figure shows a single use instant cold pack with labels indicating an inner bag of water surrounded by white particulate ammonium nitrate.

As noted at the beginning of this module, spontaneous solution formation is favored, but not guaranteed, by exothermic dissolution processes. While many soluble compounds do, indeed, dissolve with the release of heat, some dissolve endothermically. Ammonium nitrate (NH_4NO_3) is one such example and is used to make instant cold packs for treating injuries like the one pictured in Figure **10.1.5**. A thin-walled plastic bag of water is sealed inside a larger bag with solid NH_4NO_3. When the smaller bag is broken, a solution of NH_4NO_3 forms, absorbing heat from the surroundings (the injured area to which the pack is applied) and providing a cold compress that decreases swelling. Endothermic dissolutions such as this one require a greater energy input to

separate the solute species than is recovered when the solutes are solvated, but they are spontaneous nonetheless due to the increase in disorder that accompanies formation of the solution.



Video 10.1.1*: Watch this brief video illustrating endothermic and exothermic dissolution processes.*

Summary

A solution forms when two or more substances combine physically to yield a mixture that is homogeneous at the molecular level. The solvent is the most concentrated component and determines the physical state of the solution. The solutes are the other components typically present at concentrations less than that of the solvent. Solutions may form endothermically or exothermically, depending upon the relative magnitudes of solute and solvent intermolecular attractive forces. Ideal solutions form with no appreciable change in energy.

Footnotes

1. If bubbles of gas are observed within the liquid, the mixture is not homogeneous and, thus, not a solution.

Glossary

alloy
: solid mixture of a metallic element and one or more additional elements

ideal solution
: solution that forms with no accompanying energy change

solvation
: exothermic process in which intermolecular attractive forces between the solute and solvent in a solution are established

spontaneous process
: physical or chemical change that occurs without the addition of energy from an external source

---

This page titled 10.1: The Dissolution Process is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

- **11.2: The Dissolution Process** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

10.2: 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 **10.2.1**). In this section, we will describe one of the most common ways in which the relative compositions of mixtures may be quantified.



Figure **10.2.1**: 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)

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. Solutions occur frequently in nature and have also been implemented in many forms of manmade technology. We will explore a more thorough treatment of solution properties in the chapter on solutions and colloids, but here we will introduce some of the basic properties of solutions.

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:

$$M = \frac{\text{mol solute}}{\text{L solution}} \tag{10.2.1}$$

Example 10.2.1: 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:

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

Exercise 10.2.1

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

Example 10.2.2: 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 **10.2.1**?

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*:

$$M = \frac{\text{mol solute}}{\text{L solution}} \tag{10.2.2}$$

Multiple \label

Exercise 10.2.2

What volume (mL) of the sweetened tea described in Example **10.2.1** contains the same amount of sugar (mol) as 10 mL of the soft drink in this example?

Answer

80 mL

Example 10.2.3: Calculating Molar Concentrations from the Mass of Solute

Distilled white vinegar (Figure **10.2.2**) 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 **10.2.3**: Distilled white vinegar is a solution of acetic acid in water.

A label on a container is shown. The label has a picture of a salad with the words “Distilled White Vinegar,” and, “Reduced with water to 5% acidity,” written above it.

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:

$$M = \frac{\text{mol solute}}{\text{L solution}} = \frac{25.2\ \text{g}\ \ce{CH3CO2H} \times \frac{1\ \text{mol}\ \ce{CH3CO2H}}{60.052\ \text{g}\ \ce{CH3CO2H}}}{0.500\ \text{L solution}} = 0.839\ M \tag{10.2.3}$$

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

Nov 29, 2019, 5:24 PM

$$M = \frac{\text{mol solute}}{\text{L solution}} = 0.839\ M \tag{10.2.4}$$

? Exercise 10.2.3

Calculate the molarity of 6.52 g of $\ce{CoCl2}$ (128.9 g/mol) dissolved in an aqueous solution with a total volume of 75.0 mL.

Answer

0.674 M

✓ Example 10.2.4: 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 **10.2.3**:

$$M = \frac{\text{mol solute}}{\text{L solution}} \tag{10.2.5}$$

$$\text{mol solute} = M \times \text{L solution} \tag{10.2.6}$$

$$\text{mol solute} = 5.30\ \frac{\text{mol NaCl}}{\text{L}} \times 0.250\ \text{L} = 1.325\ \text{mol NaCl} \tag{10.2.7}$$

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

$$1.325\ \text{mol NaCl} \times \frac{58.44\ \text{g NaCl}}{\text{mol NaCl}} = 77.4\ \text{g NaCl} \tag{10.2.8}$$

? Exercise 10.2.4

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 **10.2.3**, it is important to refrain from rounding any intermediate calculation results, which can lead to rounding errors in the final result. In Example **10.2.4**, 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 **10.2.5**). This eliminates intermediate steps so that only the final result is rounded.

✓ Example 10.2.5: Determining the Volume of Solution

In Example **10.2.3**, 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:

$$\text{g solute} \times \frac{\text{mol solute}}{\text{g solute}} = \text{mol solute} \tag{10.2.9}$$

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

$$\text{mol solute} \times \frac{\text{L solution}}{\text{mol solute}} = \text{L solution} \tag{10.2.10}$$

Combining these two steps into one yields:

$$\text{g solute} \times \frac{\text{mol solute}}{\text{g solute}} \times \frac{\text{L solution}}{\text{mol solute}} = \text{L solution} \tag{10.2.11}$$

$$75.6\ \text{g}\ CH_3CO_2H \left(\frac{\text{mol}\ CH_3CO_2H}{60.05\ \text{g}}\right)\left(\frac{\text{L solution}}{0.839\ \text{mol}\ CH_3CO_2H}\right) = 1.50\ \text{L solution} \tag{10.2.12}$$

? Exercise 10.2.5:

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

Answer

0.370 L

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 **10.2.2**).

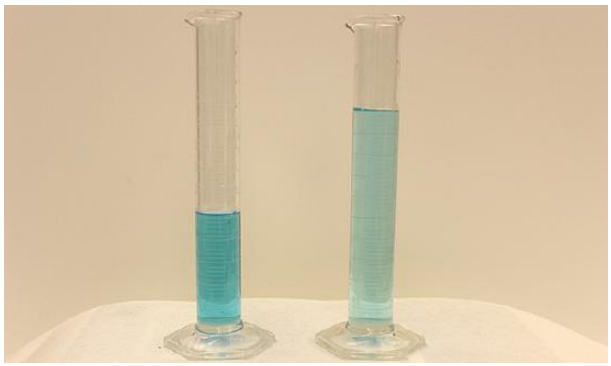


Figure **10.2.2**: Both solutions contain the same mass of copper nitrate. The solution on the right is more dilute because the copper nitrate is dissolved in more solvent. (credit: Mark Ott).

This figure shows two graduated cylinders side-by-side. The first has about half as much blue liquid as the second. The blue liquid is darker in the first cylinder than in the second.

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 **10.2.3**).



Figure **10.2.3**: 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)

This figure shows two photos. In the first, there is an empty glass container, 4.75 g of K M n O subscript 4 powder on a white circle, and a bottle of distilled water. In the second photo the powder and about half the water have been added to the glass container. The liquid in the glass container is almost black in color.

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:

$$n = ML$$

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

$$n_1 = M_1L_1$$

$$n_2 = M_2L_2$$

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:

$$M_1L_1 = M_2L_2$$

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:

$$C_1V_1 = C_2V_2$$

where C and V are concentration and volume, respectively.

Example 10.2.6: 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:

$$C_1V_1 = C_2V_2$$

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

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:

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

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

Exercise 10.2.6

What is the concentration of the solution that results from diluting 25.0 mL of a 2.04-M solution of CH3OH to 500.0 mL?

Answer

0.102 M CH_3OH

Example 10.2.7: 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 10.2.7

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

✓ Example 10.2.8: 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 10.2.8

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

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.

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 10.2: Molarity is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

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

10.3: Other Units for Solution Concentrations

Learning Objectives

- Define the concentration units of mass percentage, volume percentage, mass-volume percentage, parts-per-million (ppm), and parts-per-billion (ppb)
- Perform computations relating a solution's concentration and its components' volumes and/or masses using these units

In the previous section, we introduced molarity, a very useful measurement unit for evaluating the concentration of solutions. However, molarity is only one measure of concentration. In this section, we will introduce some other units of concentration that are commonly used in various applications, either for convenience or by convention.

Mass Percentage

Earlier in this chapter, we introduced percent composition as a measure of the relative amount of a given element in a compound. Percentages are also commonly used to express the composition of mixtures, including solutions. The mass percentage of a solution component is defined as the ratio of the component's mass to the solution's mass, expressed as a percentage:

$$\text{mass percentage} = \frac{\text{mass of component}}{\text{mass of solution}} \times 100\% \tag{10.3.1}$$

We are generally most interested in the mass percentages of solutes, but it is also possible to compute the mass percentage of solvent.

Mass percentage is also referred to by similar names such as *percent mass*, *percent weight*, *weight/weight percent*, and other variations on this theme. The most common symbol for mass percentage is simply the percent sign, %, although more detailed symbols are often used including %mass, %weight, and (w/w)%. Use of these more detailed symbols can prevent confusion of mass percentages with other types of percentages, such as volume percentages (to be discussed later in this section).

Mass percentages are popular concentration units for consumer products. The label of a typical liquid bleach bottle (Figure 10.3.1) cites the concentration of its active ingredient, sodium hypochlorite (NaOCl), as being 7.4%. A 100.0-g sample of bleach would therefore contain 7.4 g of NaOCl.



Figure 10.3.1: Liquid bleach is an aqueous solution of sodium hypochlorite (NaOCl). This brand has a concentration of 7.4% NaOCl by mass.

The sides of two cylindrical containers are shown. Each container's label is partially visible. The left container's label reads "Bleach." The right label contains more information about the product including the phrase, "Contains: Sodium hypochlorite 7.4 %."

Example 10.3.1: Calculation of Percent by Mass

A 5.0-g sample of spinal fluid contains 3.75 mg (0.00375 g) of glucose. What is the percent by mass of glucose in spinal fluid?

Solution

The spinal fluid sample contains roughly 4 mg of glucose in 5000 mg of fluid, so the mass fraction of glucose should be a bit less than one part in 1000, or about 0.1%. Substituting the given masses into the equation defining mass percentage yields:

$$\%\,\text{glucose} = \frac{3.75\ \text{mg glucose} \times \frac{1\ \text{g}}{1000\ \text{mg}}}{5.0\ \text{g spinal fluid}} = 0.075\%$$

The computed mass percentage agrees with our rough estimate (it's a bit less than 0.1%).

Note that while any mass unit may be used to compute a mass percentage (mg, g, kg, oz, and so on), the same unit must be used for both the solute and the solution so that the mass units cancel, yielding a dimensionless ratio. In this case, we converted the units of solute in the numerator from mg to g to match the units in the denominator. We could just as easily have converted the denominator from g to mg instead. As long as identical mass units are used for both solute and solution, the computed mass percentage will be correct.

? Exercise 10.3.1

A bottle of a tile cleanser contains 135 g of **HCl** and 775 g of water. What is the percent by mass of **HCl** in this cleanser?

Answer

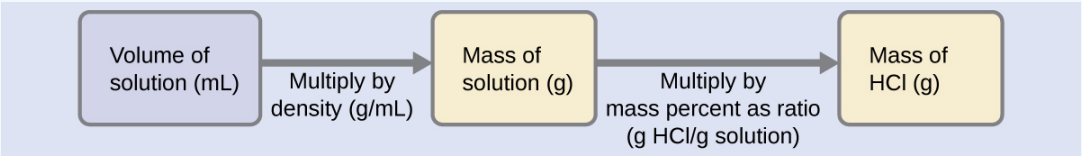
14.8%

✓ Example 10.3.2: Calculations using Mass Percentage

"Concentrated" hydrochloric acid is an aqueous solution of 37.2% **HCl** that is commonly used as a laboratory reagent. The density of this solution is 1.19 g/mL. What mass of **HCl** is contained in 0.500 L of this solution?

Solution

The HCl concentration is near 40%, so a 100-g portion of this solution would contain about 40 g of HCl. Since the solution density isn't greatly different from that of water (1 g/mL), a reasonable estimate of the HCl mass in 500 g (0.5 L) of the solution is about five times greater than that in a 100 g portion, or $5 \times 40 = 200\ \text{g}$. To derive the mass of solute in a solution from its mass percentage, we need to know the corresponding mass of the solution. Using the solution density given, we can convert the solution's volume to mass, and then use the given mass percentage to calculate the solute mass. This mathematical approach is outlined in this flowchart:



A diagram of three boxes connected by a right-facing arrow in between each is shown. The box on the left contains the phrase, "Volume of solution (m L)," the middle box reads, "Mass of solution (g)," while the one on the right contains the phrase, "Mass of H C l (g)." There is a phrase under the left arrow that says, "Multiply by density (g / m L)" and under the right arrow it states, "Multiply by mass percent as ratio (g H C l / g solution)."

For proper unit cancellation, the 0.500-L volume is converted into 500 mL, and the mass percentage is expressed as a ratio, 37.2 g HCl/g solution:

$$500\ \text{mL solution}\left(\frac{1.19\ \text{g solution}}{\text{mL solution}}\right)\left(\frac{37.2\ \text{g HCl}}{100\ \text{g solution}}\right) = 221\ \text{g HCl}$$

This mass of HCl is consistent with our rough estimate of approximately 200 g.

? Exercise 10.3.2

What volume of concentrated HCl solution contains 125 g of HCl?

Answer

282 mL

Volume Percentage

Liquid volumes over a wide range of magnitudes are conveniently measured using common and relatively inexpensive laboratory equipment. The concentration of a solution formed by dissolving a liquid solute in a liquid solvent is therefore often expressed as a volume percentage, %vol or (v/v)%:

$$\text{volume percentage} = \frac{\text{volume solute}}{\text{volume solution}} \times 100\% \tag{10.3.2}$$

Example 10.3.3: Calculations using Volume Percentage

Rubbing alcohol (isopropanol) is usually sold as a 70%vol aqueous solution. If the density of isopropyl alcohol is 0.785 g/mL, how many grams of isopropyl alcohol are present in a 355 mL bottle of rubbing alcohol?

Solution

Per the definition of volume percentage, the isopropanol volume is 70% of the total solution volume. Multiplying the isopropanol volume by its density yields the requested mass:

$$\begin{aligned} &355 \text{ mL solution} \left(\frac{70 \text{ mL isopropyl alcohol}}{100 \text{ mL solution}}\right)\left(\frac{0.785 \text{ g isopropyl alcohol}}{1 \text{ mL isopropyl alcohol}}\right) \\ &= 195 \text{ g isopropyl alcohol} \end{aligned}$$

Exercise 10.3.3

Wine is approximately 12% ethanol (CH_3CH_2OH) by volume. Ethanol has a molar mass of 46.06 g/mol and a density 0.789 g/mL. How many moles of ethanol are present in a 750-mL bottle of wine?

Answer

1.5 mol ethanol

Mass-Volume Percentage

“Mixed” percentage units, derived from the mass of solute and the volume of solution, are popular for certain biochemical and medical applications. A mass-volume percent is a ratio of a solute’s mass to the solution’s volume expressed as a percentage. The specific units used for solute mass and solution volume may vary, depending on the solution. For example, physiological saline solution, used to prepare intravenous fluids, has a concentration of 0.9% mass/volume (m/v), indicating that the composition is 0.9 g of solute per 100 mL of solution. The concentration of glucose in blood (commonly referred to as “blood sugar”) is also typically expressed in terms of a mass-volume ratio. Though not expressed explicitly as a percentage, its concentration is usually given in milligrams of glucose per deciliter (100 mL) of blood (Figure 10.3.2).



(a) (b)

Figure 10.3.2: “Mixed” mass-volume units are commonly encountered in medical settings. (a) The NaCl concentration of physiological saline is 0.9% (m/v). (b) This device measures glucose levels in a sample of blood. The normal range for glucose concentration in blood (fasting) is around 70–100 mg/dL. (credit a: modification of work by “The National Guard”/Flickr; credit b: modification of work by Biswarup Ganguly).

Two pictures are shown labeled a and b. Picture a depicts a clear, colorless solution in a plastic bag being held in a person’s hand. Picture b shows a person’s hand holding a detection meter with a digital readout screen while another hand holds someone’s finger up to the end of the meter. The meter is pressed to the drop of blood that is at the end of the person’s finger.

Parts per Million and Parts per Billion

Very low solute concentrations are often expressed using appropriately small units such as parts per million (ppm) or parts per billion (ppb). Like percentage ("part per hundred") units, ppm and ppb may be defined in terms of masses, volumes, or mixed mass-volume units. There are also ppm and ppb units defined with respect to numbers of atoms and molecules.

The mass-based definitions of ppm and ppb are given here:

$$\text{ppm} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^6 \text{ ppm} \tag{10.3.3}$$

$$\text{ppb} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^9 \text{ ppb} \tag{10.3.4}$$

Both ppm and ppb are convenient units for reporting the concentrations of pollutants and other trace contaminants in water. Concentrations of these contaminants are typically very low in treated and natural waters, and their levels cannot exceed relatively low concentration thresholds without causing adverse effects on health and wildlife. For example, the EPA has identified the maximum safe level of fluoride ion in tap water to be 4 ppm. Inline water filters are designed to reduce the concentration of fluoride and several other trace-level contaminants in tap water (Figure 10.3.3).



(a) (b)

Figure 10.3.3: (a) In some areas, trace-level concentrations of contaminants can render unfiltered tap water unsafe for drinking and cooking. (b) Inline water filters reduce the concentration of solutes in tap water. (credit a: modification of work by Jenn Durfey; credit b: modification of work by "vastateparkstaff"/Wikimedia commons).

Two pictures are shown labeled a and b. Picture a depicts a clear, colorless solution in a plastic bag being held in a person's hand. Picture b shows a person's hand holding a detection meter with a digital readout screen while another hand holds someone's finger up to the end of the meter. The meter is pressed to the drop of blood that is at the end of the person's finger.

Example 10.3.4: Parts per Million and Parts per Billion Concentrations

According to the EPA, when the concentration of lead in tap water reaches 15 ppb, certain remedial actions must be taken. What is this concentration in ppm? At this concentration, what mass of lead (μg) would be contained in a typical glass of water (300 mL)?

Solution

The definitions of the ppm and ppb units may be used to convert the given concentration from ppb to ppm. Comparing these two unit definitions shows that ppm is 1000 times greater than ppb (1 ppm = 10^3 ppb). Thus:

$$15 \cancel{\text{ ppb}} \times \frac{1 \text{ ppm}}{10^3 \cancel{\text{ ppb}}} = 0.015 \text{ ppm}$$

The definition of the ppb unit may be used to calculate the requested mass if the mass of the solution is provided. However, only the volume of solution (300 mL) is given, so we must use the density to derive the corresponding mass. We can assume the density of tap water to be roughly the same as that of pure water (~1.00 g/mL), since the concentrations of any dissolved substances should not be very large. Rearranging the equation defining the ppb unit and substituting the given quantities yields:

$$\text{ppb} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^9 \text{ ppb}$$

$$\text{mass solute} = \frac{\text{ppb} \times \text{mass solution}}{10^9 \text{ ppb}}$$

$$\text{mass solute} = \frac{15 \text{ ppb} \times 300 \text{ mL} \times \frac{1.00 \text{ g}}{\text{mL}}}{10^9 \text{ ppb}} = 4.5 \times 10^{-6} \text{ g}$$

Finally, convert this mass to the requested unit of micrograms:

$$4.5 \times 10^{-6} \text{ g} \times \frac{1 \ \mu\text{g}}{10^{-6} \text{ g}} = 4.5 \ \mu\text{g}$$

? Exercise 10.3.4

A 50.0-g sample of industrial wastewater was determined to contain 0.48 mg of mercury. Express the mercury concentration of the wastewater in ppm and ppb units.

Answer

9.6 ppm, 9600 ppb

Summary

In addition to molarity, a number of other solution concentration units are used in various applications. Percentage concentrations based on the solution components' masses, volumes, or both are useful for expressing relatively high concentrations, whereas lower concentrations are conveniently expressed using ppm or ppb units. These units are popular in environmental, medical, and other fields where mole-based units such as molarity are not as commonly used.

Glossary

mass percentage
ratio of solute-to-solution mass expressed as a percentage

mass-volume percent
ratio of solute mass to solution volume, expressed as a percentage

parts per billion (ppb)
ratio of solute-to-solution mass multiplied by 10^9

parts per million (ppm)
ratio of solute-to-solution mass multiplied by 10^6

volume percentage
ratio of solute-to-solution volume expressed as a percentage

This page titled 10.3: Other Units for Solution Concentrations is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

- **3.4: Other Units for Solution Concentrations** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

10.4: Solubility

Learning Objectives

- Describe the effects of temperature and pressure on solubility
- State Henry's law and use it in calculations involving the solubility of a gas in a liquid
- Explain the degrees of solubility possible for liquid-liquid solutions

Imagine adding a small amount of salt to a glass of water, stirring until all the salt has dissolved, and then adding a bit more. You can repeat this process until the salt concentration of the solution reaches its natural limit, a limit determined primarily by the relative strengths of the solute-solute, solute-solvent, and solvent-solvent attractive forces discussed in the previous two modules of this chapter. You can be certain that you have reached this limit because, no matter how long you stir the solution, undissolved salt remains. The concentration of salt in the solution at this point is known as its solubility.

The solubility of a solute in a particular solvent is the maximum concentration that may be achieved under given conditions when the dissolution process is at equilibrium. Referring to the example of salt in water:

$$\mathrm{NaCl}(s) \rightleftharpoons \mathrm{Na}^+(aq) + \mathrm{Cl}^-(aq) \tag{10.4.1}$$

When a solute's concentration is equal to its solubility, the solution is said to be saturated with that solute. If the solute's concentration is less than its solubility, the solution is said to be unsaturated. A solution that contains a relatively low concentration of solute is called dilute, and one with a relatively high concentration is called concentrated.

If we add more salt to a saturated solution of salt, we see it fall to the bottom and no more seems to dissolve. In fact, the added salt does dissolve, as represented by the forward direction of the dissolution equation. Accompanying this process, dissolved salt will precipitate, as depicted by the reverse direction of the equation. The system is said to be at equilibrium when these two reciprocal processes are occurring at equal rates, and so the amount of undissolved and dissolved salt remains constant. Support for the simultaneous occurrence of the dissolution and precipitation processes is provided by noting that the number and sizes of the undissolved salt crystals will change over time, though their combined mass will remain the same.



Video **10.4.1**: Watch this impressive video showing the precipitation of sodium acetate from a supersaturated solution.

Solutions may be prepared in which a solute concentration exceeds its solubility. Such solutions are said to be supersaturated, and they are interesting examples of nonequilibrium states. For example, the carbonated beverage in an open container that has not yet "gone flat" is supersaturated with carbon dioxide gas; given time, the CO_2 concentration will decrease until it reaches its equilibrium value.

Solutions of Gases in Liquids

In an earlier module of this chapter, the effect of intermolecular attractive forces on solution formation was discussed. The chemical structures of the solute and solvent dictate the types of forces possible and, consequently, are important factors in determining solubility. For example, under similar conditions, the water solubility of oxygen is approximately three times greater than that of

helium, but 100 times less than the solubility of chloromethane, $CHCl_3$. Considering the role of the solvent's chemical structure, note that the solubility of oxygen in the liquid hydrocarbon hexane, C_6H_{14}, is approximately 20 times greater than it is in water.

Other factors also affect the solubility of a given substance in a given solvent. Temperature is one such factor, with gas solubility typically decreasing as temperature increases (Figure **10.4.1**). This is one of the major impacts resulting from the thermal pollution of natural bodies of water.

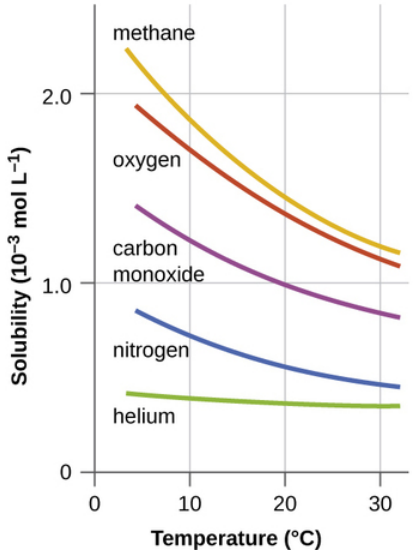


Figure **10.4.1**: The solubilities of these gases in water decrease as the temperature increases. All solubilities were measured with a constant pressure of 101.3 kPa (1 atm) of gas above the solutions.

When the temperature of a river, lake, or stream is raised abnormally high, usually due to the discharge of hot water from some industrial process, the solubility of oxygen in the water is decreased. Decreased levels of dissolved oxygen may have serious consequences for the health of the water's ecosystems and, in severe cases, can result in large-scale fish kills (Figure **10.4.2**).



(a) (b)

Figure **10.4.2**: (a) The small bubbles of air in this glass of chilled water formed when the water warmed to room temperature and the solubility of its dissolved air decreased. (b) The decreased solubility of oxygen in natural waters subjected to thermal pollution can result in large-scale fish kills. (credit a: modification of work by Liz West; credit b: modification of work by U.S. Fish and Wildlife Service)

The solubility of a gaseous solute is also affected by the partial pressure of solute in the gas to which the solution is exposed. Gas solubility increases as the pressure of the gas increases. Carbonated beverages provide a nice illustration of this relationship. The carbonation process involves exposing the beverage to a relatively high pressure of carbon dioxide gas and then sealing the beverage container, thus saturating the beverage with CO_2 at this pressure. When the beverage container is opened, a familiar hiss is heard as the carbon dioxide gas pressure is released, and some of the dissolved carbon dioxide is typically seen leaving solution in the form of small bubbles (Figure **10.4.3**). At this point, the beverage is supersaturated with carbon dioxide and, with time, the dissolved carbon dioxide concentration will decrease to its equilibrium value and the beverage will become "flat."

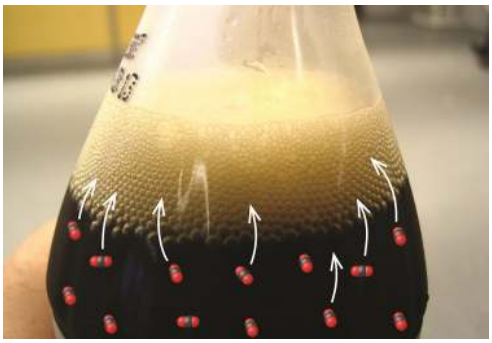


Figure 10.4.3: Opening the bottle of carbonated beverage reduces the pressure of the gaseous carbon dioxide above the beverage. The solubility of CO_2 is thus lowered, and some dissolved carbon dioxide may be seen leaving the solution as small gas bubbles. (credit: modification of work by Derrick Coetzee)

A dark brown liquid is shown in a clear, colorless container. A thick layer of beige bubbles appear at the surface of the liquid. In the liquid, thirteen small clusters of single black spheres with two red spheres attached to the left and right are shown. Red spheres represent oxygen atoms and black represent carbon atoms. Seven white arrows point upward in the container from these clusters to the bubble layer at the top of the liquid.

For many gaseous solutes, the relation between solubility, C_g, and partial pressure, P_g, is a proportional one:

$$C_g = kP_g$$

where k is a proportionality constant that depends on the identities of the gaseous solute and solvent, and on the solution temperature. This is a mathematical statement of Henry's law: The quantity of an ideal gas that dissolves in a definite volume of liquid is directly proportional to the pressure of the gas.

Example 10.4.1: Application of Henry's Law

At 20 °C, the concentration of dissolved oxygen in water exposed to gaseous oxygen at a partial pressure of 101.3 kPa (760 torr) is 1.38×10^{-3} mol L^{-1}. Use Henry's law to determine the solubility of oxygen when its partial pressure is 20.7 kPa (155 torr), the approximate pressure of oxygen in earth's atmosphere.

Solution

According to Henry's law, for an ideal solution the solubility, C_g, of a gas (1.38×10^{-3} mol L^{-1}, in this case) is directly proportional to the pressure, P_g, of the undissolved gas above the solution (101.3 kPa, or 760 torr, in this case). Because we know both C_g and P_g, we can rearrange this expression to solve for k.

$$\begin{aligned} C_g &= kP_g \\ k &= \frac{C_g}{P_g} \\ &= \frac{1.38 \times 10^{-3}\ \text{mol L}^{-1}}{101.3\ \text{kPa}} \\ &= 1.36 \times 10^{-5}\ \text{mol L}^{-1}\ \text{kPa}^{-1} \\ &\quad (1.82 \times 10^{-6}\ \text{mol L}^{-1}\ \text{torr}^{-1}) \end{aligned}$$

Now we can use k to find the solubility at the lower pressure.

$$C_g = kP_g$$

$$\begin{aligned} &1.36 \times 10^{-5}\ \text{mol L}^{-1}\ \text{kPa}^{-1} \times 20.7\ \text{kPa} \\ &(\text{or } 1.82 \times 10^{-6}\ \text{mol L}^{-1}\ \text{torr}^{-1} \times 155\ \text{torr}) \\ &= 2.82 \times 10^{-4}\ \text{mol L}^{-1} \end{aligned}$$

Note that various units may be used to express the quantities involved in these sorts of computations. Any combination of units that yield to the constraints of dimensional analysis are acceptable.

Exercise 10.4.1

Exposing a 100.0 mL sample of water at 0 °C to an atmosphere containing a gaseous solute at 20.26 kPa (152 torr) resulted in the dissolution of 1.45×10^{-3} g of the solute. Use Henry's law to determine the solubility of this gaseous solute when its pressure is 101.3 kPa (760 torr).

Answer

7.25×10^{-3} g in 100.0 mL or 0.0725 g/L

Case Study: Decompression Sickness ("The Bends")

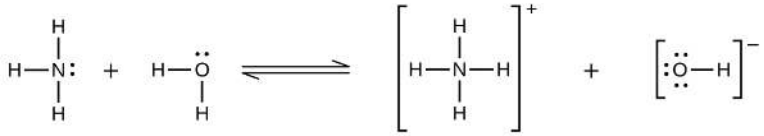
Decompression sickness (DCS), or "the bends," is an effect of the increased pressure of the air inhaled by scuba divers when swimming underwater at considerable depths. In addition to the pressure exerted by the atmosphere, divers are subjected to additional pressure due to the water above them, experiencing an increase of approximately 1 atm for each 10 m of depth. Therefore, the air inhaled by a diver while submerged contains gases at the corresponding higher ambient pressure, and the concentrations of the gases dissolved in the diver's blood are proportionally higher per Henry's law.



Figure **10.4.4**: (a) US Navy divers undergo training in a recompression chamber. (b) Divers receive hyperbaric oxygen therapy.
Two photos are shown. The first shows two people seated in a steel chamber on benches that run length of the chamber on each side. The chamber has a couple of small circular windows and an open hatch-type door. One of the two people is giving a thumbs up gesture. The second image provides a view through a small, circular window. Inside the two people can be seen with masks over their mouths and noses. The people appear to be reading.

As the diver ascends to the surface of the water, the ambient pressure decreases and the dissolved gases becomes less soluble. If the ascent is too rapid, the gases escaping from the diver's blood may form bubbles that can cause a variety of symptoms ranging from rashes and joint pain to paralysis and death. To avoid DCS, divers must ascend from depths at relatively slow speeds (10 or 20 m/min) or otherwise make several decompression stops, pausing for several minutes at given depths during the ascent. When these preventive measures are unsuccessful, divers with DCS are often provided hyperbaric oxygen therapy in pressurized vessels called decompression (or recompression) chambers (Figure **10.4.4**).

Deviations from Henry's law are observed when a chemical reaction takes place between the gaseous solute and the solvent. Thus, for example, the solubility of ammonia in water does not increase as rapidly with increasing pressure as predicted by the law because ammonia, being a base, reacts to some extent with water to form ammonium ions and hydroxide ions.



Gases can form **supersaturated solutions**. If a solution of a gas in a liquid is prepared either at low temperature or under pressure (or both), then as the solution warms or as the gas pressure is reduced, the solution may become supersaturated. In 1986, more than 1700 people in Cameroon were killed when a cloud of gas, almost certainly carbon dioxide, bubbled from Lake Nyos (Figure **10.4.5**), a deep lake in a volcanic crater. The water at the bottom of Lake Nyos is saturated with carbon dioxide by volcanic activity

beneath the lake. It is believed that the lake underwent a turnover due to gradual heating from below the lake, and the warmer, less-dense water saturated with carbon dioxide reached the surface. Consequently, tremendous quantities of dissolved CO_2 were released, and the colorless gas, which is denser than air, flowed down the valley below the lake and suffocated humans and animals living in the valley.



(a) (b)

Figure **10.4.5**: (a) It is believed that the 1986 disaster that killed more than 1700 people near Lake Nyos in Cameroon resulted when a large volume of carbon dioxide gas was released from the lake. (b) A CO_2 vent has since been installed to help outgas the lake in a slow, controlled fashion and prevent a similar catastrophe from happening in the future. (credit a: modification of work by Jack Lockwood; credit b: modification of work by Bill Evans)

Two photos are shown. The first is an aerial view of a lake surrounded by green hills. The second shows a large body of water with a fountain sending liquid up into the air several yards or meters above the surface of the water.

Solutions of Liquids in Liquids

We know that some liquids mix with each other in all proportions; in other words, they have infinite mutual solubility and are said to be miscible. Ethanol, sulfuric acid, and ethylene glycol (popular for use as antifreeze, pictured in Figure **10.4.6**) are examples of liquids that are completely miscible with water. Two-cycle motor oil is miscible with gasoline.



Figure **10.4.6**: Water and antifreeze are miscible; mixtures of the two are homogeneous in all proportions. (credit: "dno1967"/Wikimedia commons)

Liquids that mix with water in all proportions are usually polar substances or substances that form hydrogen bonds. For such liquids, the dipole-dipole attractions (or hydrogen bonding) of the solute molecules with the solvent molecules are at least as strong as those between molecules in the pure solute or in the pure solvent. Hence, the two kinds of molecules mix easily. Likewise, nonpolar liquids are miscible with each other because there is no appreciable difference in the strengths of solute-solute, solvent-solvent, and solute-solvent intermolecular attractions. The solubility of polar molecules in polar solvents and of nonpolar molecules in nonpolar solvents is, again, an illustration of the chemical axiom "like dissolves like."

Two liquids that do not mix to an appreciable extent are called immiscible. Layers are formed when we pour immiscible liquids into the same container. Gasoline, oil (Figure **10.4.7**), benzene, carbon tetrachloride, some paints, and many other nonpolar liquids are immiscible with water. The attraction between the molecules of such nonpolar liquids and polar water molecules is ineffectively weak. The only strong attractions in such a mixture are between the water molecules, so they effectively squeeze out the molecules

of the nonpolar liquid. The distinction between immiscibility and miscibility is really one of degrees, so that miscible liquids are of infinite mutual solubility, while liquids said to be immiscible are of very low (though not zero) mutual solubility.



Figure 10.4.7: Water and oil are immiscible. Mixtures of these two substances will form two separate layers with the less dense oil floating on top of the water. (credit: "Yortw"/Flickr)

This is a photo of a clear, colorless martini glass containing a golden colored liquid layer resting on top of a clear, colorless liquid.

Two liquids, such as bromine and water, that are of moderate mutual solubility are said to be partially miscible. Two partially miscible liquids usually form two layers when mixed. In the case of the bromine and water mixture, the upper layer is water, saturated with bromine, and the lower layer is bromine saturated with water. Since bromine is nonpolar, and, thus, not very soluble in water, the water layer is only slightly discolored by the bright orange bromine dissolved in it. Since the solubility of water in bromine is very low, there is no noticeable effect on the dark color of the bromine layer (Figure 10.4.8).



Figure 10.4.8: Bromine (the deep orange liquid on the left) and water (the clear liquid in the middle) are partially miscible. The top layer in the mixture on the right is a saturated solution of bromine in water; the bottom layer is a saturated solution of water in bromine. (credit: Paul Flowers)

This figure shows three test tubes. The first test tube holds a dark orange-brown substance. The second test tube holds a clear substance. The amount of substance in both test tubes is the same. The third test tube holds a dark orange-brown substance on the bottom with a lighter orange substance on top. The amount of substance in the third test tube is almost double of the first two.

Solutions of Solids in Liquids

The dependence of solubility on temperature for a number of inorganic solids in water is shown by the solubility curves in Figure 10.4.9. Reviewing these data indicate a general trend of increasing solubility with temperature, although there are exceptions, as illustrated by the ionic compound cerium sulfate.

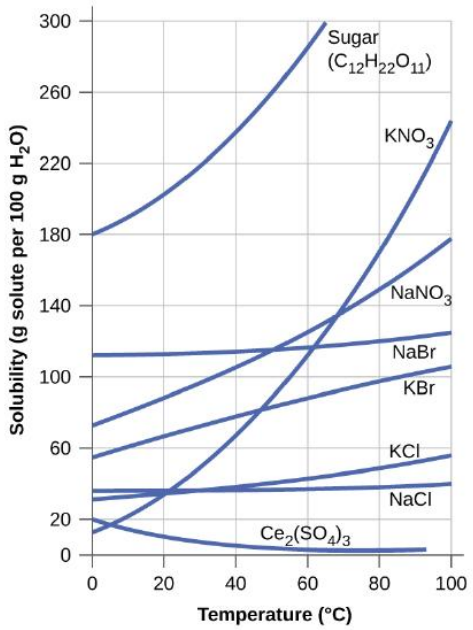


Figure **10.4.9**: This graph shows how the solubility of several solids changes with temperature.

This shows a graph of the solubility of sugar C subscript 12 H subscript 22 O subscript 11, K N O subscript 3, N a N O subscript 3, N a B r, K B r, N a subscript 2 S O subscript 4, K C l, and C e subscript 2 left parenthesis S O subscript 4 right parenthesis subscript 3 in g solute per 100 g H subscript 2 O at temperatures ranging from 0 degrees Celsius to 100 degrees Celsius. At 0 degrees Celsius, solubilities are approximately 180 for sugar C subscript 12 H subscript 22 O subscript 11, 115 for K N O subscript 3, 75 for N a N O subscript 3, 115 for N a B r, 55 for K B r, 7 for N a subscript 2 S O subscript 4, 25 for K C l, and 20 for C e subscript 2 left parenthesis S O subscript 4 right parenthesis subscript 3. At 0 degrees Celsius, solubilities are approximately 180 for sugar C subscript 12 H subscript 22 O subscript 11, 115 for K N O subscript 3, 75 for N a N O subscript 3, 115 for N a B r, 55 for K B r, 7 for N a subscript 2 S O subscript 4, 25 for K C l, and 20 for C e subscript 2 left parenthesis S O subscript 4 right parenthesis subscript 3. At 100 degrees Celsius, sugar C subscript 12 H subscript 22 O subscript 11 has exceeded the upper limit of solubility indicated on the graph, 240 for K N O subscript 3, 178 for N a N O subscript 3, 123 for N a B r, 105 for K B r, 52 for N a subscript 2 S O subscript 4, 58 for K C l, and the graph for C e subscript 2 left parenthesis S O subscript 4 right parenthesis subscript 3 stops at about 92 degrees Celsius where the solubility is nearly zero. The graph for N a subscript 2 S O subscript 4 is shown in red. All others substances are shown in blue. The solubility of this substance increases until about 30 degrees Celsius and declines beyond that point with increasing temperature.

The temperature dependence of solubility can be exploited to prepare supersaturated solutions of certain compounds. A solution may be saturated with the compound at an elevated temperature (where the solute is more soluble) and subsequently cooled to a lower temperature without precipitating the solute. The resultant solution contains solute at a concentration greater than its equilibrium solubility at the lower temperature (i.e., it is supersaturated) and is relatively stable. Precipitation of the excess solute can be initiated by adding a seed crystal (see the video in the Link to Learning earlier in this module) or by mechanically agitating the solution. Some hand warmers, such as the one pictured in Figure **10.4.10**, take advantage of this behavior.



Figure **10.4.10**: This hand warmer produces heat when the sodium acetate in a supersaturated solution precipitates. Precipitation of the solute is initiated by a mechanical shockwave generated when the flexible metal disk within the solution is “clicked.” (credit: modification of work by “Velela”/Wikimedia Commons)

Three photos of hand warmers are shown side by side with an arrow pointing from the first photo to the second, and another arrow pointing from the second photo to the third. The first packet contains a clear colorless liquid and a small metal disc can be seen. In the second packet, the disc can’t be seen and a dispersion of white liquid is beginning. In the third packet, all of the liquid is white.



Video 10.4.2: This video shows the crystallization process occurring in a hand warmer.

Summary

The extent to which one substance will dissolve in another is determined by several factors, including the types and relative strengths of intermolecular attractive forces that may exist between the substances' atoms, ions, or molecules. This tendency to dissolve is quantified as substance's solubility, its maximum concentration in a solution at equilibrium under specified conditions. A saturated solution contains solute at a concentration equal to its solubility. A supersaturated solution is one in which a solute's concentration exceeds its solubility—a nonequilibrium (unstable) condition that will result in solute precipitation when the solution is appropriately perturbed. Miscible liquids are soluble in all proportions, and immiscible liquids exhibit very low mutual solubility. Solubilities for gaseous solutes decrease with increasing temperature, while those for most, but not all, solid solutes increase with temperature. The concentration of a gaseous solute in a solution is proportional to the partial pressure of the gas to which the solution is exposed, a relation known as Henry's law.

Key Equations

- $C_g = kP_g$

Glossary

Henry's law
law stating the proportional relationship between the concentration of dissolved gas in a solution and the partial pressure of the gas in contact with the solution

immiscible
of negligible mutual solubility; typically refers to liquid substances

miscible
mutually soluble in all proportions; typically refers to liquid substances

partially miscible
of moderate mutual solubility; typically refers to liquid substances

saturated
of concentration equal to solubility; containing the maximum concentration of solute possible for a given temperature and pressure

solubility
extent to which a solute may be dissolved in water, or any solvent

supersaturated

of concentration that exceeds solubility; a nonequilibrium state

unsaturated

of concentration less than solubility

This page titled 10.4: Solubility is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

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

10.5: Colligative Properties

Learning Objectives

- Express concentrations of solution components using mole fraction and molality
- Describe the effect of solute concentration on various solution properties (vapor pressure, boiling point, freezing point, and osmotic pressure)
- Perform calculations using the mathematical equations that describe these various colligative effects
- Describe the process of distillation and its practical applications
- Explain the process of osmosis and describe how it is applied industrially and in nature

The properties of a solution are different from those of either the pure solute(s) or solvent. Many solution properties are dependent upon the chemical identity of the solute. Compared to pure water, a solution of hydrogen chloride is more acidic, a solution of ammonia is more basic, a solution of sodium chloride is more dense, and a solution of sucrose is more viscous. There are a few solution properties, however, that depend *only* upon the total concentration of solute species, regardless of their identities. These colligative properties include vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure. This small set of properties is of central importance to many natural phenomena and technological applications, as will be described in this module.

Mole Fraction and Molality

Several units commonly used to express the concentrations of solution components were introduced in an earlier chapter of this text, each providing certain benefits for use in different applications. For example, molarity (M) is a convenient unit for use in stoichiometric calculations, since it is defined in terms of the molar amounts of solute species:

$$M = \frac{\text{mol solute}}{\text{L solution}} \tag{10.5.1}$$

Because solution volumes vary with temperature, molar concentrations will likewise vary. When expressed as molarity, the concentration of a solution with identical numbers of solute and solvent species will be different at different temperatures, due to the contraction/expansion of the solution. More appropriate for calculations involving many colligative properties are mole-based concentration units whose values are not dependent on temperature. Two such units are *mole fraction* (introduced in the previous chapter on gases) and *molality*.

The mole fraction, χ, of a component is the ratio of its molar amount to the total number of moles of all solution components:

$$\chi_A = \frac{\text{mol A}}{\text{total mol of all components}} \tag{10.5.2}$$

Molality is a concentration unit defined as the ratio of the numbers of moles of solute to the mass of the solvent in kilograms:

$$m = \frac{\text{mol solute}}{\text{kg solvent}} \tag{10.5.3}$$

Since these units are computed using only masses and molar amounts, they do not vary with temperature and, thus, are better suited for applications requiring temperature-independent concentrations, including several colligative properties, as will be described in this chapter module.

Example 10.5.1: Calculating Mole Fraction and Molality

The antifreeze in most automobile radiators is a mixture of equal volumes of ethylene glycol and water, with minor amounts of other additives that prevent corrosion. What are the (a) mole fraction and (b) molality of ethylene glycol, $C_2H_4(OH)_2$, in a solution prepared from 2.22×10^3 g of ethylene glycol and 2.00×10^3 g of water (approximately 2 L of glycol and 2 L of water)?

Solution

(a) The mole fraction of ethylene glycol may be computed by first deriving molar amounts of both solution components and then substituting these amounts into the unit definition.

$$\text{mol } C_2H_4(OH)_2 = 2220 \text{ g} \times \frac{1 \text{ mol } C_2H_4(OH)_2}{62.07 \text{ g } C_2H_4(OH)_2} = 35.8 \text{ mol } C_2H_4(OH)_2$$

$$\text{mol } H_2O = 2000 \text{ g} \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 111 \text{ mol } H_2O$$

$$\chi_{\text{ethylene glycol}} = \frac{35.8 \text{ mol } C_2H_4(OH)_2}{(35.8 + 111) \text{ mol total}} = 0.245$$

Notice that mole fraction is a dimensionless property, being the ratio of properties with identical units (moles).

(b) To find molality, we need to know the moles of the solute and the mass of the solvent (in kg).

First, use the given mass of ethylene glycol and its molar mass to find the moles of solute:

$$2220 \text{ g } C_2H_4(OH)_2 \left(\frac{\text{mol } C_2H_2(OH)_2}{62.07 \text{ g}} \right) = 35.8 \text{ mol } C_2H_4(OH)_2$$

Then, convert the mass of the water from grams to kilograms:

$$2000 \text{ g } H_2O \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) = 2 \text{ kg } H_2O$$

Finally, calculate molarity per its definition:

$$\text{molality} = \frac{\text{mol solute}}{\text{kg solvent}}$$

$$\text{molality} = \frac{35.8 \text{ mol } C_2H_4(OH)_2}{2 \text{ kg } H_2O}$$

$$\text{molality} = 17.9 \, m$$

? Exercise 10.5.1

What are the mole fraction and molality of a solution that contains 0.850 g of ammonia, NH_3, dissolved in 125 g of water?

Answer

7.14×10^{-3}; 0.399 *m*

✓ Example 10.5.2: Converting Mole Fraction and Molal Concentrations

Calculate the mole fraction of solute and solvent in a 3.0 *m* solution of sodium chloride.

Solution

Converting from one concentration unit to another is accomplished by first comparing the two unit definitions. In this case, both units have the same numerator (moles of solute) but different denominators. The provided molal concentration may be written as:

$$\frac{3.0 \text{ mol NaCl}}{1.0 \text{ kg } H_2O}$$

The numerator for this solution's mole fraction is, therefore, 3.0 mol NaCl. The denominator may be computed by deriving the molar amount of water corresponding to 1.0 kg

$$1.0 \text{ kg } H_2O \left(\frac{1000 \text{ g}}{1 \text{ kg}} \right) \left(\frac{\text{mol } H_2O}{18.02 \text{ g}} \right) = 55 \text{ mol } H_2O$$

and then substituting these molar amounts into the definition for mole fraction.

$$X_{H_2O} = \frac{\text{mol } H_2O}{\text{mol NaCl} + \text{mol } H_2O}$$
$$X_{H_2O} = \frac{55 \text{ mol } H_2O}{3.0 \text{ mol NaCl} + 55 \text{ mol } H_2O}$$
$$X_{H_2O} = 0.95$$
$$X_{NaCl} = \frac{\text{mol NaCl}}{\text{mol NaCl} + \text{mol } H_2O}$$
$$X_{NaCl} = \frac{3.0 \text{ mol NaCl}}{3.0 \text{ mol NaCl} + 55 \text{ mol } H_2O}$$
$$X_{NaCl} = 0.052$$

? Exercise 10.5.2

The mole fraction of iodine, I_2, dissolved in dichloromethane, CH_2Cl_2, is 0.115. What is the molal concentration, *m*, of iodine in this solution?

Answer

1.50 *m*

Vapor Pressure Lowering

As described in the chapter on liquids and solids, the equilibrium vapor pressure of a liquid is the pressure exerted by its gaseous phase when vaporization and condensation are occurring at equal rates:

$$\text{liquid} \rightleftharpoons \text{gas} \tag{10.5.4}$$

Dissolving a nonvolatile substance in a volatile liquid results in a lowering of the liquid's vapor pressure. This phenomenon can be rationalized by considering the effect of added solute molecules on the liquid's vaporization and condensation processes. To vaporize, solvent molecules must be present at the surface of the solution. The presence of solute decreases the surface area available to solvent molecules and thereby reduces the rate of solvent vaporization. Since the rate of condensation is unaffected by the presence of solute, the net result is that the vaporization-condensation equilibrium is achieved with fewer solvent molecules in the vapor phase (i.e., at a lower vapor pressure) (Figure 10.5.1). While this kinetic interpretation is useful, it does not account for several important aspects of the colligative nature of vapor pressure lowering. A more rigorous explanation involves the property of *entropy*, a topic of discussion in a later text chapter on thermodynamics. For purposes of understanding the lowering of a liquid's vapor pressure, it is adequate to note that the greater entropy of a solution in comparison to its separate solvent and solute serves to effectively stabilize the solvent molecules and hinder their vaporization. A lower vapor pressure results, and a correspondingly higher boiling point as described in the next section of this module.

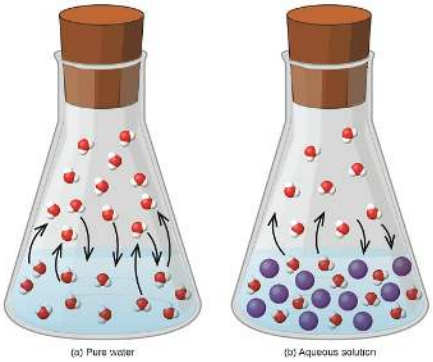


Figure **10.5.1**: The presence of nonvolatile solutes lowers the vapor pressure of a solution by impeding the evaporation of solvent molecules.

This figure contains two images. Figure a is labeled “pure water.” It shows a beaker half-filled with liquid. In the liquid, eleven molecules are evenly dispersed in the liquid each consisting of one central red sphere and two slightly smaller white spheres are shown. Four molecules near the surface of the liquid have curved arrows drawn from them pointing to the space above the liquid in the beaker. Above the liquid, twelve molecules are shown, with arrows pointing from three of them into the liquid below. Figure b is labeled “Aqueous solution.” It is similar to figure a except that eleven blue spheres, slightly larger in size than the molecules, are dispersed evenly in the liquid. Only four curved arrows appear in this diagram with two from the molecules in the liquid pointing to the space above and two from molecules in the space above the liquid pointing into the liquid below.

The relationship between the vapor pressures of solution components and the concentrations of those components is described by Raoult’s law: *The partial pressure exerted by any component of an ideal solution is equal to the vapor pressure of the pure component multiplied by its mole fraction in the solution.*

$$P_A = X_A P_A^\circ \tag{10.5.5}$$

where P_A is the partial pressure exerted by component A in the solution, P_A° is the vapor pressure of pure A, and X_A is the mole fraction of A in the solution. (Mole fraction is a concentration unit introduced in the chapter on gases.)

Recalling that the total pressure of a gaseous mixture is equal to the sum of partial pressures for all its components (Dalton’s law of partial pressures), the total vapor pressure exerted by a solution containing *i* components is

$$P_{solution} = \sum_i P_i = \sum_i X_i P_i^\circ \tag{10.5.6}$$

A nonvolatile substance is one whose vapor pressure is negligible ($P^\circ \approx 0$), and so the vapor pressure above a solution containing only nonvolatile solutes is due only to the solvent:

$$P_{solution} = X_{solvent} P_{solvent}^\circ \tag{10.5.7}$$

Example 10.5.3: Calculation of a Vapor Pressure

Compute the vapor pressure of an ideal solution containing 92.1 g of glycerin, $C_3H_5(OH)_3$, and 184.4 g of ethanol, C_2H_5OH, at 40 °C. The vapor pressure of pure ethanol is 0.178 atm at 40 °C. Glycerin is essentially nonvolatile at this temperature.

Solution

Since the solvent is the only volatile component of this solution, its vapor pressure may be computed per Raoult’s law as:

$$P_{solution} = X_{solvent} P_{solvent}^\circ$$

First, calculate the molar amounts of each solution component using the provided mass data.

$$92.1 \text{ g } \cancel{C_3H_5(OH)_3} \times \frac{1 \text{ mol } C_3H_5(OH)_3}{92.094 \text{ g } \cancel{C_3H_5(OH)_3}} = 1.00 \text{ mol } C_3H_5(OH)_3$$

$$184.4 \text{ g } \cancel{C_2H_5OH} \times \frac{1 \text{ mol } C_2H_5OH}{46.069 \text{ g } \cancel{C_2H_5OH}} = 4.000 \text{ mol } C_2H_5OH$$

Next, calculate the mole fraction of the solvent (ethanol) and use Raoult’s law to compute the solution’s vapor pressure.

$$X_{C_2H_5OH} = \frac{4.000\ \text{mol}}{(1.00\ \text{mol} + 4.000\ \text{mol})} = 0.800$$

$$P_{solv} = X_{solv} P^{\circ}_{solv} = 0.800 \times 0.178\ \text{atm} = 0.142\ \text{atm}$$

? Exercise 10.5.3

A solution contains 5.00 g of urea, $CO(NH_2)_2$ (a nonvolatile solute) and 0.100 kg of water. If the vapor pressure of pure water at 25 °C is 23.7 torr, what is the vapor pressure of the solution?

Answer

23.4 torr

Elevation of the Boiling Point of a Solvent

As described in the chapter on liquids and solids, the *boiling point* of a liquid is the temperature at which its vapor pressure is equal to ambient atmospheric pressure. Since the vapor pressure of a solution is lowered due to the presence of nonvolatile solutes, it stands to reason that the solution's boiling point will subsequently be increased. Compared to pure solvent, a solution, therefore, will require a higher temperature to achieve any given vapor pressure, including one equivalent to that of the surrounding atmosphere. The increase in boiling point observed when nonvolatile solute is dissolved in a solvent, ΔT_b, is called boiling point elevation and is directly proportional to the molal concentration of solute species:

$$\Delta T_b = K_b m \tag{10.5.8}$$

where

- K_b is the boiling point elevation constant, or the *ebullioscopic constant* and
- m is the molal concentration (molality) of all solute species.

Boiling point elevation constants are characteristic properties that depend on the identity of the solvent. Values of K_b for several solvents are listed in Table 10.5.1.

Table 10.5.1: Boiling Point Elevation and Freezing Point Depression Constants for Several Solvents

Solvent	Boiling Point (°C at 1 atm)	K_b (Cm^{-1})	Freezing Point (°C at 1 atm)	K_f (Cm^{-1})
water	100.0	0.512	0.0	1.86
hydrogen acetate	118.1	3.07	16.6	3.9
benzene	80.1	2.53	5.5	5.12
chloroform	61.26	3.63	−63.5	4.68
nitrobenzene	210.9	5.24	5.67	8.1

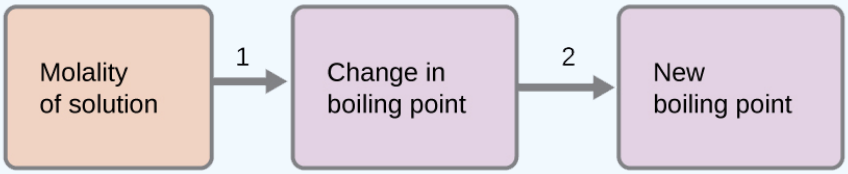
The extent to which the vapor pressure of a solvent is lowered and the boiling point is elevated depends on the total number of solute particles present in a given amount of solvent, not on the mass or size or chemical identities of the particles. A 1 *m* aqueous solution of sucrose (342 g/mol) and a 1 *m* aqueous solution of ethylene glycol (62 g/mol) will exhibit the same boiling point because each solution has one mole of solute particles (molecules) per kilogram of solvent.

✓ Example 10.5.4: Calculating the Boiling Point of a Solution

What is the boiling point of a 0.33 *m* solution of a nonvolatile solute in benzene?

Solution

Use the equation relating boiling point elevation to solute molality to solve this problem in two steps.



1. *Calculate the change in boiling point.*
   $\Delta T_b = K_b m = 2.53\ °C\ m^{-1} \times 0.33\ m = 0.83\ °C$

- *Add the boiling point elevation to the pure solvent's boiling point.*
  $\text{Boiling temperature} = 80.1\ °C + 0.83\ °C = 80.9\ °C$

Exercise 10.5.4

What is the boiling point of the antifreeze described in Example 10.5.4?

Answer

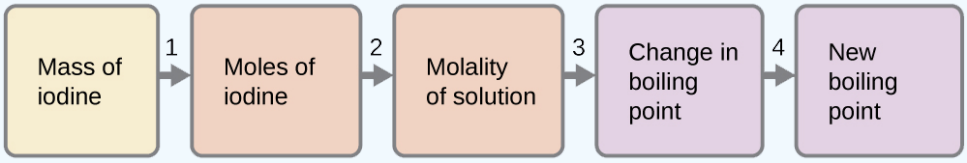
109.2 °C

Example 10.5.5: The Boiling Point of an Iodine Solution

Find the boiling point of a solution of 92.1 g of iodine, I_2, in 800.0 g of chloroform, $CHCl_3$, assuming that the iodine is nonvolatile and that the solution is ideal.

Solution

We can solve this problem using four steps.



1. *Convert from grams to moles of I_2 using the molar mass of I_2 in the unit conversion factor.*

Result: 0.363 mol

Determine the molality of the solution from the number of moles of solute and the mass of solvent, in kilograms.

Result: 0.454 *m*

Use the direct proportionality between the change in boiling point and molal concentration to determine how much the boiling point changes.

Result: 1.65 °C

Determine the new boiling point from the boiling point of the pure solvent and the change.

Result: 62.91 °C

Check each result as a self-assessment.

Exercise 10.5.5: glycerin:Water Solution

What is the boiling point of a solution of 1.0 g of glycerin, $C_3H_5(OH)_3$, in 47.8 g of water? Assume an ideal solution.

Answer

100.12 °C

Distillation of Solutions

Distillation is a technique for separating the components of mixtures that is widely applied in both in the laboratory and in industrial settings. It is used to refine petroleum, to isolate fermentation products, and to purify water. This separation technique involves the controlled heating of a sample mixture to selectively vaporize, condense, and collect one or more components of interest. A typical apparatus for laboratory-scale distillations is shown in Figure **10.5.2**.

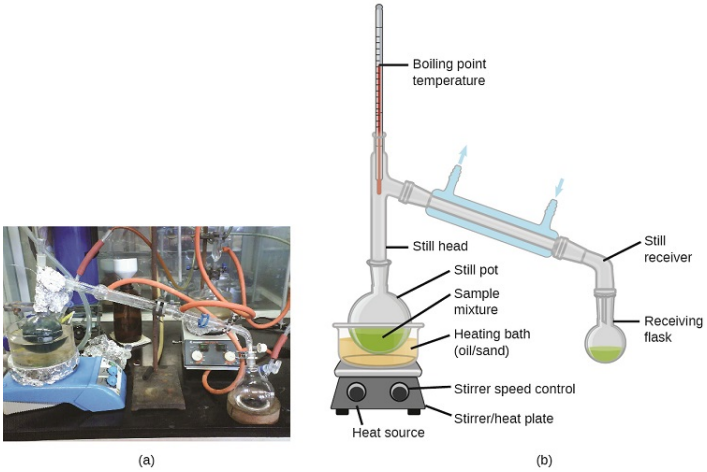


Figure **10.5.2**: A typical laboratory distillation unit is shown in (a) a photograph and (b) a schematic diagram of the components. (credit a: modification of work by "Rifleman82"/Wikimedia commons; credit b: modification of work by "Slashme"/Wikimedia Commons)

Figure a contains a photograph of a common laboratory distillation unit. Figure b provides a diagram labeling typical components of a laboratory distillation unit, including a stirrer/heat plate with heat and stirrer speed control, a heating bath of oil or sand, stirring means such as boiling chips, a still pot, a still head, a thermometer for boiling point temperature reading, a condenser with a cool water inlet and outlet, a still receiver with a vacuum or gas inlet, a receiving flask for holding distillate, and a cooling bath.

Oil refineries use large-scale *fractional distillation* to separate the components of crude oil. The crude oil is heated to high temperatures at the base of a tall *fractionating column*, vaporizing many of the components that rise within the column. As vaporized components reach adequately cool zones during their ascent, they condense and are collected. The collected liquids are simpler mixtures of hydrocarbons and other petroleum compounds that are of appropriate composition for various applications (e.g., diesel fuel, kerosene, gasoline), as depicted in Figure **10.5.3**.

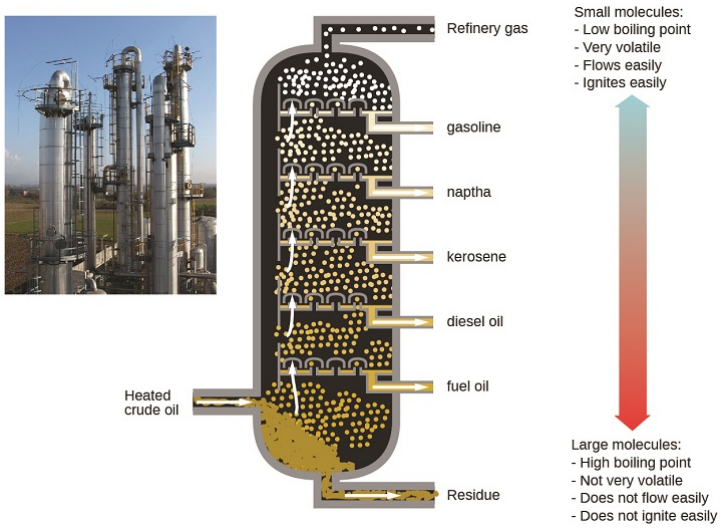


Figure **10.5.3**: Crude oil is a complex mixture that is separated by large-scale fractional distillation to isolate various simpler mixtures.

This figure contains a photo of a refinery, showing large columnar structures. A diagram of a fractional distillation column used in separating crude oil is also shown. Near the bottom of the column, an arrow pointing into the column shows a point of entry for heated crude oil. The column contains several layers at which different components are removed. At the very bottom, residue materials are removed as indicated by an arrow out of the column. At each successive level, different materials are removed proceeding from the bottom to the top of the column. The materials are fuel oil, followed by diesel oil, kerosene, naptha, gasoline, and refinery gas at the very top. To the right of the column diagram, a double sided arrow is shown that is blue at the top and gradually changes color to red moving downward. The blue top of the arrow is labeled, “small molecules: low boiling point, very volatile, flows easily, ignites easily.” The red bottom of the arrow is labeled, “large molecules: high boiling point, not very volatile, does not flow easily, does not ignite easily.”

Depression of the Freezing Point of a Solvent

Solutions freeze at lower temperatures than pure liquids. This phenomenon is exploited in “de-icing” schemes that use salt (Figure **10.5.4**), calcium chloride, or urea to melt ice on roads and sidewalks, and in the use of ethylene glycol as an “antifreeze” in automobile radiators. Seawater freezes at a lower temperature than fresh water, and so the Arctic and Antarctic oceans remain unfrozen even at temperatures below 0 °C (as do the body fluids of fish and other cold-blooded sea animals that live in these oceans).



Figure **10.5.4**: Rock salt (NaCl), calcium chloride ($CaCl_2$), or a mixture of the two are used to melt ice. (credit: modification of work by Eddie Welker)

The decrease in freezing point of a dilute solution compared to that of the pure solvent, ΔT_f, is called the freezing point depression and is directly proportional to the molal concentration of the solute

$$\Delta T_f = K_f m \tag{10.5.9}$$

where

- m is the *molal* concentration of the solute in the solvent and
- K_f is called the freezing point depression constant (or *cryoscopic constant*).

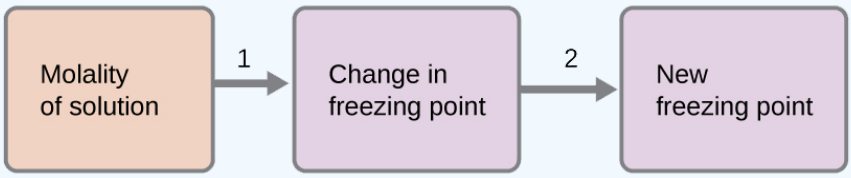
Just as for boiling point elevation constants, these are characteristic properties whose values depend on the chemical identity of the solvent. Values of K_f for several solvents are listed in Table **10.5.1**.

Example 10.5.5: Calculation of the Freezing Point of a Solution

What is the freezing point of the 0.33 *m* solution of a nonvolatile nonelectrolyte solute in benzene described in Example **10.5.4**?

Solution

Use the equation relating freezing point depression to solute molality to solve this problem in two steps.



1. *Calculate the change in freezing point.*

$$\Delta T_f = K_f m = 5.12\ ^\circ\text{C}\ m^{-1} \times 0.33\ m = 1.7\ ^\circ\text{C}$$

2. *Subtract the freezing point change observed from the pure solvent's freezing point.*

$$\text{Freezing Temperature} = 5.5\ ^\circ\text{C} - 1.7\ ^\circ\text{C} = 3.8\ ^\circ\text{C}$$

Exercise 10.5.6

What is the freezing point of a 1.85 *m* solution of a nonvolatile nonelectrolyte solute in nitrobenzene?

Answer

−9.3 °C

Colligative Properties and De-Icing

Sodium chloride and its group 2 analogs calcium and magnesium chloride are often used to de-ice roadways and sidewalks, due to the fact that a solution of any one of these salts will have a freezing point lower than 0 °C, the freezing point of pure water. The group 2 metal salts are frequently mixed with the cheaper and more readily available sodium chloride ("rock salt") for use on roads, since they tend to be somewhat less corrosive than the NaCl, and they provide a larger depression of the freezing point, since they dissociate to yield three particles per formula unit, rather than two particles like the sodium chloride.

Because these ionic compounds tend to hasten the corrosion of metal, they would not be a wise choice to use in antifreeze for the radiator in your car or to de-ice a plane prior to takeoff. For these applications, covalent compounds, such as ethylene or propylene glycol, are often used. The glycols used in radiator fluid not only lower the freezing point of the liquid, but they elevate the boiling point, making the fluid useful in both winter and summer. Heated glycols are often sprayed onto the surface of airplanes prior to takeoff in inclement weather in the winter to remove ice that has already formed and prevent the formation of more ice, which would be particularly dangerous if formed on the control surfaces of the aircraft (Video **10.5.1**).



Video* 10.5.1*: *Freezing point depression is exploited to remove ice from the control surfaces of aircraft.*

Phase Diagram for an Aqueous Solution of a Nonelectrolyte

The colligative effects on vapor pressure, boiling point, and freezing point described in the previous section are conveniently summarized by comparing the phase diagrams for a pure liquid and a solution derived from that liquid. Phase diagrams for water and an aqueous solution are shown in Figure 10.5.5.

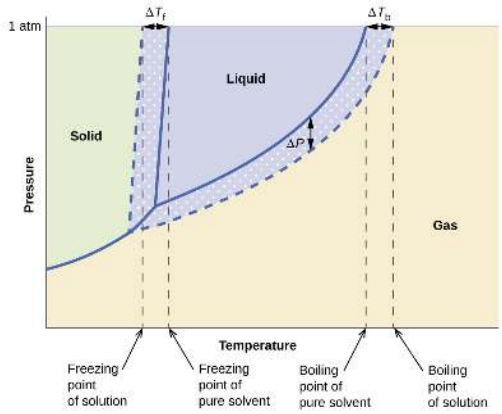


Figure 10.5.5: These phase diagrams show water (solid curves) and an aqueous solution of nonelectrolyte (dashed curves).

This phase diagram indicates the pressure in atmospheres of water and a solution at various temperatures. The graph shows the freezing point of water and the freezing point of the solution, with the difference between these two values identified as delta T subscript f. The graph shows the boiling point of water and the boiling point of the solution, with the difference between these two values identified as delta T subscript b. Similarly, the difference in the pressure of water and the solution at the boiling point of water is shown and identified as delta P. This difference in pressure is labeled vapor pressure lowering. The lower level of the vapor pressure curve for the solution as opposed to that of pure water shows vapor pressure lowering in the solution. Background colors on the diagram indicate the presence of water and the solution in the solid state to the left, liquid state in the central upper region, and gas to the right.

The liquid-vapor curve for the solution is located *beneath* the corresponding curve for the solvent, depicting the vapor pressure *lowering*, ΔP, that results from the dissolution of nonvolatile solute. Consequently, at any given pressure, the solution's boiling point is observed at a higher temperature than that for the pure solvent, reflecting the boiling point elevation, ΔT_b, associated with the presence of nonvolatile solute. The solid-liquid curve for the solution is displaced left of that for the pure solvent, representing the freezing point depression, ΔTf, that accompanies solution formation. Finally, notice that the solid-gas curves for the solvent and its solution are identical. This is the case for many solutions comprising liquid solvents and nonvolatile solutes. Just as for vaporization, when a solution of this sort is frozen, it is actually just the *solvent* molecules that undergo the liquid-to-solid transition, forming pure solid solvent that excludes solute species. The solid and gaseous phases, therefore, are composed solvent only, and so transitions between these phases are not subject to colligative effects.

Osmosis and Osmotic Pressure of Solutions

A number of natural and synthetic materials exhibit *selective permeation*, meaning that only molecules or ions of a certain size, shape, polarity, charge, and so forth, are capable of passing through (permeating) the material. Biological cell membranes provide elegant examples of selective permeation in nature, while dialysis tubing used to remove metabolic wastes from blood is a more simplistic technological example. Regardless of how they may be fabricated, these materials are generally referred to as semipermeable membranes.

Consider the apparatus illustrated in Figure **10.5.6**, in which samples of pure solvent and a solution are separated by a membrane that only solvent molecules may permeate. Solvent molecules will diffuse across the membrane in both directions. Since the concentration of *solvent* is greater in the pure solvent than the solution, these molecules will diffuse from the solvent side of the membrane to the solution side at a faster rate than they will in the reverse direction. The result is a net transfer of solvent molecules from the pure solvent to the solution. Diffusion-driven transfer of solvent molecules through a semipermeable membrane is a process known as osmosis.

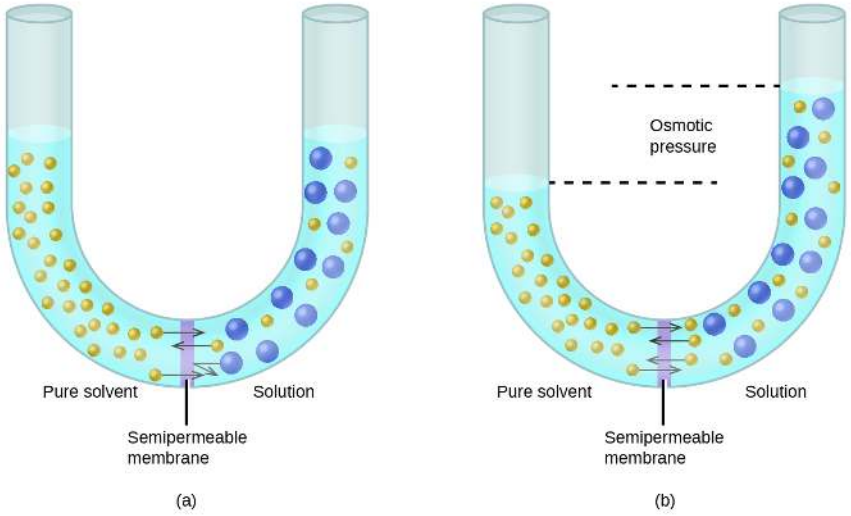


Figure **10.5.6**: Osmosis results in the transfer of solvent molecules from a sample of low (or zero) solute concentration to a sample of higher solute concentration.

The figure shows two U shaped tubes with a semi permeable membrane placed at the base of the U. In figure a, pure solvent is present and indicated by small yellow spheres to the left of the membrane. To the right, a solution exists with larger blue spheres intermingled with some small yellow spheres. At the membrane, arrows pointing from three small yellow spheres on both sides of the membrane cross over the membrane. An arrow drawn from one of the large blue spheres does not cross the membrane, but rather is reflected back from the surface of the membrane. The levels of liquid in both sides of the U shaped tube are equal. In figure b, arrows again point from small yellow spheres across the semipermeable membrane from both sides. This diagram shows the level of liquid in the left, pure solvent, side to be significantly lower than the liquid level on the right. Dashed lines are drawn from these two liquid levels into the middle of the U-shaped tube and between them is the term osmotic pressure.

When osmosis is carried out in an apparatus like that shown in Figure **10.5.6**, the volume of the solution increases as it becomes diluted by accumulation of solvent. This causes the level of the solution to rise, increasing its hydrostatic pressure (due to the weight of the column of solution in the tube) and resulting in a faster transfer of solvent molecules back to the pure solvent side. When the pressure reaches a value that yields a reverse solvent transfer rate equal to the osmosis rate, bulk transfer of solvent ceases. This pressure is called the osmotic pressure (Π) of the solution. The osmotic pressure of a dilute solution is related to its solute molarity, M, and absolute temperature, T, according to the equation

$$\Pi = MRT \tag{10.5.10}$$

where R is the universal gas constant.

Example 10.5.7: Calculation of Osmotic Pressure

What is the osmotic pressure (atm) of a 0.30 *M* solution of glucose in water that is used for intravenous infusion at body temperature, 37 °C?

Solution

We can find the osmotic pressure, \(\Pi\), using Equation 10.5.10, where *T* is on the Kelvin scale (310 K) and the value of *R* is expressed in appropriate units (0.08206 L atm/mol K).

$$\begin{aligned}\Pi &= MRT \\ &= 0.03\ \text{mol/L} \times 0.08206\ \text{L atm/mol K} \times 310\ \text{K} \\ &= 7.6\ \text{atm}\end{aligned}$$

Exercise 10.5.7

What is the osmotic pressure (atm) a solution with a volume of 0.750 L that contains 5.0 g of methanol, CH_3OH, in water at 37 °C?

Answer

5.3 atm

If a solution is placed in an apparatus like the one shown in Figure 10.5.7, applying pressure greater than the osmotic pressure of the solution reverses the osmosis and pushes solvent molecules from the solution into the pure solvent. This technique of reverse osmosis is used for large-scale desalination of seawater and on smaller scales to produce high-purity tap water for drinking.

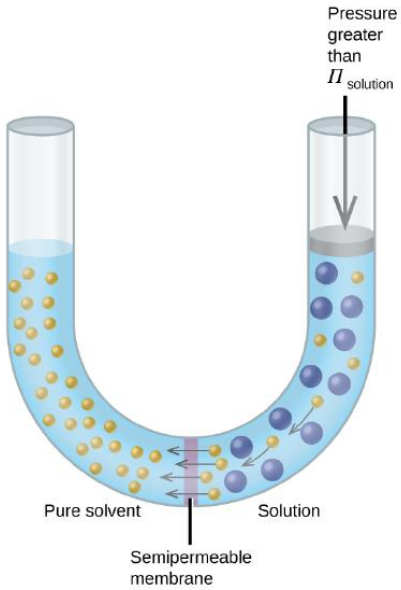


Figure 10.5.7: Applying a pressure greater than the osmotic pressure of a solution will reverse osmosis. Solvent molecules from the solution are pushed into the pure solvent.

The figure shows a U shaped tube with a semi permeable membrane placed at the base of the U. Pure solvent is present and indicated by small yellow spheres to the left of the membrane. To the right, a solution exists with larger blue spheres intermingled with some small yellow spheres. At the membrane, arrows point from four small yellow spheres to the left of the membrane. On the right side of the U, there is a disk that is the same width of the tube and appears to block it. The disk is at the same level as the solution. An arrow points down from the top of the tube to the disk and is labeled, “Pressure greater than Π subscript solution.”

Examples of osmosis are evident in many biological systems because cells are surrounded by semipermeable membranes. Carrots and celery that have become limp because they have lost water can be made crisp again by placing them in water. Water moves into the carrot or celery cells by osmosis. A cucumber placed in a concentrated salt solution loses water by osmosis and absorbs some salt to become a pickle. Osmosis can also affect animal cells. Solute concentrations are particularly important when solutions are

injected into the body. Solutes in body cell fluids and blood serum give these solutions an osmotic pressure of approximately 7.7 atm. Solutions injected into the body must have the same osmotic pressure as blood serum; that is, they should be isotonic with blood serum. If a less concentrated solution, a hypotonic solution, is injected in sufficient quantity to dilute the blood serum, water from the diluted serum passes into the blood cells by osmosis, causing the cells to expand and rupture. This process is called hemolysis. When a more concentrated solution, a hypertonic solution, is injected, the cells lose water to the more concentrated solution, shrivel, and possibly die in a process called *crenation* (Figure 11.5.8).

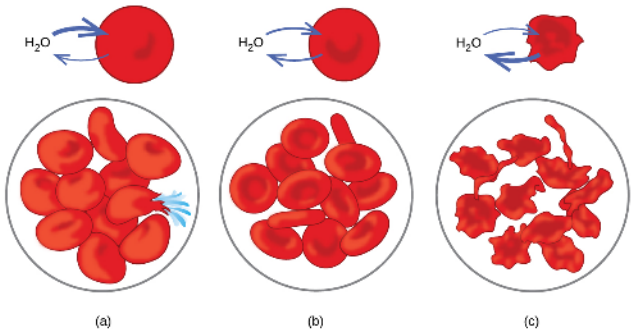


Figure **10.5.8**: Red blood cell membranes are water permeable and will (a) swell and possibly rupture in a hypotonic solution; (b) maintain normal volume and shape in an isotonic solution; and (c) shrivel and possibly die in a hypertonic solution. (credit a/b/c: modifications of work by “LadyofHats”/Wikimedia commons)

This figure shows three scenarios relating to red blood cell membranes. In a, H subscript 2 O has two arrows drawn from it pointing into a red disk. Beneath it in a circle are eleven similar disks with a bulging appearance, one of which appears to have burst with blue liquid erupting from it. In b, the image is similar except that rather than having two arrows pointing into the red disk, one points in and a second points out toward the H subscript 2 O. In the circle beneath, twelve of the red disks are present. In c, both arrows are drawn from a red shriveled disk toward the H subscript 2 O. In the circle below, twelve shriveled disks are shown.

Determination of Molar Masses

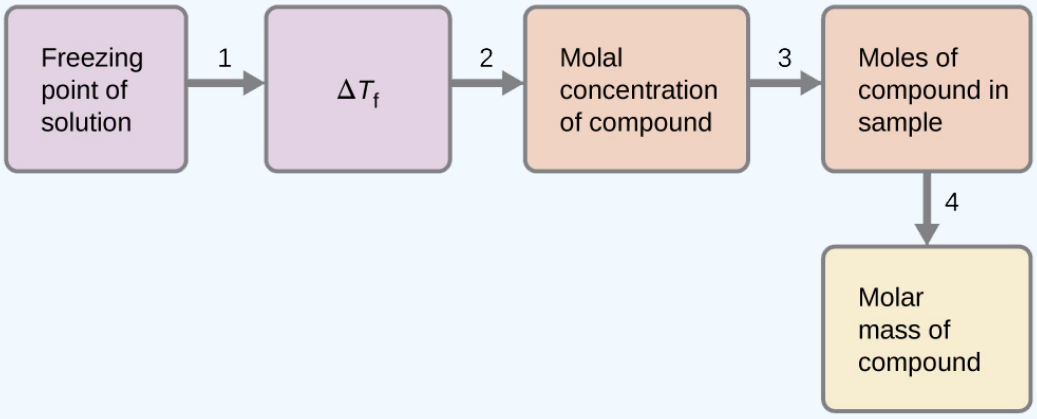
Osmotic pressure and changes in freezing point, boiling point, and vapor pressure are directly proportional to the concentration of solute present. Consequently, we can use a measurement of one of these properties to determine the molar mass of the solute from the measurements.

✔ Example 10.5.8: Determining Molar Mass from Freezing Point Depression

A solution of 4.00 g of a nonelectrolyte dissolved in 55.0 g of benzene is found to freeze at 2.32 °C. What is the molar mass of this compound?

Solution

We can solve this problem using the following steps.



https://chem.libretexts.org/@go/page/216778

1. *Determine the change in freezing point from the observed freezing point and the freezing point of pure benzene* (Table 11.5.1).

$$\Delta T_f = 5.5\ ^\circ\text{C} - 2.32\ ^\circ\text{C} = 3.2\ ^\circ\text{C}$$

1. *Determine the molal concentration from K_f, the freezing point depression constant for benzene* (Table 11.5.1), *and* ΔT_f.

\(\Delta T_\ce{f}=K_\ce{f}m\)

$$m = \frac{\Delta T_f}{K_f} = \frac{3.2\ ^\circ\text{C}}{5.12\ ^\circ\text{C}m^{-1}} = 0.63\ m$$

1. *Determine the number of moles of compound in the solution from the molal concentration and the mass of solvent used to make the solution.*

$$\text{Moles of solute} = \frac{0.62\ \text{mol solute}}{1.00\ \cancel{\text{kg solvent}}} \times 0.0550\ \cancel{\text{kg solvent}} = 0.035\ \text{mol}$$

2. *Determine the molar mass from the mass of the solute and the number of moles in that mass.*

\(\mathrm{Molar\: mass=\dfrac{4.00\:g}{0.034\:mol}=1.2×10^2\:g/mol}\)

Exercise 10.5.8

A solution of 35.7 g of a nonelectrolyte in 220.0 g of chloroform has a boiling point of 64.5 °C. What is the molar mass of this compound?

Answer

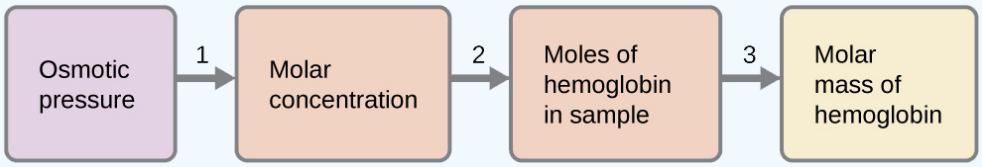
1.8×10^2 g/mol

Example 10.5.9: Determination of a Molar Mass from Osmotic Pressure

A 0.500 L sample of an aqueous solution containing 10.0 g of hemoglobin has an osmotic pressure of 5.9 torr at 22 °C. What is the molar mass of hemoglobin?

Solution

Here is one set of steps that can be used to solve the problem:



1.

$$\Pi = \frac{5.9\ \text{torr} \times 1\ \text{atm}}{760\ \text{torr}} = 7.8 \times 10^{-3}\ \text{atm}$$

$$\Pi = MRT$$

$$M = \frac{\Pi}{RT} = \frac{7.8 \times 10^{-3}\ \text{atm}}{(0.08206\ \text{L atm/mol K})(295\ \text{K})} = 3.2 \times 10^{-4}\ \text{M}$$

1. $$\text{moles of hemoglobin} = \frac{3.2 \times 10^{-4}\ \text{mol}}{1\ \cancel{\text{L solution}}} \times 0.500\ \cancel{\text{L solution}} = 1.6 \times 10^{-4}\ \text{mol}$$

2. *Determine the molar mass from the mass of hemoglobin and the number of moles in that mass.*

$$\text{molar mass} = \frac{10.0\ \text{g}}{1.6 \times 10^{-4}\ \text{mol}} = 6.2 \times 10^4\ \text{g/mol}$$

Exercise 10.5.9

What is the molar mass of a protein if a solution of 0.02 g of the protein in 25.0 mL of solution has an osmotic pressure of 0.56 torr at 25 °C?

Answer

2.7×10^4 g/mol

Colligative Properties of Electrolytes

As noted previously in this module, the colligative properties of a solution depend only on the number, not on the kind, of solute species dissolved. For example, 1 mole of any nonelectrolyte dissolved in 1 kilogram of solvent produces the same lowering of the freezing point as does 1 mole of any other nonelectrolyte. However, 1 mole of sodium chloride (an electrolyte) forms *2 moles* of ions when dissolved in solution. Each individual ion produces the same effect on the freezing point as a single molecule does.

Example 10.5.10: The Freezing Point of a Solution of an Electrolyte

The concentration of ions in seawater is approximately the same as that in a solution containing 4.2 g of NaCl dissolved in 125 g of water. Assume that each of the ions in the NaCl solution has the same effect on the freezing point of water as a nonelectrolyte molecule, and determine the freezing temperature the solution (which is approximately equal to the freezing temperature of seawater).

Solution

We can solve this problem using the following series of steps.

- Convert from grams to moles of NaCl using the molar mass of NaCl in the unit conversion factor. Result: 0.072 mol NaCl
- Determine the number of moles of ions present in the solution using the number of moles of ions in 1 mole of NaCl as the conversion factor (2 mol ions/1 mol NaCl). Result: 0.14 mol ions
- Determine the molality of the ions in the solution from the number of moles of ions and the mass of solvent, in kilograms. Result: 1.1 m
- Use the direct proportionality between the change in freezing point and molal concentration to determine how much the freezing point changes. Result: 2.0 °C
- Determine the new freezing point from the freezing point of the pure solvent and the change. Result: −2.0 °C

Check each result as a self-assessment.

Exercise 10.5.10

Assume that each of the ions in calcium chloride, $CaCl_2$, has the same effect on the freezing point of water as a nonelectrolyte molecule. Calculate the freezing point of a solution of 0.724 g of $CaCl_2$ in 175 g of water.

Answer

−0.208 °C

Assuming complete dissociation, a 1.0 *m* aqueous solution of NaCl contains 2.0 mole of ions (1.0 mol Na^+ and 1.0 mol Cl^-) per each kilogram of water, and its freezing point depression is expected to be

$$\Delta T_f = 2.0 \text{ mol ions/kg water} \times 1.86 \text{ °C kg water/mol ion} = 3.7 \text{ °C}. \tag{10.5.11}$$

When this solution is actually prepared and its freezing point depression measured, however, a value of 3.4 °C is obtained. Similar discrepancies are observed for other ionic compounds, and the differences between the measured and expected colligative property values typically become more significant as solute concentrations increase. These observations suggest that the ions of sodium chloride (and other strong electrolytes) are not completely dissociated in solution.

To account for this and avoid the errors accompanying the assumption of total dissociation, an experimentally measured parameter named in honor of Nobel Prize-winning German chemist Jacobus Henricus van't Hoff is used. The van't Hoff factor (i) is defined as the ratio of solute particles in solution to the number of formula units dissolved:

$$i = \frac{\text{moles of particles in solution}}{\text{moles of formula units dissolved}} \tag{10.5.12}$$

Values for measured van't Hoff factors for several solutes, along with predicted values assuming complete dissociation, are shown in Table **10.5.2**.

Table **10.5.2**: Expected and Observed van't Hoff Factors for Several 0.050 m Aqueous Electrolyte Solutions

Electrolyte	Particles in Solution	*i* (Predicted)	*i* (Measured)
HCl	H^+, Cl^-	2	1.9
NaCl	Na^+, Cl^-	2	1.9
$MgSO_4$	Mg^{2+}, SO_4^{2-}	2	1.3
$MgCl_2$	Mg^{2+}, $2Cl^-$	3	2.7
$FeCl_3$	Fe^{3+}, $3Cl^-$	4	3.4
glucose (a non-electrolyte)	$C_{12}H_{22}O_{11}$	1	1.0

In 1923, the chemists Peter Debye and Erich Hückel proposed a theory to explain the apparent incomplete ionization of strong electrolytes. They suggested that although interionic attraction in an aqueous solution is very greatly reduced by solvation of the ions and the insulating action of the polar solvent, it is not completely nullified. The residual attractions prevent the ions from behaving as totally independent particles (Figure **10.5.9**). In some cases, a positive and negative ion may actually touch, giving a solvated unit called an ion pair. Thus, the activity, or the effective concentration, of any particular kind of ion is less than that indicated by the actual concentration. Ions become more and more widely separated the more dilute the solution, and the residual interionic attractions become less and less. Thus, in extremely dilute solutions, the effective concentrations of the ions (their activities) are essentially equal to the actual concentrations. Note that the van't Hoff factors for the electrolytes in Table **10.5.2** are for 0.05 *m* solutions, at which concentration the value of *i* for NaCl is 1.9, as opposed to an ideal value of 2.

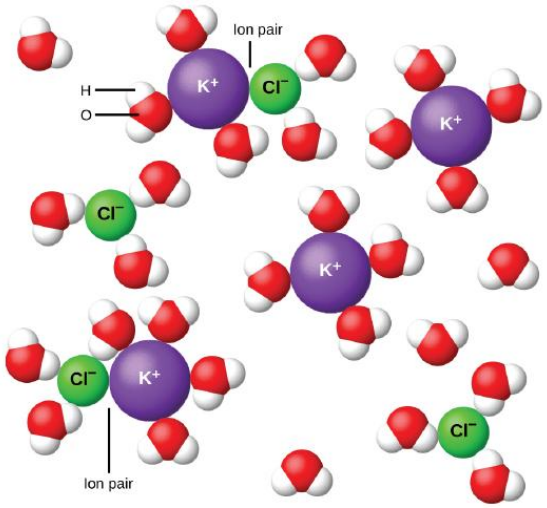


Figure **10.5.9**: Ions become more and more widely separated the more dilute the solution, and the residual interionic attractions become less.

The diagram shows four purple spheres labeled K superscript plus and four green spheres labeled C l superscript minus dispersed in H subscript 2 O as shown by clusters of single red spheres with two white spheres attached. Red spheres represent oxygen and white represent hydrogen. In two locations, the purple and green spheres are touching. In these two locations, the diagram is labeled ion pair. All red and green spheres are surrounded by the white and red H subscript 2 O clusters. The white spheres are attracted to the purple spheres and the red spheres are attracted to the green spheres.

Summary

Properties of a solution that depend only on the concentration of solute particles are called colligative properties. They include changes in the vapor pressure, boiling point, and freezing point of the solvent in the solution. The magnitudes of these properties depend only on the total concentration of solute particles in solution, not on the type of particles. The total concentration of solute particles in a solution also determines its osmotic pressure. This is the pressure that must be applied to the solution to prevent diffusion of molecules of pure solvent through a semipermeable membrane into the solution. Ionic compounds may not completely dissociate in solution due to activity effects, in which case observed colligative effects may be less than predicted.

Key Equations

- $(P_A = X_A P_A^\circ)$
- $P_{solution} = \sum_i P_i = \sum_i X_i P_i^\circ$
- $P_{solution} = X_{solvent} P_{solvent}^\circ$
- $\Delta T_b = K_b m$
- $\Delta T_f = K_f m$
- $\Pi = MRT$

Footnotes

1. A nonelectrolyte shown for comparison.

Glossary

boiling point elevation
elevation of the boiling point of a liquid by addition of a solute

boiling point elevation constant
the proportionality constant in the equation relating boiling point elevation to solute molality; also known as the ebullioscopic constant

colligative property
property of a solution that depends only on the concentration of a solute species

crenation
process whereby biological cells become shriveled due to loss of water by osmosis

freezing point depression
lowering of the freezing point of a liquid by addition of a solute

freezing point depression constant
(also, cryoscopic constant) proportionality constant in the equation relating freezing point depression to solute molality

hemolysis
rupture of red blood cells due to the accumulation of excess water by osmosis

hypertonic
of greater osmotic pressure

hypotonic
of less osmotic pressure

ion pair
solvated anion/cation pair held together by moderate electrostatic attraction

isotonic

of equal osmotic pressure

molality (*m*)
a concentration unit defined as the ratio of the numbers of moles of solute to the mass of the solvent in kilograms

osmosis
diffusion of solvent molecules through a semipermeable membrane

osmotic pressure (*Π*)
opposing pressure required to prevent bulk transfer of solvent molecules through a semipermeable membrane

Raoult's law
the partial pressure exerted by a solution component is equal to the product of the component's mole fraction in the solution and its equilibrium vapor pressure in the pure state

semipermeable membrane
a membrane that selectively permits passage of certain ions or molecules

van't Hoff factor (*i*)
the ratio of the number of moles of particles in a solution to the number of moles of formula units dissolved in the solution

---

This page titled 10.5: Colligative Properties is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

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

10.6: Colloids

Learning Objectives

- Describe the composition and properties of colloidal dispersions
- List and explain several technological applications of colloids

As a child, you may have made suspensions such as mixtures of mud and water, flour and water, or a suspension of solid pigments in water, known as tempera paint. These suspensions are heterogeneous mixtures composed of relatively large particles that are visible (or that can be seen with a magnifying glass). They are cloudy, and the suspended particles settle out after mixing. On the other hand, when we make a solution, we prepare a homogeneous mixture in which no settling occurs and in which the dissolved species are molecules or ions. Solutions exhibit completely different behavior from suspensions. A solution may be colored, but it is transparent, the molecules or ions are invisible, and they do not settle out on standing. A group of mixtures called colloids (or colloidal dispersions) exhibit properties intermediate between those of suspensions and solutions (Figure 10.6.1). The particles in a colloid are larger than most simple molecules; however, colloidal particles are small enough that they do not settle out upon standing.

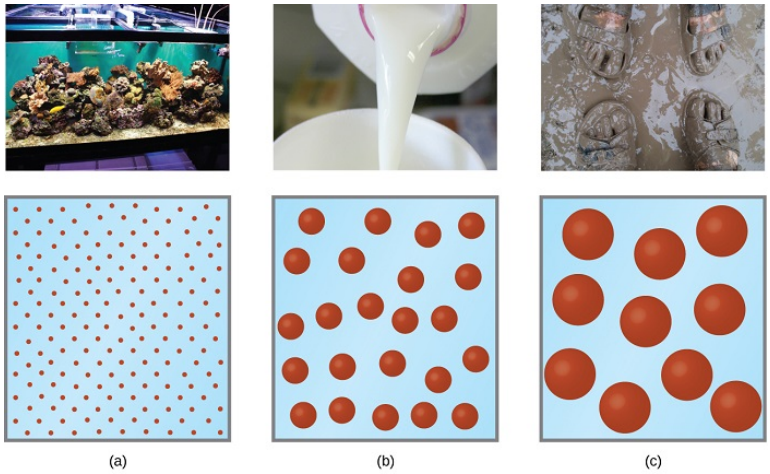


Figure 10.6.1: (a) A solution is a homogeneous mixture that appears clear, such as the saltwater in this aquarium. (b) In a colloid, such as milk, the particles are much larger but remain dispersed and do not settle. (c) A suspension, such as mud, is a heterogeneous mixture of suspended particles that appears cloudy and in which the particles can settle. (credit a photo: modification of work by Adam Wimsatt; credit b photo: modification of work by Melissa Wiese; credit c photo: modification of work by Peter Burgess)

This figure contains three photos and correponding particle diagrams. In a, a photo of an aquarium containing fish is shown. The particle diagram beneath it shows 90 tiny red spheres. In b, a photo is shown of milk being poured into a cup. The corresponding particle diagram shows about 25 medium sized red spheres.In c, a photo is shown of two pairs of sandal clad feet in mud. The particle diagram below shows 10 fairly large red spheres.

The particles in a colloid are large enough to scatter light, a phenomenon called the Tyndall effect. This can make colloidal mixtures appear cloudy or opaque, such as the searchlight beams shown in Figure 10.6.2. Clouds are colloidal mixtures. They are composed of water droplets that are much larger than molecules, but that are small enough that they do not settle out.



Figure **10.6.2**: The paths of searchlight beams are made visible when light is scattered by colloidal-size particles in the air (fog, smoke, etc.). (credit: “Bahman”/Wikimedia Commons)

The term “colloid”—from the Greek words *kolla*, meaning “glue,” and *eidos*, meaning “like”—was first used in 1861 by Thomas Graham to classify mixtures such as starch in water and gelatin. Many colloidal particles are aggregates of hundreds or thousands of molecules, but others (such as proteins and polymer molecules) consist of a single extremely large molecule. The protein and synthetic polymer molecules that form colloids may have molecular masses ranging from a few thousand to many million atomic mass units.

Analogous to the identification of solution components as “solute” and “solvent,” the components of a colloid are likewise classified according to their relative amounts. The particulate component typically present in a relatively minor amount is called the dispersed phase and the substance or solution throughout which the particulate is dispersed is called the dispersion medium. Colloids may involve virtually any combination of physical states (gas in liquid, liquid in solid, solid in gas, etc.), as illustrated by the examples of colloidal systems given in Table **10.6.1**.

Table **10.6.2**: Examples of Colloidal Systems

Dispersed Phase	Dispersion Medium	Common Examples	Name
solid	gas	smoke, dust	—
solid	liquid	starch in water, some inks, paints, milk of magnesia	sol
solid	solid	some colored gems, some alloys	—
liquid	gas	clouds, fogs, mists, sprays	aerosol
liquid	liquid	milk, mayonnaise, butter	emulsion
liquid	solid	jellies, gels, pearl, opal (H_2O in SiO_2)	gel
gas	liquid	foams, whipped cream, beaten egg whites	foam
gas	solid	pumice, floating soaps	—

Preparation of Colloidal Systems

We can prepare a colloidal system by producing particles of colloidal dimensions and distributing these particles throughout a dispersion medium. Particles of colloidal size are formed by two methods:

1. Dispersion methods: that is, by breaking down larger particles. For example, paint pigments are produced by dispersing large particles by grinding in special mills.
2. Condensation methods: that is, growth from smaller units, such as molecules or ions. For example, clouds form when water molecules condense and form very small droplets.

A few solid substances, when brought into contact with water, disperse spontaneously and form colloidal systems. Gelatin, glue, starch, and dehydrated milk powder behave in this manner. The particles are already of colloidal size; the water simply disperses them. Powdered milk particles of colloidal size are produced by dehydrating milk spray. Some atomizers produce colloidal dispersions of a liquid in air.

We can prepare an emulsion by shaking together or blending two immiscible liquids. This breaks one liquid into droplets of colloidal size, which then disperse throughout the other liquid. Oil spills in the ocean may be difficult to clean up, partly because wave action can cause the oil and water to form an emulsion. In many emulsions, however, the dispersed phase tends to coalesce, form large drops, and separate. Therefore, emulsions are usually stabilized by an emulsifying agent, a substance that inhibits the coalescence of the dispersed liquid. For example, a little soap will stabilize an emulsion of kerosene in water. Milk is an emulsion of butterfat in water, with the protein casein as the emulsifying agent. Mayonnaise is an emulsion of oil in vinegar, with egg yolk components as the emulsifying agents.

Condensation methods form colloidal particles by aggregation of molecules or ions. If the particles grow beyond the colloidal size range, drops or precipitates form, and no colloidal system results. Clouds form when water molecules aggregate and form colloid-sized particles. If these water particles coalesce to form adequately large water drops of liquid water or crystals of solid water, they settle from the sky as rain, sleet, or snow. Many condensation methods involve chemical reactions. We can prepare a red colloidal suspension of iron(III) hydroxide by mixing a concentrated solution of iron(III) chloride with hot water:

$$\mathrm{Fe^{3+}_{(aq)} + 3Cl^-_{(aq)} + 6H_2O_{(l)} \longrightarrow Fe(OH)_{3(s)} + H_3O^+_{(aq)} + 3Cl^-_{(aq)}} \tag{10.6.1}$$

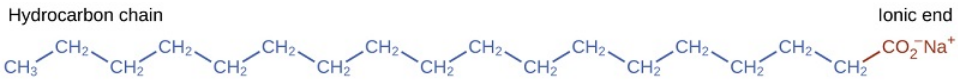
A colloidal gold sol results from the reduction of a very dilute solution of gold(III) chloride by a reducing agent such as formaldehyde, tin(II) chloride, or iron(II) sulfate:

$$\mathrm{Au^{3+} + 3\,e^- \rightarrow Au} \tag{10.6.2}$$

Some gold sols prepared in 1857 are still intact (the particles have not coalesced and settled), illustrating the long-term stability of many colloids.

Soaps and Detergents

Pioneers made soap by boiling fats with a strongly basic solution made by leaching potassium carbonate, $\mathrm{K_2CO_3}$, from wood ashes with hot water. Animal fats contain polyesters of fatty acids (long-chain carboxylic acids). When animal fats are treated with a base like potassium carbonate or sodium hydroxide, glycerol and salts of fatty acids such as palmitic, oleic, and stearic acid are formed. The salts of fatty acids are called soaps. The sodium salt of stearic acid, sodium stearate, has the formula $\mathrm{C_{17}H_{35}CO_2Na}$ and contains an uncharged nonpolar hydrocarbon chain, the $\mathrm{C_{17}H_{35}-}$ unit, and an ionic carboxylate group, the $\mathrm{-CO_2^-}$ unit (Figure 10.6.3).

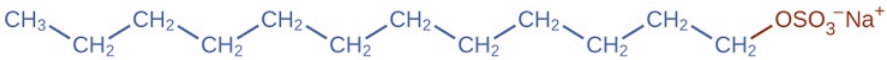


sodium stearate (soap)

Figure 10.6.3: Soaps contain a nonpolar hydrocarbon end (blue) and an ionic end (red). The ionic end is a carboxylate group. The length of the hydrocarbon end can vary from soap to soap.

This figure shows a structural formula for soap known as sodium stearate. A hydrocarbon chain composed of 18 carbon atoms and 35 hydrogen atoms is shown with an ionic end with 2 oxygen atoms and a negative charge. A positively charged N a superscript plus is also shown at the ionic end.

*Deterg*ents (soap substitutes) also contain nonpolar hydrocarbon chains, such as $\mathrm{C_{12}H_{25}—}$, and an ionic group, such as a sulfate $\mathrm{—OSO_3^-}$, or a sulfonate $\mathrm{—SO_3^-}$ (Figure 10.6.4). Soaps form insoluble calcium and magnesium compounds in hard water; detergents form water-soluble products—a definite advantage for detergents.



sodium lauryl sulfate (detergent)

Figure **10.6.4**: Detergents contain a nonpolar hydrocarbon end (blue) and an ionic end (red). The ionic end can be either a sulfate or a sulfonate. The length of the hydrocarbon end can vary from detergent to detergent.

This figure shows a structural formula for a detergent known as sodium lauryl sulfate. A hydrocarbon chain composed of 12 carbon atoms and 25 hydrogen atoms is shown with an ionic end involving a negatively charged sulfur and four oxygen atoms at the ionic end of the chain. A positively charged N a superscript plus is also shown at the ionic end.

The cleaning action of soaps and detergents can be explained in terms of the structures of the molecules involved. The hydrocarbon (nonpolar) end of a soap or detergent molecule dissolves in, or is attracted to, nonpolar substances such as oil, grease, or dirt particles. The ionic end is attracted by water (polar), illustrated in Figure **10.6.5**. As a result, the soap or detergent molecules become oriented at the interface between the dirt particles and the water so they act as a kind of bridge between two different kinds of matter, nonpolar and polar. Molecules such as this are termed amphiphilic since they have both a hydrophobic (“water-fearing”) part and a hydrophilic (“water-loving”) part. As a consequence, dirt particles become suspended as colloidal particles and are readily washed away.

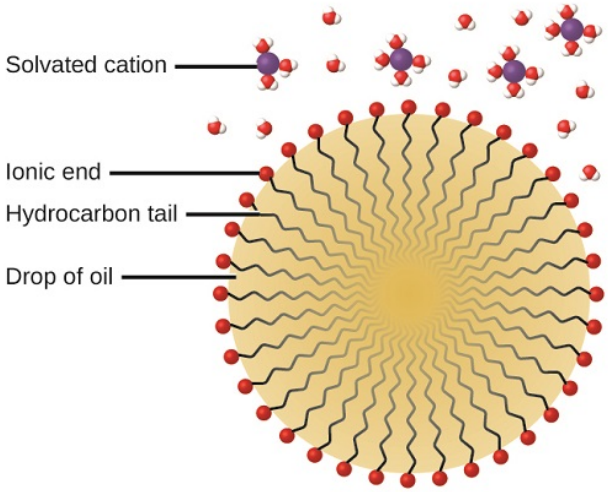


Figure **10.6.5**: This diagrammatic cross section of an emulsified drop of oil in water shows how soap or detergent acts as an emulsifier.

This figure shows a drop of oil in which approximately thirty hydrocarbon tails are oriented toward the center of the drop with ionic ends indicated as tiny red spheres on the surface of the oil drop. Solvated cations are indicated as purple spheres surrounded by clusters of H subscript 2 subscript O molecules shown as tiny clusters of red central oxygen spheres with two white hydrogen spheres attached.

Deepwater Horizon Oil Spill

The blowout of the Deepwater Horizon oil drilling rig on April 20, 2010, in the Gulf of Mexico near Mississippi began the largest marine oil spill in the history of the petroleum. In the 87 days following the blowout, an estimated 4.9 million barrels (210 million gallons) of oil flowed from the ruptured well 5000 feet below the water’s surface. The well was finally declared sealed on September 19, 2010.

Crude oil is immiscible with and less dense than water, so the spilled oil rose to the surface of the water. Floating booms, skimmer ships, and controlled burns were used to remove oil from the water’s surface in an attempt to protect beaches and wetlands along the Gulf coast. In addition to removal of the oil, attempts were also made to lessen its environmental impact by rendering it “soluble” (in the loose sense of the term) and thus allowing it to be diluted to hopefully less harmful levels by the vast volume of ocean water. This approach used 1.84 million gallons of the oil dispersant Corexit 9527, most of which was injected underwater at the site of the leak, with small amounts being sprayed on top of the spill. Corexit 9527 contains 2-butoxyethanol ($C_6H_{14}O_2$), an amphiphilic molecule whose polar and nonpolar ends are useful for emulsifying oil into small droplets, increasing the surface area of the oil and making it more available to marine bacteria for digestion (Figure **10.6.6**). While this approach avoids many of the immediate hazards that bulk oil poses to marine and coastal ecosystems, it introduces

the possibility of long-term effects resulting from the introduction of the complex and potential toxic components of petroleum into the ocean's food chain. A number of organizations are involved in monitoring the extended impact of this oil spill, including the National Oceanic and Atmospheric Administration.



(a) (b) (c)

Figure **10.6.6**: (a) This NASA satellite image shows the oil slick from the Deepwater Horizon spill. (b) A US Air Force plane sprays Corexit, a dispersant. (c) The molecular structure of 2-butoxyethanol is shown. (credit a: modification of work by "NASA, FT2, demis.nl"/Wikimedia Commons; credit b: modification of work by "NASA/MODIS Rapid Response Team"/Wikimedia Commons)

Electrical Properties of Colloidal Particles

Dispersed colloidal particles are often electrically charged. A colloidal particle of iron(III) hydroxide, for example, does not contain enough hydroxide ions to compensate exactly for the positive charges on the iron(III) ions. Thus, each individual colloidal particle bears a positive charge, and the colloidal dispersion consists of charged colloidal particles and some free hydroxide ions, which keep the dispersion electrically neutral. Most metal hydroxide colloids have positive charges, whereas most metals and metal sulfides form negatively charged dispersions. All colloidal particles in any one system have charges of the same sign. This helps keep them dispersed because particles containing like charges repel each other.

We can take advantage of the charge on colloidal particles to remove them from a variety of mixtures. If we place a colloidal dispersion in a container with charged electrodes, positively charged particles, such as iron(III) hydroxide particles, would move to the negative electrode. There, the colloidal particles lose their charge and coagulate as a precipitate.

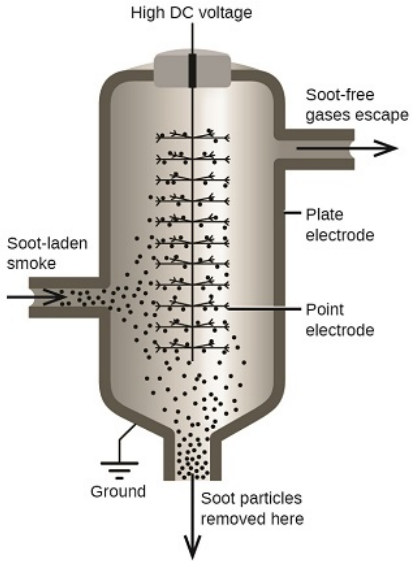


Figure **10.6.7**: In a Cottrell precipitator, positively and negatively charged particles are attracted to highly charged electrodes, where they are neutralized and deposited as dust.

This figure shows a diagram of a Cottrell precipitator. An arrow pointing into a cylindrical chamber shows the path of soot laden smoke. In the presence of high DC voltage and both point and plate electrodes, soot particles are removed at the bottom of the chamber and soot free air exits the top. A photo shows the honeycomb electrodes of a modern electrostatic precipitator.

The carbon and dust particles in smoke are often colloidally dispersed and electrically charged. The charged particles are attracted to highly charged electrodes, where they are neutralized and deposited as dust (Figure **10.6.7**. This is one of the important methods used to clean up the smoke from a variety of industrial processes. The process is also important in the recovery of valuable

products from the smoke and flue dust of smelters, furnaces, and kilns. There are also ionic air filters designed for home use to improve indoor air quality.

Gels

When we make gelatin, such as Jell-O, we are making a type of colloid (Figure **10.6.8**). Gelatin sets on cooling because the hot aqueous mixture of gelatin coagulates as it cools and the whole mass, including the liquid, sets to an extremely viscous body known as a gel, a colloid in which the dispersing medium is a solid and the dispersed phase is a liquid. It appears that the fibers of the dispersing medium form a complex three-dimensional network, the interstices being filled with the liquid medium or a dilute solution of the dispersing medium. Because the formation of a gel is accompanied by the taking up of water or some other solvent, the gel is said to be hydrated or solvated.

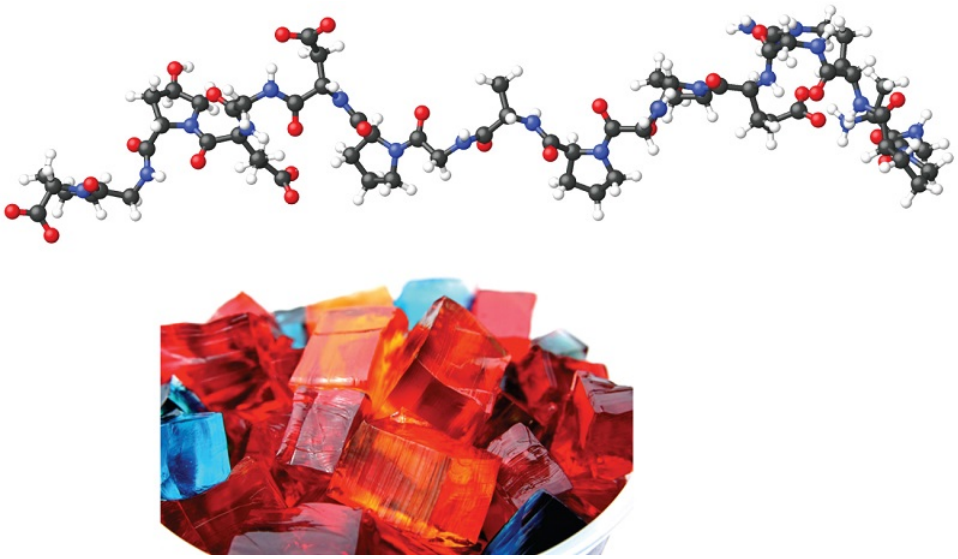


Figure **10.6.8**: Gelatin desserts are colloids in which an aqueous solution of sweeteners and flavors is dispersed throughout a medium of solid proteins. (credit photo: modification of work by Steven Depolo).

In this figure, a large molecular model of gelatin is shown with black carbon atoms, red oxygen atoms, white hydrogen atoms, and blue nitrogen atoms. A photo is shown of gelatin dessert cut into colorful rectangles.

Pectin, a carbohydrate from fruit juices, is a gel-forming substance important in jelly making. Silica gel, a colloidal dispersion of hydrated silicon dioxide, is formed when dilute hydrochloric acid is added to a dilute solution of sodium silicate. Canned Heat is a gel made by mixing alcohol and a saturated aqueous solution of calcium acetate.

Summary

Colloids are mixtures in which one or more substances are dispersed as relatively large solid particles or liquid droplets throughout a solid, liquid, or gaseous medium. The particles of a colloid remain dispersed and do not settle due to gravity, and they are often electrically charged. Colloids are widespread in nature and are involved in many technological applications.

Glossary

amphiphilic

molecules possessing both hydrophobic (nonpolar) and a hydrophilic (polar) parts

colloid

(also, colloidal dispersion) mixture in which relatively large solid or liquid particles are dispersed uniformly throughout a gas, liquid, or solid

dispersion medium

solid, liquid, or gas in which colloidal particles are dispersed

dispersed phase

substance present as relatively large solid or liquid particles in a colloid

emulsifying agent

amphiphilic substance used to stabilize the particles of some emulsions

emulsion

colloid formed from immiscible liquids

gel

colloidal dispersion of a liquid in a solid

Tyndall effect

scattering of visible light by a colloidal dispersion

This page titled 10.6: Colloids is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

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

CHAPTER OVERVIEW

11: Fundamental Equilibrium Concepts

A general chemistry Libretexts Textmap organized around the textbook
General Chemistry -Atoms First
By OpenStax

I II III IV V VI VII VIII IX X XI XII XIII XIV XV XVI XVII XVIII XIX XX XXI ● **Homework**

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.

11.1: Chemical Equilibria
11.2: Equilibrium Constants
11.3: Shifting Equilibria- Le Châtelier's Principle
11.4: Equilibrium Calculations

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: Fundamental Equilibrium Concepts is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

11.1: Chemical Equilibria

Learning Objectives

- Describe the nature of equilibrium systems
- Explain the dynamic nature of a chemical equilibrium

A chemical reaction is usually written in a way that suggests it proceeds in one direction, the direction in which we read, but all chemical reactions are reversible, and both the forward and reverse reaction occur to one degree or another depending on conditions. In a chemical equilibrium, the forward and reverse reactions occur at equal rates, and the concentrations of products and reactants remain constant. If we run a reaction in a closed system so that the products cannot escape, we often find the reaction does not give a 100% yield of products. Instead, some reactants remain after the concentrations stop changing. At this point, when there is no further change in concentrations of reactants and products, we say the reaction is at equilibrium. A mixture of reactants and products is found at equilibrium.

For example, when we place a sample of dinitrogen tetroxide (N_2O_4, a colorless gas) in a glass tube, it forms nitrogen dioxide (NO_2, a brown gas) by the reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \tag{11.1.1}$$

The color becomes darker as N_2O_4 is converted to NO_2. When the system reaches equilibrium, both N_2O_4 and NO_2 are present (Figure 11.1.1).

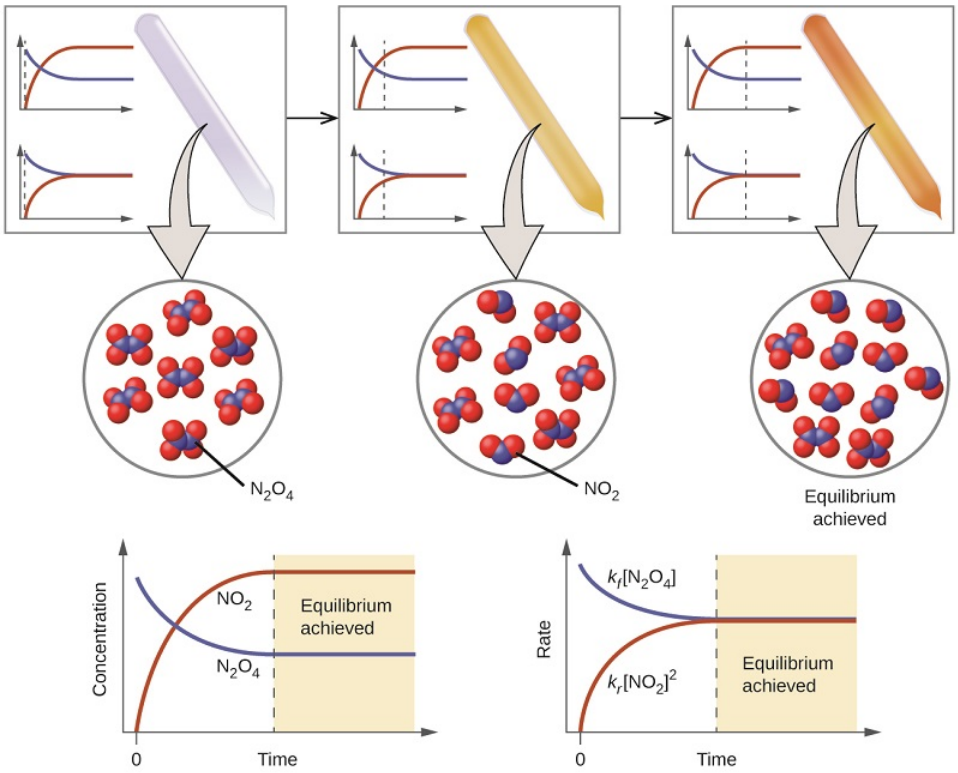


Figure **11.1.1**: A mixture of NO_2 and N_2O_4 moves toward equilibrium. Colorless N_2O_4 reacts to form brown NO_2. As the reaction proceeds toward equilibrium, the color of the mixture darkens due to the increasing concentration of NO_2.

A three-part diagram is shown. At the top of the diagram, three beakers are shown, and each one contains a sealed tube. The tube in the left beaker is full of a colorless gas which is connected to a zoom-in view of the particles in the tube by a downward-facing arrow. This particle view shows seven particles, each composed of two connected blue spheres. Each blue sphere is connected to two red spheres. The tube in the middle beaker is full of a light brown gas which is connected to a zoom-in view of the particles in the tube by a downward-facing arrow. This particle view shows nine particles, five of which are composed of two connected blue spheres. Each blue sphere is connected to two red spheres. The remaining four are composed of two red spheres connected to a blue sphere. The tube in the right beaker is full of a brown gas which is connected to a zoom-in view of the particles in the tube by a downward-facing arrow. This particle view shows eleven particles, three of which are composed of two connected blue spheres. Each blue sphere is connected to two red spheres. The remaining eight are composed of two red spheres connected to a blue sphere. At the bottom of the image are two graphs. The left graph has a y-axis labeled, “Concentration,” and an x-axis labeled, “Time.” A red line labeled, “N O subscript 2,” begins in the bottom left corner of the graph at a point labeled, “0,” and rises near the highest point on the y-axis before it levels off and becomes horizontal. A blue line labeled, “N subscript 2 O subscript 4,” begins near the highest point on the y-axis and drops below the midpoint of the y-axis before leveling off. The right graph has a y-axis labeled, “Rate,” and an x-axis labeled, “Time.” A red line labeled, “k subscript f, [N subscript 2 O subscript 4],” begins in the bottom left corner of the graph at a point labeled, “0,” and rises near the middle of the y-axis before it levels off and becomes horizontal. A blue line labeled, “k subscript f, [N O subscript 2] superscript 2,” begins near the highest point on the y-axis and drops to the same point on the y-axis as the red line before leveling off. The point where both lines become horizontal is labeled, “Equilibrium achieved.”

The formation of NO_2 from N_2O_4 is a reversible reaction, which is identified by the equilibrium arrow (⇌). All reactions are reversible, but many reactions, for all practical purposes, proceed in one direction until the reactants are exhausted and will reverse only under certain conditions. Such reactions are often depicted with a one-way arrow from reactants to products. Many other reactions, such as the formation of NO_2 from N_2O_4, are reversible under more easily obtainable conditions and, therefore, are named as such. In a reversible reaction, the reactants can combine to form products and the products can react to form the reactants. Thus, not only can N_2O_4 decompose to form NO_2, but the NO_2 produced can react to form N_2O_4. As soon as the forward reaction produces any NO_2, the reverse reaction begins and NO_2 starts to react to form N_2O_4. At equilibrium, the concentrations of N_2O_4 and NO_2 no longer change because the rate of formation of NO_2 is exactly equal to the rate of consumption of NO_2, and the rate of formation of N_2O_4 is exactly equal to the rate of consumption of N_2O_4. *Chemical equilibrium is a dynamic process*: As with the swimmers and the sunbathers, the numbers of each remain constant, yet there is a flux back and forth between them (Figure **11.1.2**).



Figure 11.1.2: These jugglers provide an illustration of dynamic equilibrium. Each throws clubs to the other at the same rate at which he receives clubs from that person. Because clubs are thrown continuously in both directions, the number of clubs moving in each direction is constant, and the number of clubs each juggler has at a given time remains (roughly) constant.

In a chemical equilibrium, the forward and reverse reactions do not stop, rather they continue to occur at the same rate, leading to constant concentrations of the reactants and the products. Plots showing how the reaction rates and concentrations change with respect to time are shown in Figure 11.1.1.

We can detect a state of equilibrium because the concentrations of reactants and products do not appear to change. However, it is important that we verify that the absence of change is due to equilibrium and not to a reaction rate that is so slow that changes in concentration are difficult to detect.

We use a double arrow when writing an equation for a reversible reaction. Such a reaction may or may not be at equilibrium. For example, Figure 11.1.1 shows the reaction:

$$\mathrm{N_2O_4\,(g)} \rightleftharpoons \mathrm{2\,NO_2\,(g)} \tag{11.1.2}$$

When we wish to speak about one particular component of a reversible reaction, we use a single arrow. For example, in the equilibrium shown in Figure 11.1.1, the rate of the forward reaction

$$\mathrm{2\,NO_2\,(g)} \rightarrow \mathrm{N_2O_4\,(g)} \tag{11.1.3}$$

is equal to the rate of the backward reaction

$$\mathrm{N_2O_4\,(g)} \rightarrow \mathrm{2\,NO_2\,(g)} \tag{11.1.4}$$

Equilibrium and Soft Drinks

The connection between chemistry and carbonated soft drinks goes back to 1767, when Joseph Priestley (1733–1804; mostly known today for his role in the discovery and identification of oxygen) discovered a method of infusing water with carbon dioxide to make carbonated water. In 1772, Priestly published a paper entitled “Impregnating Water with Fixed Air.” The paper describes dripping oil of vitriol (today we call this sulfuric acid, but what a great way to describe sulfuric acid: “oil of vitriol” literally means “liquid nastiness”) onto chalk (calcium carbonate). The resulting CO_2 falls into the container of water beneath the vessel in which the initial reaction takes place; agitation helps the gaseous CO_2 mix into the liquid water.

$$\mathrm{H_2SO_4\,(l) + CaCO_3\,(s)} \rightarrow \mathrm{CO_2\,(g) + H_2O\,(l) + CaSO_4\,(aq)}$$

Carbon dioxide is slightly soluble in water. There is an equilibrium reaction that occurs as the carbon dioxide reacts with the water to form carbonic acid (H_2CO_3). Since carbonic acid is a weak acid, it can dissociate into protons (H^+) and hydrogen carbonate ions (HCO_3^-).

$$\mathrm{CO_2\,(aq) + H_2O\,(l)} \rightleftharpoons \mathrm{H_2CO_3\,(aq)} \rightleftharpoons \mathrm{HCO_3^-\,(aq) + H^+\,(aq)}$$

Today, CO_2 can be pressurized into soft drinks, establishing the equilibrium shown above. Once you open the beverage container, however, a cascade of equilibrium shifts occurs. First, the CO_2 gas in the air space on top of the bottle escapes, causing the equilibrium between gas-phase CO_2 and dissolved or aqueous CO_2 to shift, lowering the concentration of CO_2 in the soft drink. Less CO_2 dissolved in the liquid leads to carbonic acid decomposing to dissolved CO_2 and H_2O. The lowered

carbonic acid concentration causes a shift of the final equilibrium. As long as the soft drink is in an open container, the CO_2 bubbles up out of the beverage, releasing the gas into the air (Figure **11.1.3**). With the lid off the bottle, the CO_2 reactions are no longer at equilibrium and will continue until no more of the reactants remain. This results in a soft drink with a much lowered CO_2 concentration, often referred to as "flat."



Figure **11.1.3**: When a soft drink is opened, several equilibrium shifts occur. (credit: modification of work by "D Coetzee"/Flickr)

A bottle of soda sitting on the ground is shown with a large amount of fizz-filled liquid spewing out of the top.

Sublimation of Bromine

Let us consider the evaporation of bromine as a second example of a system at equilibrium.

$$Br_2(l) \rightleftharpoons Br_2(g)$$

An equilibrium can be established for a physical change—like this liquid to gas transition—as well as for a chemical reaction. Figure **11.1.4** shows a sample of liquid bromine at equilibrium with bromine vapor in a closed container. When we pour liquid bromine into an empty bottle in which there is no bromine vapor, some liquid evaporates, the amount of liquid decreases, and the amount of vapor increases. If we cap the bottle so no vapor escapes, the amount of liquid and vapor will eventually stop changing and an equilibrium between the liquid and the vapor will be established. If the bottle were not capped, the bromine vapor would escape and no equilibrium would be reached.



Figure **11.1.4**: An equilibrium is pictured between liquid bromine, $Br_2(l)$, the dark liquid, and bromine vapor, $Br_2(g)$, the orange gas. Because the container is sealed, bromine vapor cannot escape and equilibrium is maintained. (credit: Bromine [images-of-elements.com]).

A glass container is shown that is filled with an orange-brown gas and a small amount of dark orange liquid.

Summary

A reaction is at equilibrium when the amounts of reactants or products no longer change. Chemical equilibrium is a dynamic process, meaning the rate of formation of products by the forward reaction is equal to the rate at which the products re-form reactants by the reverse reaction.

Glossary

equilibrium

in chemical reactions, the state in which the conversion of reactants into products and the conversion of products back into reactants occur simultaneously at the same rate; state of balance

reversible reaction

chemical reaction that can proceed in both the forward and reverse directions under given conditions

---

This page titled 11.1: Chemical Equilibria is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

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

11.2: Equilibrium Constants

Learning Objectives

- Derive reaction quotients from chemical equations representing homogeneous and heterogeneous reactions
- Calculate values of reaction quotients and equilibrium constants, using concentrations and pressures
- Relate the magnitude of an equilibrium constant to properties of the chemical system

Now that we have a symbol (⇌) to designate reversible reactions, we will need a way to express mathematically how the amounts of reactants and products affect the equilibrium of the system. A general equation for a reversible reaction may be written as follows:

$$mA + nB + \rightleftharpoons xC + yD \tag{11.2.1}$$

We can write the reaction quotient (Q) for this equation. When evaluated using concentrations, it is called Q_c. We use brackets to indicate molar concentrations of reactants and products.

$$Q_c = \frac{[C]^x[D]^y}{[A]^m[B]^n} \tag{11.2.2}$$

The reaction quotient is equal to the molar concentrations of the products of the chemical equation (multiplied together) over the reactants (also multiplied together), with each concentration raised to the power of the coefficient of that substance in the balanced chemical equation. For example, the reaction quotient for the reversible reaction

$$2\,NO_{2(g)} \rightleftharpoons N_2O_{4(g)} \tag{11.2.3}$$

is given by this expression:

$$Q_c = \frac{[N_2O_4]}{[NO_2]^2} \tag{11.2.4}$$

Example 11.2.1: Writing Reaction Quotient Expressions

Write the expression for the reaction quotient for each of the following reactions:

a. $3\,O_{2(g)} \rightleftharpoons 2\,O_{3(g)}$
b. $N_{2(g)} + 3\,H_{2(g)} \rightleftharpoons 2\,NH_{3(g)}$
c. $4\,NH_{3(g)} + 7\,O_{2(g)} \rightleftharpoons 4\,NO_{2(g)} + 6\,H_2O_{(g)}$

Solution

a. $Q_c = \frac{[O_3]^2}{[O_2]^3}$
b. $Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$
c. $Q_c = \frac{[NO_2]^4[H_2O]^6}{[NH_3]^4[O_2]^7}$

Exercise 11.2.1

Write the expression for the reaction quotient for each of the following reactions:

a. $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$
b. $C_4H_8(g) \rightleftharpoons 2\,C_2H_4(g)$
c. $2\,C_4H_{10}(g) + 13\,O_2(g) \rightleftharpoons 8\,CO_2(g) + 10\,H_2O(g)$

Answer a

$$Q_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

Answer b

$$Q_c = \frac{[C_2H_4]^2}{[C_4H_8]}$$

Answer c

$$Q_c = \frac{[CO_2]^8[H_2O]^{10}}{[C_4H_{10}]^2[O_2]^{13}}$$

The numeric value of Q_c for a given reaction varies; it depends on the concentrations of products and reactants present at the time when Q_c is determined. When pure reactants are mixed, Q_c is initially zero because there are no products present at that point. As the reaction proceeds, the value of Q_c increases as the concentrations of the products increase and the concentrations of the reactants simultaneously decrease (Figure 11.2.1). When the reaction reaches equilibrium, the value of the reaction quotient no longer changes because the concentrations no longer change.

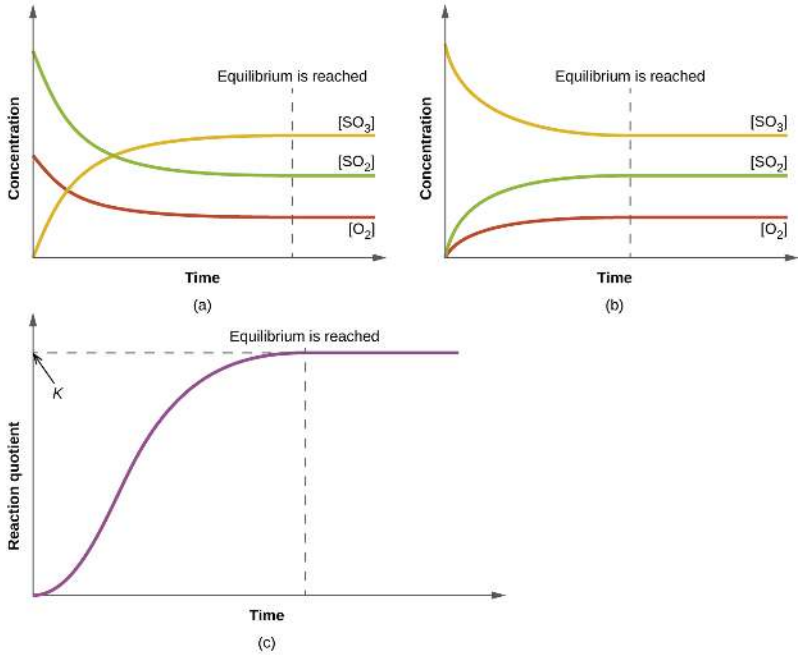


Figure 11.2.1: (a) The change in the concentrations of reactants and products is depicted as the $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ reaction approaches equilibrium. (b) The change in concentrations of reactants and products is depicted as the reaction $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ approaches equilibrium. (c) The graph shows the change in the value of the reaction quotient as the reaction approaches equilibrium.

Three graphs are shown and labeled, “a,” “b,” and “c.” All three graphs have a vertical dotted line running through the middle labeled, “Equilibrium is reached.” The y-axis on graph a is labeled, “Concentration,” and the x-axis is labeled, “Time.” Three curves are plotted on graph a. The first is labeled, “[S O subscript 2];” this line starts high on the y-axis, ends midway down the y-axis, has a steep initial slope and a more gradual slope as it approaches the far right on the x-axis. The second curve on this graph is labeled, “[O subscript 2];” this line mimics the first except that it starts and ends about fifty percent lower on the y-axis. The third curve is the inverse of the first in shape and is labeled, “[S O subscript 3].” The y-axis on graph b is labeled, “Concentration,” and the x-axis is labeled, “Time.” Three curves are plotted on graph b. The first is labeled, “[S O subscript 2];” this line starts low on the y-axis, ends midway up the y-axis, has a steep initial slope and a more gradual slope as it approaches the far right on the x-axis. The second curve on this graph is labeled, “[O subscript 2];” this line mimics the first except that it ends about fifty percent lower on the y-axis. The third curve is the inverse of the first in shape and is labeled, “[S O subscript 3].” The y-axis on graph c is labeled, “Reaction Quotient,” and the x-axis is labeled, “Time.” A single curve is plotted on graph c. This curve begins at the bottom of the y-axis and rises steeply up near the top of the y-axis, then levels off into a horizontal line. The top point of this line is labeled, “k.”

When a mixture of reactants and products of a reaction reaches equilibrium at a given temperature, its reaction quotient always has the same value. This value is called the equilibrium constant (K) of the reaction at that temperature. As for the reaction quotient, when evaluated in terms of concentrations, it is noted as K_c.

That a reaction quotient always assumes the same value at equilibrium can be expressed as:

$$Q_c \text{ at equilibrium} = K_c = \frac{[C]^x[D]^y\ldots}{[A]^m[B]^n\ldots} \tag{11.2.5}$$

This equation is a mathematical statement of the law of mass action: When a reaction has attained equilibrium at a given temperature, the reaction quotient for the reaction always has the same value.

Example 11.2.2: Evaluating a Reaction Quotient

Gaseous nitrogen dioxide forms dinitrogen tetroxide according to this equation:

$$2\,NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$$

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 equilibrium constant for the reaction?

Solution

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,

$$Q_c = \frac{[N2O4]}{[NO2]^2} = \frac{0}{0.10^2} = 0$$

b. At equilibrium, the value of the equilibrium constant is equal to the value of the reaction quotient. At equilibrium,

$$K_c = Q_c = \frac{[N2O4]}{[NO2]^2} = \frac{0.042}{0.016^2} = 1.6 \times 10^2.$$

The equilibrium constant is 1.6×10^2.

Note that dimensional analysis would suggest the unit for this K_c value should be M^{-1}. However, it is common practice to omit units for K_c values computed as described here, since it is the magnitude of an equilibrium constant that relays useful information. As will be discussed later in this module, the rigorous approach to computing equilibrium constants uses dimensionless quantities derived from activities instead of molar concentrations, and so K_c values are truly unitless.

Exercise 11.2.2

For the reaction

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$$

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 equilibrium constant, K_c?

Answer

K_c = 4.3

The magnitude of an equilibrium constant is a measure of the yield of a reaction when it reaches equilibrium. A large value for K_c indicates that equilibrium is attained only after the reactants have been largely converted into products. A small value of K_c—much less than 1—indicates that equilibrium is attained when only a small proportion of the reactants have been converted into products.

Once a value of K_c is known for a reaction, it can be used to predict directional shifts when compared to the value of Q_c. A system that is not at equilibrium will proceed in the direction that establishes equilibrium. The data in Figure 11.2.2 illustrate this. When heated to a consistent temperature, 800 °C, different starting mixtures of CO, H_2O, CO_2, and H_2 react to reach compositions adhering to the same equilibrium (the value of Q_c changes until it equals the value of K_c). This value is 0.640, the equilibrium constant for the reaction under these conditions.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \quad K_c = 0.640 \quad T = 800°C \tag{11.2.6}$$

It is important to recognize that an equilibrium can be established starting either from reactants or from products, or from a mixture of both. For example, equilibrium was established from Mixture 2 in Figure **11.2.2** when the products of the reaction were heated in a closed container. In fact, one technique used to determine whether a reaction is truly at equilibrium is to approach equilibrium starting with reactants in one experiment and starting with products in another. If the same value of the reaction quotient is observed when the concentrations stop changing in both experiments, then we may be certain that the system has reached equilibrium.

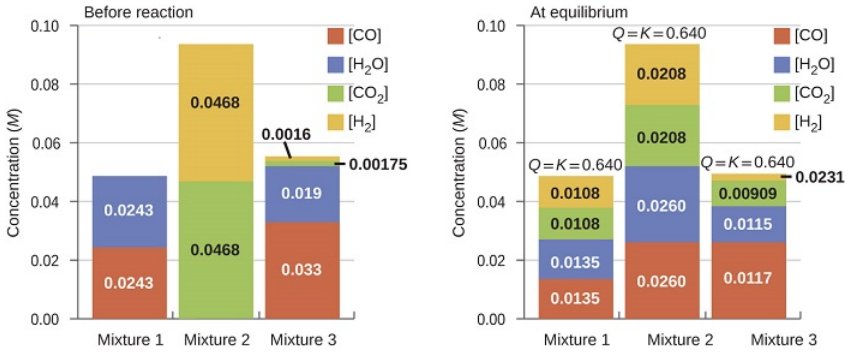


Figure **11.2.2**: Concentrations of three mixtures are shown before and after reaching equilibrium at 800 °C for the so-called water gas shift reaction (Equation 11.2.6).

Two sets of bar graphs are shown. The left is labeled, “Before reaction,” and the right is labeled, “At equilibrium.” Both graphs have y-axes labeled, “Concentration (M),” and three bars on the x-axes labeled, “Mixture 1,” “Mixture 2,” and “Mixture 3.” The y-axis has a scale beginning at 0.00 and ending at 0.10, with measurement increments of 0.02. The bars on the graphs are color coded and a key is provided with a legend. Red is labeled, “C O;” blue is labeled, “H subscript 2 O;” green is labeled, “C O subscript 2,” and yellow is labeled, “H subscript 2.” The graph on the left shows the red bar for mixture one just above 0.02 and the blue bar near 0.05. For mixture two, the green bar is near 0.05, and the yellow bar is near 0.09. For mixture 3, the red bar is near 0.01, the blue bar is slightly above that with green and yellow topping it off at 0.02. On the right graph, the bar for mixture one shows the red bar slightly above 0.01, the blue bar stacked on it rising slightly above 0.02, the green rising near 0.04, and the yellow bar reaching near 0.05. A label above this bar reads, “Q equals 0.640.” The bar for mixture two shows the red bar slightly above 0.02, the blue bar stacked on it rising near 0.05, the green rising near 0.07, and the yellow bar reaching near 0.10. A label above this bar reads “Q equals 0.640.” The bar for mixture three shows the red bar near 0.01, the blue bar stacked on it rising slightly above 0.01, the green rising near 0.02, and the yellow bar reaching 0.02. A label above this bar reads “Q equals 0.640”.

Example 11.2.3: Predicting the Direction of Reaction

Given here are the starting concentrations of reactants and products for three experiments involving this reaction:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

with $K_c = 0.64$. Determine in which direction the reaction proceeds as it goes to equilibrium in each of the three experiments shown.

Reactant/Products for Three Experiments

Reactants/Products	Experiment 1	Experiment 2	Experiment 3
$[CO]_i$	0.0203 M	0.011 M	0.0094 M
$[H_2O]_i$	0.0203 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

Solution

Experiment 1:

$$Q_c = \frac{[CO2][H2]}{[CO][H2O]} = \frac{(0.0040)(0.0040)}{(0.0203)(0.0203)} = 0.039.$$

$Q_c < K_c$ (0.039 < 0.64)

The reaction will shift to the right.

Experiment 2:

$$Q_c = \frac{[CO2][H2]}{[CO][H2O]} = \frac{(0.037)(0.046)}{(0.011)(0.0011)} = 1.4 \times 10^2$$

$Q_c > K_c$ (140 > 0.64)

The reaction will shift to the left.

Experiment 3:

$$Q_c = \frac{[CO2][H2]}{[CO][H2O]} = \frac{(0.0015)(0.0076)}{(0.0094)(0.0025)} = 0.48$$

$Q_c < K_c$ (0.48 < 0.64)

The reaction will shift to the right.

Exercise 11.2.3

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:

$$2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g) \quad K_c = 4.6 \times 10^4$$

(b) A 5.0-L flask containing 17 g of NH_3, 14 g of N_2, and 12 g of H_2:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \quad K_c = 0.060$$

(c) A 2.00-L flask containing 230 g of SO_3(g):

$$2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g) \quad K_c = 0.230$$

Answer a

$Q_c = 6.45 \times 10^3$, shifts right.

Answer b

$Q_c = 0.12$, shifts left.

Answer c

$Q_c = 0$, shifts right

In Example **11.2.2**, it was mentioned that the common practice is to omit units when evaluating reaction quotients and equilibrium constants. It should be pointed out that using concentrations in these computations is a convenient but simplified approach that sometimes leads to results that seemingly conflict with the law of mass action. For example, equilibria involving aqueous ions often exhibit equilibrium constants that vary quite significantly (are *not* constant) at high solution concentrations. This may be avoided by computing K_c values using the *activities* of the reactants and products in the equilibrium system instead of their concentrations. The activity of a substance is a measure of its effective concentration under specified conditions. While a detailed discussion of this important quantity is beyond the scope of an introductory text, it is necessary to be aware of a few important aspects:

- Activities are dimensionless (**unitless**) quantities and are in essence “adjusted” concentrations.
- For relatively dilute solutions, a solute's activity and its molar concentration are roughly equal.
- Activities for pure condensed phases (solids and liquids) are equal to 1.
- Activities for solvents in dilute solutions are equal to 1.

As a consequence of this last two aspects, Q_c and K_c expressions do not contain terms for solids or liquids or solvents in dilute solutions (being numerically equal to 1, these terms have no effect on the expression's value). Several examples of equilibria yielding such expressions will be encountered in this section.

Homogeneous Equilibria

A homogeneous equilibrium is one in which all of the reactants and products are present in a single solution (by definition, a homogeneous mixture). In this chapter, we will concentrate on the two most common types of homogeneous equilibria: those occurring in liquid-phase solutions and those involving exclusively gaseous species. Reactions between solutes in liquid solutions belong to one type of homogeneous equilibria. The chemical species involved can be molecules, ions, or a mixture of both. Several examples are provided here:

Example 1

$$\mathrm{C_2H_2}(aq) + 2\,\mathrm{Br_2}(aq) \rightleftharpoons \mathrm{C_2H_2Br_4}(aq) \tag{11.2.7}$$

with associated equilibrium constant

$$K_c = \frac{[C2H2Br4]}{[C2H2][Br2]^2} \tag{11.2.8}$$

Example 2

$$\mathrm{I_2}(aq) + \mathrm{I^-}(aq) \rightleftharpoons \mathrm{I_3^-}(aq) \tag{11.2.9}$$

with associated equilibrium constant

$$K_c = \frac{[I3-]}{[I2][I-]} \tag{11.2.10}$$

Example 3

$$\mathrm{Hg_2^{2+}}(aq) + \mathrm{NO_3^-}(aq) + 3\,\mathrm{H_3O^+}(aq) \rightleftharpoons 2\,\mathrm{Hg^{2+}}(aq) + \mathrm{HNO_2}(aq) + 4\,\mathrm{H_2O}(l) \tag{11.2.11}$$

with associated equilibrium constant

$$K_c = \frac{[Hg^2+]^2[HNO2]}{[Hg2^2+][NO3-][H3O+]^3} \tag{11.2.12}$$

Example 4

$$\mathrm{HF}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{F^-}(aq) \tag{11.2.13}$$

with associated equilibrium constant

$$K_c = \frac{[H3O+][F-]}{[HF]} \tag{11.2.14}$$

Example 5

$$\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq) \tag{11.2.15}$$

with associated equilibrium constant

$$K_c = \frac{[NH4+][OH-]}{[NH3]} \tag{11.2.16}$$

In each of these examples, the equilibrium system is an aqueous solution, as denoted by the *aq* annotations on the solute formulas. Since $H_2O(l)$ is the solvent for these solutions, it is assigned an activity of 1, and thus **does not** appear explicitly as a term in the K_c expression, as discussed earlier, even though it may also appear as a reactant or product in the chemical equation.

Reactions in which all reactants and products are gases represent a second class of homogeneous equilibria. We use molar concentrations in the following examples, but we will see shortly that partial pressures of the gases may be used as well:

Example 1

$$\mathrm{C_2H_6}(g) \rightleftharpoons \mathrm{C_2H_4}(g) + \mathrm{H_2}(g) \tag{11.2.17}$$

with associated equilibrium constant

$$K_c = \frac{[C2H4][H2]}{[C2H6]} \tag{11.2.18}$$

Example 2

$$3\,\mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{O_3}(g) \tag{11.2.19}$$

with associated equilibrium constant

$$K_c = \frac{[O3]^2}{[O2]^3} \tag{11.2.20}$$

Example 3

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{NH_3}(g) \tag{11.2.21}$$

with associated equilibrium constant

$$K_c = \frac{[NH3]^2}{[N2][H2]^3} \tag{11.2.22}$$

Example 4

$$\mathrm{C_3H_8}(g) + 5\,\mathrm{O_2}(g) \rightleftharpoons 3\,\mathrm{CO_2}(g) + 4\,\mathrm{H_2O}(g) \tag{11.2.23}$$

with associated equilibrium constant

$$K_c = \frac{[CO2]^3[H2O]^4}{[C3H8][O2]^5} \tag{11.2.24}$$

Note that the concentration of $\mathrm{H_2O}_{(g)}$ has been included in the last example because water is not the solvent in this gas-phase reaction and its concentration (and activity) changes.

Whenever gases are involved in a reaction, the partial pressure of each gas can be used instead of its concentration in the equation for the reaction quotient because the partial pressure of a gas is directly proportional to its concentration at constant temperature. This relationship can be derived from the ideal gas equation, where M is the molar concentration of gas, $\frac{n}{V}$.

$$PV = nRT \tag{11.2.25}$$

$$P = \left(\frac{n}{V}\right)RT \tag{11.2.26}$$

$$= MRT \tag{11.2.27}$$

Thus, at constant temperature, the pressure of a gas is **directly proportional** to its concentration. Using the partial pressures of the gases, we can write the reaction quotient for the system

$$\mathrm{C_2H_6}(g) \rightleftharpoons \mathrm{C_2H_4}(g) + \mathrm{H_2}(g) \tag{11.2.28}$$

by following the same guidelines for deriving concentration-based expressions:

$$Q_P = \frac{P_{\mathrm{C_2H_4}} P_{\mathrm{H_2}}}{P_{\mathrm{C_2H_6}}} \tag{11.2.29}$$

In this equation we use Q_P to indicate a reaction quotient written with partial pressures: $P_{\mathrm{C_2H_6}}$ is the partial pressure of C_2H_6; $P_{\mathrm{H_2}}$, the partial pressure of H_2; and $P_{\mathrm{C_2H_6}}$, the partial pressure of C_2H_4. At equilibrium:

$$K_P = Q_P = \frac{P_{\mathrm{C_2H_4}} P_{\mathrm{H_2}}}{P_{\mathrm{C_2H_6}}} \tag{11.2.30}$$

The subscript P in the symbol K_P designates an equilibrium constant derived using partial pressures instead of concentrations. The equilibrium constant, K_P, is still a constant, but its numeric value may differ from the equilibrium constant found for the same reaction by using concentrations.

Conversion between a value for K_c, an equilibrium constant expressed in terms of concentrations, and a value for K_P, an equilibrium constant expressed in terms of pressures, is straightforward (a K or Q without a subscript could be either concentration or pressure).

The equation relating K_c and K_P is derived as follows. For the gas-phase reaction:

$$m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D} \tag{11.2.31}$$

with

$$K_P = \frac{(P_C)^x (P_D)^y}{(P_A)^m (P_B)^n} \tag{11.2.32}$$

$$= \frac{([\mathrm{C}] \times RT)^x ([\mathrm{D}] \times RT)^y}{([\mathrm{A}] \times RT)^m ([\mathrm{B}] \times RT)^n} \tag{11.2.33}$$

$$= \frac{[\mathrm{C}]^x [\mathrm{D}]^y}{[\mathrm{A}]^m [\mathrm{B}]^n} \times \frac{(RT)^{x+y}}{(RT)^{m+n}} \tag{11.2.34}$$

$$= K_c (RT)^{(x+y)-(m+n)} \tag{11.2.35}$$

$$= K_c (RT)^{\Delta n} \tag{11.2.36}$$

The relationship between K_c and K_P is

$$K_P = K_c (RT)^{\Delta n} \tag{11.2.37}$$

In this equation, Δn is the difference between the sum of the coefficients of the *gaseous* products and the sum of the coefficients of the *gaseous* reactants in the reaction (the change in moles of gas between the reactants and the products). For the gas-phase reaction $m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D}$, we have

$$\Delta n = (x + y) - (m + n) \tag{11.2.38}$$

Example 11.2.4: Calculation of K_P

Write the equations for the conversion of K_c to K_P for each of the following reactions:

a. $\mathrm{C_2H_6}(g) \rightleftharpoons \mathrm{C_2H_4}(g) + \mathrm{H_2}(g)$
b. $\mathrm{CO}(g) + \mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO_2}(g) + \mathrm{H_2}(g)$
c. $\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{NH_3}(g)$
d. K_c is equal to 0.28 for the following reaction at 900 °C:

$$\mathrm{CS_2}(g) + 4\,\mathrm{H_2}(g) \rightleftharpoons \mathrm{CH_4}(g) + 2\,\mathrm{H_2S}(g)$$

What is K_P at this temperature?

Solution

(a) $\Delta n = (2) - (1) = 1$

$$K_P = K_c (RT)^{\Delta n} = K_c (RT)^1 = K_c (RT)$$

(b) $\Delta n = (2) - (2) = 0$

$$K_P = K_c (RT)^{\Delta n} = K_c (RT)^0 = K_c$$

(c) $\Delta n = (2) - (1 + 3) = -2$

$$K_P = K_c (RT)^{\Delta n} = K_c (RT)^{-2} = \frac{K_c}{(RT)^2}$$

d) $K_P = K_c (\mathrm{RT})^{\Delta n} = (0.28)[(0.0821)(1173)]^{-2} = 3.0 \times 10^{-5}$

? Exercise 11.2.4

Write the equations for the conversion of K_c to K_P for each of the following reactions, which occur in the gas phase:

a. $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$
b. $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$
c. $C_3H_8(g) + 5\,O_2(g) \rightleftharpoons 3\,CO_2(g) + 4\,H_2O(g)$
d. At 227 °C, the following reaction has K_c = 0.0952:

$$CH_3OH(g) \rightleftharpoons CO(g) + 2\,H_2(g)$$

What would be the value of K_P at this temperature?

Answer a

$K_P = K_c\,(RT)^{-1}$

Answer b

$K_P = K_c\,(RT)$

Answer c

$K_P = K_c\,(RT)$;

Answer d

160 or 1.6×10^2

Heterogeneous Equilibria

A heterogeneous equilibrium is a system in which reactants and products are found in two or more phases. The phases may be any combination of solid, liquid, or gas phases, and solutions. When dealing with these equilibria, remember that solids and pure liquids do not appear in equilibrium constant expressions (the activities of pure solids, pure liquids, and solvents are 1).

Some heterogeneous equilibria involve chemical changes:

Example 1

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,Cl^-(aq) \tag{11.2.39}$$

with associated equilibrium constant

$$K_c = [Pb^{2+}][Cl^-]^2 \tag{11.2.40}$$

Example 1

$$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) \tag{11.2.41}$$

with associated equilibrium constant

$$K_c = \frac{1}{[CO_2]} \tag{11.2.42}$$

Example 1

$$C(s) + 2\,S(g) \rightleftharpoons CS_2(g) \tag{11.2.43}$$

with associated equilibrium constant

$$K_c = \frac{[CS2]}{[S]^2} \tag{11.2.44}$$

Other heterogeneous equilibria involve phase changes, for example, the evaporation of liquid bromine, as shown in the following equation:

$$Br_2(l) \rightleftharpoons Br_2(g) \tag{11.2.45}$$

with associated equilibrium constant

$$K_c = [\mathrm{Br_2}] \tag{11.2.46}$$

We can write equations for reaction quotients of heterogeneous equilibria that involve gases, using **partial pressures** instead of concentrations. Two examples are:

$$\mathrm{CaO}(s) + \mathrm{CO_2}(g) \rightleftharpoons \mathrm{CaCO_3}(s) \tag{11.2.47}$$

with associated equilibrium constant

$$K_P = \frac{1}{P_{\mathrm{CO_2}}} \tag{11.2.48}$$

$$\mathrm{C}(s) + 2\,\mathrm{S}(g) \rightleftharpoons \mathrm{CS_2}(g) \tag{11.2.49}$$

with associated equilibrium constant

$$K_P = \frac{P_{\mathrm{CS_2}}}{(P_{\mathrm{S}})^2} \tag{11.2.50}$$

Summary

For any reaction that is at equilibrium, the reaction quotient Q is equal to the equilibrium constant K for the reaction. If a reactant or product is a pure solid, a pure liquid, or the solvent in a dilute solution, the concentration of this component does not appear in the expression for the equilibrium constant. At equilibrium, the values of the concentrations of the reactants and products are constant. Their particular values may vary depending on conditions, but the value of the reaction quotient will always equal K (K_c when using concentrations or K_P when using partial pressures).

A homogeneous equilibrium is an equilibrium in which all components are in the same phase. A heterogeneous equilibrium is an equilibrium in which components are in two or more phases. We can decide whether a reaction is at equilibrium by comparing the reaction quotient with the equilibrium constant for the reaction.

Key Equations

- $Q = \dfrac{[\mathrm{C}]^x[\mathrm{D}]^y}{[\mathrm{A}]^m[\mathrm{B}]^n}$ where $m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D}$
- $Q_P = \dfrac{(P_C)^x(P_D)^y}{(P_A)^m(P_B)^n}$ where $m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D}$
- $P = MRT$
- $K_P = K_c\,(RT)^{\Delta n}$

Glossary

equilibrium constant (K)
value of the reaction quotient for a system at equilibrium

heterogeneous equilibria
equilibria between reactants and products in different phases

homogeneous equilibria
equilibria within a single phase

K_c
equilibrium constant for reactions based on concentrations of reactants and products

K_P
equilibrium constant for gas-phase reactions based on partial pressures of reactants and products

law of mass action

when a reversible reaction has attained equilibrium at a given temperature, the reaction quotient remains constant

reaction quotient (*Q*)

ratio of the product of molar concentrations (or pressures) of the products to that of the reactants, each concentration (or pressure) being raised to the power equal to the coefficient in the equation

---

This page titled 11.2: Equilibrium Constants is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

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

11.3: Shifting Equilibria- Le Châtelier's Principle

Learning Objectives

- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Chatelier's principle

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 $Q = K$.

Predicting the Direction of a Reversible Reaction

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 11.3.1 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 11.3.1: (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. $\mathbf{Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)}$. *(c) Silver nitrate has been added to the solution in (b), precipitating some of the SCN− as the white solid AgSCN.* $\mathbf{Ag^+(aq) + SCN^-(aq) \rightleftharpoons AgSCN(s)}$. *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).*

Three capped test tubes held vertically in clamps are shown in pictures labeled, "a," "b," and "c." The test tube in picture a is half filled with a clear, orange liquid. The test tube in picture b is half filled with a dark, burgundy liquid. The test tube in picture c is half filled with a slightly cloudy, orange liquid.

The effect of a change in concentration on a system at equilibrium is illustrated further by the equilibrium of this chemical reaction:

$$\mathbf{H_{2(g)} + I_{2(g)} \rightleftharpoons 2\,HI_{(g)}} \tag{11.3.1}$$

$$K_c = 50.0 \text{ at } 400°C \tag{11.3.2}$$

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:

$$Q_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.692)^2}{(0.374)(0.153)} = 50.0 = K_c \tag{11.3.3}$$

We have stressed this system by introducing additional H_2. The stress is relieved when the reaction shifts to the right, using up some (but not all) of the excess H_2, reducing the amount of uncombined I_2, and forming additional HI.

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, O_2, and NO_2 are at equilibrium:

$$2\,NO\,(g) + O_2\,(g) \rightleftharpoons 2\,NO_2\,(g) \tag{11.3.4}$$

The formation of additional amounts of NO_2 decreases the total number of molecules in the system because each time two molecules of NO_2 form, a total of three molecules of NO and 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 NO_2 into NO and O_2, which tends to restore the pressure.

Now consider this reaction:

$$N_2\,(g) + O_2\,(g) \rightleftharpoons 2\,NO\,(g) \tag{11.3.5}$$

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.

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.

$$\mathrm{H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)} \quad \Delta H = -9.4\ \mathrm{kJ\ (exothermic)} \tag{11.3.6}$$

Because this reaction is exothermic, we can write it with heat as a product.

$$\mathrm{H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) + heat} \tag{11.3.7}$$

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 $\mathrm{NO_2}$ and $\mathrm{N_2O_4}$ in this reaction

$$\mathrm{N_2O_4(g) \rightleftharpoons 2\,NO_2(g)} \quad \Delta H = 57.20\ \mathrm{kJ} \tag{11.3.8}$$

The positive ΔH value tells us that the reaction is endothermic and could be written

$$\mathrm{heat + N_2O_4(g) \rightleftharpoons 2\,NO_2(g)} \tag{11.3.9}$$

At higher temperatures, the gas mixture has a deep brown color, indicative of a significant amount of brown $\mathrm{NO_2}$ 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 $\mathrm{N_2O_4}$ increases, and the concentration of brown $\mathrm{NO_2}$ decreases, causing the brown color to fade.

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

$$\mathrm{N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)} \tag{11.3.10}$$

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.

$$\mathrm{N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)}$$

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 ($\mathrm{N_2}$) 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.

It has long been known that nitrogen and hydrogen react to form ammonia. However, it became possible to manufacture ammonia in useful quantities by the reaction of nitrogen and hydrogen only in the early 20th century after the factors that influence its equilibrium were understood.

To be practical, an industrial process must give a large yield of product relatively quickly. One way to increase the yield of ammonia is to increase the pressure on the system in which N_2, H_2, and NH_3 are at equilibrium or are coming to equilibrium.

$$\mathrm{N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)} \tag{11.3.11}$$

The formation of additional amounts of ammonia reduces the total pressure exerted by the system and somewhat reduces the stress of the increased pressure.

Although increasing the pressure of a mixture of N_2, H_2, and NH_3 will increase the yield of ammonia, at low temperatures, the rate of formation of ammonia is slow. At room temperature, for example, the reaction is so slow that if we prepared a mixture of N_2 and H_2, no detectable amount of ammonia would form during our lifetime. The formation of ammonia from hydrogen and nitrogen is an exothermic process:

$$\mathrm{N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g)} \quad \Delta H = -92.2\ \mathrm{kJ} \tag{11.3.12}$$

Thus, increasing the temperature to increase the rate lowers the yield. If we lower the temperature to shift the equilibrium to favor the formation of more ammonia, equilibrium is reached more slowly because of the large decrease of reaction rate with decreasing temperature.

Part of the rate of formation lost by operating at lower temperatures can be recovered by using a catalyst. The net effect of the catalyst on the reaction is to cause equilibrium to be reached more rapidly. In the commercial production of ammonia, conditions of about 500 °C, 150–900 atm, and the presence of a catalyst are used to give the best compromise among rate, yield, and the cost of the equipment necessary to produce and contain high-pressure gases at high temperatures (Figure **11.3.2**).

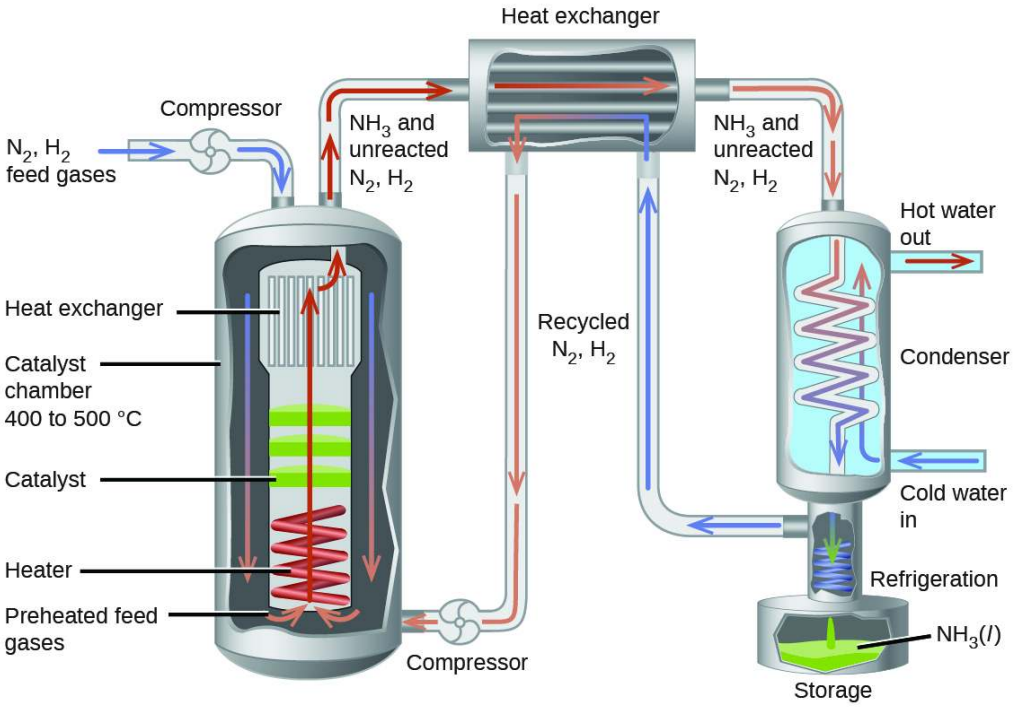


Figure **11.3.2**: Commercial production of ammonia requires heavy equipment to handle the high temperatures and pressures required. This schematic outlines the design of an ammonia plant.

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 **11.3.1**: 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.

Glossary

Le Chatelier's principle
when a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance

position of equilibrium
concentrations or partial pressures of components of a reaction at equilibrium (commonly used to describe conditions before a disturbance)

stress
change to a reaction's conditions that may cause a shift in the equilibrium

This page titled 11.3: Shifting Equilibria- Le Châtelier’s Principle is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

- **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.

11.4: Equilibrium Calculations

Learning Objectives

- Write equations representing changes in concentration and pressure for chemical species in equilibrium systems
- Use algebra to perform various types of equilibrium calculations

We know that at equilibrium, the value of the reaction quotient of any reaction is equal to its equilibrium constant. Thus, we can use the mathematical expression for Q to determine a number of quantities associated with a reaction at equilibrium or approaching equilibrium. While we have learned to identify in which direction a reaction will shift to reach equilibrium, we want to extend that understanding to quantitative calculations. We do so by evaluating the ways that the concentrations of products and reactants change as a reaction approaches equilibrium, keeping in mind the stoichiometric ratios of the reaction. This algebraic approach to equilibrium calculations will be explored in this section.

Changes in concentrations or pressures of reactants and products occur as a reaction system approaches equilibrium. In this section we will see that we can relate these changes to each other using the coefficients in the balanced chemical equation describing the system. We use the decomposition of ammonia as an example.

On heating, ammonia reversibly decomposes into nitrogen and hydrogen according to this equation:

$$2\,\mathrm{NH_3}(g) \rightleftharpoons \mathrm{N_2}(g) + 3\,\mathrm{H_2}(g)$$

If a sample of ammonia decomposes in a closed system and the concentration of N_2 increases by 0.11 M, the change in the N_2 concentration, $\Delta[N_2]$, the final concentration minus the initial concentration, is 0.11 M. The change is positive because the concentration of N_2 increases.

The change in the H_2 concentration, $\Delta[H_2]$, is also positive—the concentration of H_2 increases as ammonia decomposes. The chemical equation tells us that the change in the concentration of H_2 is three times the change in the concentration of N_2 because for each mole of N_2 produced, 3 moles of H_2 are produced.

$$\begin{aligned}\Delta[\mathrm{H_2}] &= 3 \times \Delta[\mathrm{N_2}] \\ &= 3 \times (0.11\ M) \\ &= 0.33\ M\end{aligned}$$

The change in concentration of NH_3, $\Delta[NH_3]$, is twice that of $\Delta[N_2]$; the equation indicates that 2 moles of NH_3 must decompose for each mole of N_2 formed. However, the change in the NH_3 concentration is negative because the concentration of ammonia *decreases* as it decomposes.

$$\begin{aligned}\Delta[\mathrm{NH_3}] &= -2 \times \Delta[\mathrm{N_2}] \\ &= -2 \times (0.11\ M) \\ &= -0.22\ M\end{aligned}$$

We can relate these relationships directly to the coefficients in the equation

$$\begin{array}{ccccc} 2\,\mathrm{NH_3}(g) & \rightleftharpoons & \mathrm{N_2}(g) & + & 3\,\mathrm{H_2}(g) \\ \Delta[\mathrm{NH_3}] = -2 \times \Delta[\mathrm{N_2}] & & \Delta[\mathrm{N_2}] = 0.11\ M & & \Delta[\mathrm{H_2}] = 3 \times \Delta[\mathrm{N_2}] \end{array} \quad \begin{array}{r} (11.4.1) \\ (11.4.2) \end{array}$$

Note that all the changes on one side of the arrows are of the same sign and that all the changes on the other side of the arrows are of the opposite sign.

If we did not know the magnitude of the change in the concentration of N_2, we could represent it by the symbol x.

$$\Delta[\mathrm{N_2}] = x$$

The changes in the other concentrations would then be represented as:

$$\Delta[\mathrm{H_2}] = 3 \times \Delta[\mathrm{N_2}] = 3x$$

$$\Delta[\mathrm{NH_3}] = -2 \times \Delta[\mathrm{N_2}] = -2x$$

The coefficients in the Δ terms are identical to those in the balanced equation for the reaction.

$$2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g) \tag{11.4.3}$$
$$-2x \qquad x \qquad 3x \tag{11.4.4}$$

The simplest way for us to find the coefficients for the concentration changes in any reaction is to use the coefficients in the balanced chemical equation. The sign of the coefficient is positive when the concentration increases; it is negative when the concentration decreases.

Example 11.4.1: Determining Relative Changes in Concentration

Complete the changes in concentrations for each of the following reactions.

(a)

$$C_2H_2(g) + 2\,Br_2(g) \rightleftharpoons C_2H_2Br_4(g) \tag{11.4.5}$$
$$x \qquad \_\_\_\_ \qquad \_\_\_\_ \tag{11.4.6}$$

(b)

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq) \tag{11.4.7}$$
$$\_\_\_\_ \qquad \_\_\_\_ \qquad x \tag{11.4.8}$$

(c)

$$C_3H_8(g) + 5\,O_2(g) \rightleftharpoons 3\,CO_2(g) + 4\,H_2O(g) \tag{11.4.9}$$
$$x \qquad \_\_\_\_ \qquad \_\_\_\_ \qquad \_\_\_\_ \tag{11.4.10}$$

Solution

(a)

$$C_2H_2(g) + 2\,Br_2(g) \rightleftharpoons C_2H_2Br_4(g) \tag{11.4.11}$$
$$x \qquad 2x \qquad -x \tag{11.4.12}$$

(b)

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq) \tag{11.4.13}$$
$$-x \qquad -x \qquad x \tag{11.4.14}$$

(c)

$$C_3H_8(g) + 5\,O_2(g) \rightleftharpoons 3\,CO_2(g) + 4\,H_2O(g) \tag{11.4.15}$$
$$x \qquad 5x \qquad -3x \qquad -4x \tag{11.4.16}$$

Exercise 11.4.1

Complete the changes in concentrations for each of the following reactions:

(a)

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g) \tag{11.4.17}$$
$$\_\_\_\_ \qquad x \qquad \_\_\_\_ \tag{11.4.18}$$

(b)

$$C_4H_8(g) \rightleftharpoons 2\,C_2H_4(g) \tag{11.4.19}$$
$$\_\_\_\_ \qquad -2x \tag{11.4.20}$$

(c)

$$4\,NH_3(g) + 7\,H_2O(g) \rightleftharpoons 4\,NO_2(g) + 6\,H_2O(g) \tag{11.4.21}$$
$$\_\_\_\_ \qquad \_\_\_\_ \qquad \_\_\_\_ \qquad \_\_\_\_ \tag{11.4.22}$$

Answer a

$2x$, x, $-2x$

Answer b

x, $-2x$

Answer c

$4x$, $7x$, $-4x$, $-6x$ or $-4x$, $-7x$, $4x$, $6x$

Calculations Involving Equilibrium Concentrations

Because the value of the reaction quotient of any reaction at equilibrium is equal to its equilibrium constant, we can use the mathematical expression for Q_c (i.e., *the law of mass action*) to determine a number of quantities associated with a reaction at equilibrium. It may help if we keep in mind that $Q_c = K_c$ (at equilibrium) in all of these situations and that there are only three basic types of calculations:

1. **Calculation of an equilibrium constant**. If concentrations of reactants and products at equilibrium are known, the value of the equilibrium constant for the reaction can be calculated.
2. **Calculation of missing equilibrium concentrations**. If the value of the equilibrium constant and all of the equilibrium concentrations, except one, are known, the remaining concentration can be calculated.
3. **Calculation of equilibrium concentrations from initial concentrations**. If the value of the equilibrium constant and a set of concentrations of reactants and products that are not at equilibrium are known, the concentrations at equilibrium can be calculated.

A similar list could be generated using Q_P, K_P, and partial pressure. We will look at solving each of these cases in sequence.

Calculation of an Equilibrium Constant

Since the law of mass action is the only equation we have to describe the relationship between K_c and the concentrations of reactants and products, any problem that requires us to solve for K_c must provide enough information to determine the reactant and product concentrations at equilibrium. Armed with the concentrations, we can solve the equation for K_c, as it will be the only unknown.

Example 11.4.1 showed us how to determine the equilibrium constant of a reaction if we know the concentrations of reactants and products at equilibrium. The following example shows how to use the stoichiometry of the reaction and a combination of initial concentrations and equilibrium concentrations to determine an equilibrium constant. This technique, commonly called an ICE table —for **I**nitial, **C**hange, and **E**quilibrium–will be helpful in solving many equilibrium problems. A chart is generated beginning with the equilibrium reaction in question. Underneath the reaction the initial concentrations of the reactants and products are listed—these conditions are usually provided in the problem and we consider no shift toward equilibrium to have happened. The next row of data is the change that occurs as the system shifts toward equilibrium—do not forget to consider the reaction stoichiometry as described in a previous section of this chapter. The last row contains the concentrations once equilibrium has been reached.

Example 11.4.2: Calculation of an Equilibrium Constant

Iodine molecules react reversibly with iodide ions to produce triiodide ions.

$$\mathrm{I_2}(aq) + \mathrm{I^-}(aq) \rightleftharpoons \mathrm{I_3^-}(aq)$$

If a solution with the concentrations of I_2 and I^- both equal to 1.000×10^{-3} M before reaction gives an equilibrium concentration of I_2 of 6.61×10^{-4} M, what is the equilibrium constant for the reaction?

Solution

We will begin this problem by calculating the changes in concentration as the system goes to equilibrium. Then we determine the equilibrium concentrations and, finally, the equilibrium constant. First, we set up a table with the initial concentrations, the changes in concentrations, and the equilibrium concentrations using $-x$ as the change in concentration of I_2.

	I_2	+ I^- ⇌	I_3^-
Initial concentration (M)	1.000×10^{-3}	1.000×10^{-3}	0
Change (M)	$-x$	$-x$	$+x$
Equilibrium concentration (M)	$1.000 \times 10^{-3} - x$	$1.000 \times 10^{-3} - x$	x

Since the equilibrium concentration of I_2 is given, we can solve for x. At equilibrium the concentration of I_2 is 6.61×10^{-4} M so that

$$1.000 \times 10^{-3} - x = 6.61 \times 10^{-4}$$

$$x = 1.000 \times 10^{-3} - 6.61 \times 10^{-4}$$

$$= 3.39 \times 10^{-4}\ M$$

Now we can fill in the table with the concentrations at equilibrium.

	I_2 + I^- ⇌ I_3^-		
Initial concentration (*M*)	1.000×10^{-3}	1.000×10^{-3}	0
Change (*M*)	$-x = -3.39 \times 10^{-4}$	$-x$	$+x$
Equilibrium concentration (*M*)	6.61×10^{-4}	6.61×10^{-4}	3.39×10^{-4}

We now calculate the value of the equilibrium constant.

$$K_c = Q_c = \frac{[I3-]}{[I2][I-]}$$

$$= \frac{3.39 \times 10^{-4}\ M}{(6.61 \times 10^{-4}\ M)(6.61 \times 10^{-4}\ M)} = 776$$

Exercise 11.4.2

Ethanol and acetic acid react and form water and ethyl acetate, the solvent responsible for the odor of some nail polish removers.

$$C_2H_5OH + CH_3CO_2H \rightleftharpoons CH_3CO_2C_2H_5 + H_2O$$

When 1 mol each of C_2H_5OH and CH_3CO_2H are allowed to react in 1 L of the solvent dioxane, equilibrium is established when $\frac{1}{3}$ mol of each of the reactants remains. Calculate the equilibrium constant for the reaction. (Note: Water is not a solvent in this reaction.)

Answer

$K_c = 4$

Calculation of a Missing Equilibrium Concentration

If we know the equilibrium constant for a reaction and know the concentrations at equilibrium of all reactants and products except one, we can calculate the missing concentration.

Example 11.4.3: Calculation of a Missing Equilibrium Concentration

Nitrogen oxides are air pollutants produced by the reaction of nitrogen and oxygen at high temperatures. At 2000 °C, the value of the equilibrium constant for the reaction, $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, is 4.1×10^{-4}. Find the concentration of NO(g) in an equilibrium mixture with air at 1 atm pressure at this temperature. In air, $[N_2]$ = 0.036 mol/L and $[O_2]$ 0.0089 mol/L.

Solution

We are given all of the equilibrium concentrations except that of NO. Thus, we can solve for the missing equilibrium concentration by rearranging the equation for the equilibrium constant.

$$K_c = Q_c = \frac{[NO]^2}{[N2][O2]}$$

$$[NO]^2 = K_c[N_2][O_2]$$

$$[NO] = \sqrt{K_c[N_2][O_2]}$$

$$= \sqrt{(4.1 \times 10^{-4})(0.036)(0.0089)}$$

$$= \sqrt{1.31 \times 10^{-7}}$$

$$= 3.6 \times 10^{-4}$$

Thus [NO] is 3.6×10^{-4} mol/L at equilibrium under these conditions.

We can check our answer by substituting all equilibrium concentrations into the expression for the reaction quotient to see whether it is equal to the equilibrium constant.

$$Q_c = \frac{[NO]^2}{[N2][O2]}$$

$$= \frac{(3.6 \times 10^{-4})^2}{(0.036)(0.0089)}$$

$$= 4.0 \times 10^{-4} = K_c$$

The answer checks; our calculated value gives the equilibrium constant within the error associated with the significant figures in the problem.

? Exercise 11.4.3

The equilibrium constant for the reaction of nitrogen and hydrogen to produce ammonia at a certain temperature is 6.00×10^{-2}. Calculate the equilibrium concentration of ammonia if the equilibrium concentrations of nitrogen and hydrogen are 4.26 *M* and 2.09 *M*, respectively.

Answer

1.53 mol/L

Calculation of Changes in Concentration

If we know the equilibrium constant for a reaction and a set of concentrations of reactants and products that are *not at equilibrium*, we can calculate the changes in concentrations as the system comes to equilibrium, as well as the new concentrations at equilibrium. The typical procedure can be summarized in four steps.

1. Determine the direction the reaction proceeds to come to equilibrium.
   - Write a balanced chemical equation for the reaction.
   - If the direction in which the reaction must proceed to reach equilibrium is not obvious, calculate Q_c from the initial concentrations and compare to K_c to determine the direction of change.
2. Determine the relative changes needed to reach equilibrium, then write the equilibrium concentrations in terms of these changes.
   - Define the changes in the initial concentrations that are needed for the reaction to reach equilibrium. Generally, we represent the smallest change with the symbol *x* and express the other changes in terms of the smallest change.
   - Define missing equilibrium concentrations in terms of the initial concentrations and the changes in concentration determined in (a).
3. Solve for the change and the equilibrium concentrations.
   - Substitute the equilibrium concentrations into the expression for the equilibrium constant, solve for *x*, and check any assumptions used to find *x*.
   - Calculate the equilibrium concentrations.
4. Check the arithmetic.
   - Check the calculated equilibrium concentrations by substituting them into the equilibrium expression and determining whether they give the equilibrium constant.

Sometimes a particular step may differ from problem to problem—it may be more complex in some problems and less complex in others. However, every calculation of equilibrium concentrations from a set of initial concentrations will involve these steps.

In solving equilibrium problems that involve changes in concentration, sometimes it is convenient to set up an ICE table, as described in the previous section.

Example 11.4.4: Calculation of Concentration as a Reaction Equilibrates

Under certain conditions, the equilibrium constant for the decomposition of $PCl_5(g)$ into $PCl_3(g)$ and $Cl_2(g)$ is 0.0211. What are the equilibrium concentrations of PCl_5, PCl_3, and Cl_2 if the initial concentration of PCl_5 was 1.00 *M*?

Solution

Use the stepwise process described earlier.

1. The balanced equation for the decomposition of PCl_5 is

$$\mathbf{PCl_5}(g) \rightleftharpoons \mathbf{PCl_3}(g) + \mathbf{Cl_2}(g)$$

Because we have no products initially, $Q_c = 0$ and the reaction will proceed to the right.

- Let us represent the increase in concentration of PCl_3 by the symbol *x*. The other changes may be written in terms of *x* by considering the coefficients in the chemical equation.

$$\mathbf{PCl_5}(g) \rightleftharpoons \mathbf{PCl_3}(g) + \mathbf{Cl_2}(g) \tag{11.4.23}$$

$$-x \qquad x \qquad x \tag{11.4.24}$$

- The changes in concentration and the expressions for the equilibrium concentrations are:

	$PCl_5 \rightleftharpoons PCl_3 + Cl_2$		
Initial concentration (*M*)	1.00	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium concentration (*M*)	$1.00 - x$	$0 + x = x$	$0 + x = x$

This table has two main columns and four rows. The first row for the first column does not have a heading and then has the following in the first column: Initial concentration (M), Change (M), Equilibrium concentration (M). The second column has the header, “P C l subscript 5 equilibrium arrow P C l subscript 3 plus C l subscript 2.” Under the second column is a subgroup of three rows and three columns. The first column has the following: 1.00, negative x, 1.00 minus x. The second column has the following: 0, positive x, 0 plus x equals x. The third column has the following: 0, positive x, 0 plus x equals x.

- Substituting the equilibrium concentrations into the equilibrium constant equation gives

$$K_c = \frac{[PCl3][Cl2]}{[PCl5]} = 0.0211$$

$$= \frac{(x)(x)}{(1.00 - x)}$$

This equation contains only one variable, *x*, the change in concentration. We can write the equation as a quadratic equation and solve for *x* using the quadratic formula.

$$0.0211 = \frac{(x)(x)}{(1.00 - x)}$$

$$0.0211(1.00 - x) = x^2$$

$$x^2 + 0.0211x - 0.0211 = 0$$

An equation of the form $ax^2 + bx + c = 0$ can be rearranged to solve for *x*:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

In this case, $a = 1$, $b = 0.0211$, and $c = -0.0211$. Substituting the appropriate values for *a*, *b*, and *c* yields:

$$x = \frac{-0.0211 \pm \sqrt{(0.0211)^2 - 4(1)(-0.0211)}}{2(1)}$$

$$= \frac{-0.0211 \pm \sqrt{(4.45 \times 10^{-4}) + (8.44 \times 10^{-2})}}{2}$$

$$= \frac{-0.0211 \pm 0.291}{2}$$

Hence

$$x = \frac{-0.0211 + 0.291}{2} = 0.135$$

or

$$x = \frac{-0.0211 - 0.291}{2} = -0.156$$

Quadratic equations often have two different solutions, one that is physically possible and one that is physically impossible (an extraneous root). In this case, the second solution (−0.156) is physically impossible because we know the change must be a positive number (otherwise we would end up with negative values for concentrations of the products). Thus, x = 0.135 M.

The equilibrium concentrations are

$[PCl_5] = 1.00 - 0.135 = 0.87\ M$
$[PCl_3] = x = 0.135\ M$
$[Cl_2] = x = 0.135\ M$

- Substitution into the expression for K_c (to check the calculation) gives

$$K_c = \frac{[PCl3][Cl2]}{[PCl5]} = \frac{(0.135)(0.135)}{0.87} = 0.021$$

The equilibrium constant calculated from the equilibrium concentrations is equal to the value of K_c given in the problem (when rounded to the proper number of significant figures). Thus, the calculated equilibrium concentrations check.

? Exercise 11.4.4A

Acetic acid, CH_3CO_2H, reacts with ethanol, C_2H_5OH, to form water and ethyl acetate, $CH_3CO_2C_2H_5$.

$$CH_3CO_2H + C_2H_5OH \rightleftharpoons CH_3CO_2C_2H_5 + H_2O$$

The equilibrium constant for this reaction with dioxane as a solvent is 4.0. What are the equilibrium concentrations when a mixture that is 0.15 M in CH_3CO_2H, 0.15 M in C_2H_5OH, 0.40 M in $CH_3CO_2C_2H_5$, and 0.40 M in H_2O are mixed in enough dioxane to make 1.0 L of solution?

Answer

$[CH_3CO_2H]$ = 0.36 M, $[C_2H_5OH]$ = 0.36 M, $[CH_3CO_2C_2H_5]$ = 0.17 M, $[H_2O]$ = 0.17 M

? Exercise 11.4.4B

A 1.00-L flask is filled with 1.00 moles of H_2 and 2.00 moles of I_2. The value of the equilibrium constant for the reaction of hydrogen and iodine reacting to form hydrogen iodide is 50.5 under the given conditions. What are the equilibrium concentrations of H_2, I_2, and HI in moles/L?

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

Answer

$[H_2]$ = 0.06 M, $[I_2]$ = 1.06 M, [HI] = 1.88 M

Sometimes it is possible to use chemical insight to find solutions to equilibrium problems without actually solving a quadratic (or more complicated) equation. First, however, it is useful to verify that equilibrium can be obtained starting from two extremes: all (or mostly) reactants and all (or mostly) products.

Consider the ionization of 0.150 M HA, a weak acid.

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq) \quad K_c = 6.80 \times 10^{-4}$$

The most obvious way to determine the equilibrium concentrations would be to start with only reactants. This could be called the "all reactant" starting point. Using x for the amount of acid ionized at equilibrium, this is the ICE table and solution.

	$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$		
Initial concentration (M)	0.150	0	0
Change (M)	$-x$	x	x
Equilibrium concentration (M)	$0.150 - x$	x	x

This table has two main columns and four rows. The first row for the first column does not have a heading and then has the following: Initial pressure (M), Change (M), Equilibrium (M). The second column has the header, “H A (a q) equilibrium arrow H superscript plus sign (a q) plus A subscript negative sign (a q).” Under the second column is a subgroup of three columns and three rows. The first column has the following: 0.150, negative x, 0.150 minus x. The second column has the following: 0, x, x. The third column has the following: 0, x, x.

Setting up and solving the quadratic equation gives

$$K_c = \frac{[H+][A-]}{[HA]} = \frac{(x)(x)}{(0.150 - x)} = 6.80 \times 10^{-4}$$
$$x^2 + 6.80 \times 10^{-4}x - 1.02 \times 10^{-4} = 0$$
$$x = -6.80 \times 10^{-4} \pm \sqrt{(6.80 \times 10^{-4})^2 - (4)(1)(-1.02 \times 10^{-4})}(2)(1)$$
$$x = 0.00977\ M \text{ or } -0.0104\ M$$

Using the positive (physical) root, the equilibrium concentrations are

$$[\mathrm{HA}] = 0.150 - x = 0.140\ M$$
$$[\mathrm{H^+}] = [\mathrm{A^-}] = x = 0.00977\ M$$

A less obvious way to solve the problem would be to assume all the HA ionizes first, then the system comes to equilibrium. This could be called the “all product” starting point. Assuming all of the HA ionizes gives

$$[\mathrm{HA}] = 0.150 - 0.150 = 0\ M$$
$$[\mathrm{H^+}] = 0 + 0.150 = 0.150\ M$$
$$[\mathrm{A^-}] = 0 + 0.150 = 0.150\ M$$

Using these as initial concentrations and “y” to represent the concentration of HA at equilibrium, this is the ICE table for this starting point.

	$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$		
Initial concentration (M)	0	0.150	0.150
Change (M)	$+y$	$-y$	$-y$
Equilibrium concentration (M)	y	$0.150 - y$	$0.150 - y$

This table has two main columns and four rows. The first row for the first column does not have a heading and then has the following: Initial pressure (M), Change (M), Equilibrium (M). The second column has the header, “H A (a q) equilibrium arrow H superscript plus sign (a q) plus A subscript negative sign (a q).” Under the second column is a subgroup of three columns and three rows. The first column has the following: 0, positive y, y. The second column has the following: 0.150, negative y, 0.150 minus y. The third column has the following: 0.150, negative y, and 0.150 minus y.

Setting up and solving the quadratic equation gives

$$K_c = \frac{[H+][A-]}{[HA]} = \frac{(0.150 - y)(0.150 - y)}{(y)} = 6.80 \times 10^{-4}$$
$$6.80 \times 10^{-4}y = 0.0225 - 0.300y + y^2$$

Retain a few extra significant figures to minimize rounding problems.

$$y^2 - 0.30068y + 0.022500 = 0$$

$$y = \frac{0.30068 \pm \sqrt{(0.30068)^2 - (4)(1)(0.022500)}}{(2)(1)}$$

$$y = \frac{0.30068 \pm 0.020210}{2}$$

Rounding each solution to three significant figures gives

$$y = 0.160\ M \text{ or } y = 0.140\ M$$

Using the physically significant root (0.140 M) gives the equilibrium concentrations as

$$[\mathrm{HA}] = y = 0.140\ M$$
$$[\mathrm{H^+}] = 0.150 - y = 0.010\ M$$
$$[\mathrm{A^-}] = 0.150 - y = 0.010\ M$$

Thus, the two approaches give the same results (to three *decimal places*), and show that *both* starting points lead to the same equilibrium conditions. The "all reactant" starting point resulted in a relatively small change (x) because the system was close to equilibrium, while the "all product" starting point had a relatively large change (y) that was nearly the size of the initial concentrations. It can be said that a system that starts "close" to equilibrium will require only a "small" change in conditions (x) to reach equilibrium.

Recall that a small K_c means that very little of the reactants form products and a large K_c means that most of the reactants form products. If the system can be arranged so it starts "close" to equilibrium, then if the change (x) is small compared to any initial concentrations, it can be neglected. Small is usually defined as resulting in an error of less than 5%. The following two examples demonstrate this.

Example 11.4.5: Approximate Solution Starting Close to Equilibrium

What are the concentrations at equilibrium of a 0.15 M solution of HCN?

$$\mathrm{HCN}(aq) \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{CN^-}(aq) \quad K_c = 4.9 \times 10^{-10}$$

Solution

Using "x" to represent the concentration of each product at equilibrium gives this ICE table.

	$\mathrm{HCN}(aq) \rightleftharpoons$	$\mathrm{H^+}(aq)$	+ $\mathrm{CN^-}(aq)$
Initial concentration (M)	0.15	0	0
Change (M)	$-x$	x	x
Equilibrium concentration (M)	$0.15 - x$	x	x

This table has two main columns and four rows. The first row for the first column does not have a heading and then has the following: Initial pressure (M), Change (M), Equilibrium (M). The second column has the header, "H C N (a q) equilibrium arrow H superscript plus sign (a q) plus C N subscript negative sign (a q)." Under the second column is a subgroup of three columns and three rows. The first column has the following: 0.15, negative x, 0.15 minus x. The second column has the following: 0, x, x. The third column has the following: 0, x, x.

The exact solution may be obtained using the quadratic formula with

$$K_c = \frac{(x)(x)}{0.15 - x}$$

solving

$$x^2 + 4.9 \times 10^{-10} - 7.35 \times 10^{-11} = 0$$

$$x = 8.56 \times 10^{-6}\ M\ (3 \text{ sig. figs.}) = 8.6 \times 10^{-6}\ M\ (2 \text{ sig. figs.})$$

Thus $[H^+] = [CN^-] = x = 8.6 \times 10^{-6}\ M$ and $[HCN] = 0.15 - x = 0.15\ M$.

In this case, chemical intuition can provide a simpler solution. From the equilibrium constant and the initial conditions, x must be small compared to 0.15 M. More formally, if $x \ll 0.15$, then $0.15 - x \approx 0.15$. If this assumption is true, then it simplifies obtaining x

$$K_c = \frac{(x)(x)}{0.15 - x} \approx \frac{x^2}{0.15}$$

$$4.9 \times 10^{-10} = \frac{x^2}{0.15}$$

$$x^2 = (0.15)(4.9 \times 10^{-10}) = 7.4 \times 10^{-11}$$

$$x = \sqrt{7.4 \times 10^{-11}} = 8.6 \times 10^{-6}\ M$$

In this example, solving the exact (quadratic) equation and using approximations gave the same result to two significant figures. While most of the time the approximation is a bit different from the exact solution, as long as the error is less than 5%, the approximate solution is considered valid. In this problem, the 5% applies to IF $(0.15 - x) \approx 0.15\ M$, so if

$$\frac{x}{0.15} \times 100\% = \frac{8.6 \times 10^{-6}}{0.15} \times 100\% = 0.006\%$$

is less than 5%, as it is in this case, the assumption is valid. The approximate solution is thus a valid solution.

? Exercise 11.4.5

What are the equilibrium concentrations in a 0.25 M NH_3 solution?

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \quad K_c = 1.8 \times 10^{-5}$$

Assume that x is much less than 0.25 M and calculate the error in your assumption.

Answer

$[OH^-] = [NH_4^+] = 0.0021\ M$; $[NH_3] = 0.25\ M$, error = 0.84%

The second example requires that the original information be processed a bit, but it still can be solved using a small x approximation.

✓ Example 11.4.6: Approximate Solution After Shifting Starting Concentration

Copper(II) ions form a complex ion in the presence of ammonia

$$Cu^{2+}(aq) + 4\,NH_3(aq) \rightleftharpoons Cu(NH_3)_4{}^{2+}(aq) \quad K_c = 5.0 \times 10^{13} = \frac{[Cu(NH3)4^2+]}{[Cu^2 + (aq)][NH3]^4}$$

If 0.010 mol Cu^{2+} is added to 1.00 L of a solution that is 1.00 M NH_3 what are the concentrations when the system comes to equilibrium?

Solution The initial concentration of copper(II) is 0.010 M. The equilibrium constant is very large so it would be better to start with as much product as possible because “all products” is much closer to equilibrium than “all reactants.” Note that Cu^{2+} is the limiting reactant; if all 0.010 M of it reacts to form product the concentrations would be

$$[Cu^{2+}] = 0.010 - 0.010 = 0\ M$$

$$[Cu(NH_3)_4{}^{2+}] = 0.010\ M$$

$$[NH_3] = 1.00 - 4 \times 0.010 = 0.96\ M$$

Using these “shifted” values as initial concentrations with x as the free copper(II) ion concentration at equilibrium gives this ICE table.

	$Cu^{2+}(aq)$ +	$4NH_3(aq) \rightleftharpoons$	$Cu(NH_3)_4{}^{2+}(aq)$
Initial concentration (*M*)	0	0.96	0.010
Change (*M*)	$+x$	$+4x$	$-x$
Equilibrium concentration (*M*)	x	$0.96 + 4x$	$0.010 - x$

This table has two main columns and four rows. The first row for the first column does not have a heading and then has the following: Initial pressure (M), Change (M), Equilibrium (M). The second column has the header, “C u superscript 2 positive sign (a q) plus 4 N H subscript 3 (a q) equilibrium arrow C u (N H subscript 3) subscript 4 superscript 2 positive sign (a q).” Under the second column is a subgroup of three columns and three rows. The first column has the following: 0, positive x, x. The second column has the following: 0.96, positive 4 x, 0.96 plus 4 x. The third column has the following: 0.010, negative x, 0.010 minus x.

Since we are starting close to equilibrium, x should be small so that

$$0.96 + 4x \approx 0.96\ M$$

$$0.010 - x \approx 0.010\ M$$

$$K_c = \frac{(0.010 - x)}{x(0.96 - 4x)^4} \approx \frac{(0.010)}{x(0.96)^4} = 5.0 \times 10^{13}$$

$$x = \frac{(0.010)}{K_c(0.96)^4} = 2.4 \times 10^{-16}\ M$$

Select the smallest concentration for the 5% rule.

$$\frac{2.4 \times 10^{-16}}{0.010} \times 100\% = 2 \times 10^{-12}\%$$

This is much less than 5%, so the assumptions are valid. The concentrations at equilibrium are

$$[Cu^{2+}] = x = 2.4 \times 10^{-16}\ M$$
$$[NH_3] = 0.96 - 4x = 0.96\ M$$
$$[Cu(NH_3)_4{}^{2+}] = 0.010 - x = 0.010\ M$$

By starting with the maximum amount of product, this system was near equilibrium and the change (x) was very small. With only a small change required to get to equilibrium, the equation for x was greatly simplified and gave a valid result well within the 5% error maximum.

? Exercise 11.4.6

What are the equilibrium concentrations when 0.25 mol Ni^{2+} is added to 1.00 L of 2.00 *M* NH_3 solution?

$$Ni^{2+}(aq) + 6\,NH_3(aq) \rightleftharpoons Ni(NH_3)_6{}^{2+}(aq)$$

with $K_c = 5.5 \times 10^8$.

With such a large equilibrium constant, first form as much product as possible, then assume that only a small amount (x) of the product shifts left. Calculate the error in your assumption.

Answer

$[Ni(NH_3)_6{}^{2+}] = 0.25\ M$, $[NH_3] = 0.50\ M$, $[Ni^{2+}] = 2.9 \times 10^{-8}\ M$, error = $1.2 \times 10^{-5}\%$

Summary

The ratios of the rate of change in concentrations of a reaction are equal to the ratios of the coefficients in the balanced chemical equation. The sign of the coefficient of X is positive when the concentration increases and negative when it decreases. We learned to approach three basic types of equilibrium problems. When given the concentrations of the reactants and products at equilibrium, we can solve for the equilibrium constant; when given the equilibrium constant and some of the concentrations involved, we can

solve for the missing concentrations; and when given the equilibrium constant and the initial concentrations, we can solve for the concentrations at equilibrium.

This page titled 11.4: Equilibrium Calculations is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

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

CHAPTER OVERVIEW

12: Acid-Base Equilibria

A general chemistry Libretexts Textmap organized around the textbook
General Chemistry -Atoms First
By OpenStax

I II III IV V VI VII VIII IX X XI XII XIII XIV XV XVI XVII XVIII XIX XX XXI ● **Homework**

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.

12.1: Brønsted-Lowry Acids and Bases
12.2: pH and pOH
12.3: Relative Strengths of Acids and Bases
12.4: Polyprotic Acids
12.5: Buffers
12.6: Acid-Base Titrations

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 12: Acid-Base Equilibria is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

12.1: Brønsted-Lowry Acids and Bases

Learning Objectives

- 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

Acids and bases have been known for a long time. When Robert Boyle characterized them in 1680, he noted that acids dissolve many substances, change the color of certain natural dyes (for example, they change litmus from blue to red), and lose these characteristic properties after coming into contact with alkalis (bases). 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.

In an earlier chapter on chemical reactions, we defined acids and bases as Arrhenius did: We identified an acid as a compound that dissolves in water to yield hydronium ions (H_3O^+) and a base as a compound that dissolves in water to yield hydroxide ions (OH^-). This definition is not wrong; it is simply limited.

Later, we extended the definition of an acid or a base using the more general definition proposed in 1923 by the Danish chemist Johannes Brønsted and the English chemist Thomas Lowry. Their definition centers on the proton, H^+. A proton is what remains when a normal hydrogen atom, ^1_1H, loses an electron. 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 the transfer of a proton from a proton donor (acid) to a proton acceptor (base). In a subsequent chapter of this text we will introduce the most general model of acid-base behavior introduced by the American chemist G. N. Lewis.

Acids may be compounds such as HCl or H_2SO_4, organic acids like acetic acid (CH_3COOH) or ascorbic acid (vitamin C), or H_2O. Anions (such as HSO_4^-, $H_2PO_4^-$, HS^-, and HCO_3^-) and cations (such as H_3O^+, NH_4^+, and $[Al(H_2O)_6]^{3+}$) may also act as acids. Bases fall into the same three categories. Bases may be neutral molecules (such as H_2O, NH_3, and CH_3NH_2), anions (such as OH^-, HS^-, HCO_3^-, CO_3^{2-}, F^-, and PO_4^{3-}), or cations (such as $[Al(H_2O)_5OH]^{2+}$). The most familiar bases are ionic compounds such as $NaOH$ and $Ca(OH)_2$, which contain the hydroxide ion, OH^-. The hydroxide ion in these compounds accepts a proton from acids to form water:

$$H^+ + OH^- \rightarrow H_2O \tag{12.1.1}$$

We call the product that remains after an acid donates a proton the conjugate base of the acid. This species is a base because it can accept a proton (to re-form the acid):

$$\text{acid} \rightleftharpoons \text{proton} + \text{conjugate base} \tag{12.1.2}$$

$$HF \rightleftharpoons H^+ + F^- \tag{12.1.3}$$

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \tag{12.1.4}$$

$$H_2O \rightleftharpoons H^+ + OH^- \tag{12.1.5}$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \tag{12.1.6}$$

$$NH_4^+ \rightleftharpoons H^+ + NH_3 \tag{12.1.7}$$

We call the product that results when a base accepts a proton the base's conjugate acid. This species is an acid because it can give up a proton (and thus re-form the base):

$$\text{base} + \text{proton} \rightleftharpoons \text{conjugate acid} \tag{12.1.8}$$

$$OH^- + H^+ \rightleftharpoons H_2O \tag{12.1.9}$$

$$H_2O + H^+ \rightleftharpoons H_3O^+ \tag{12.1.10}$$

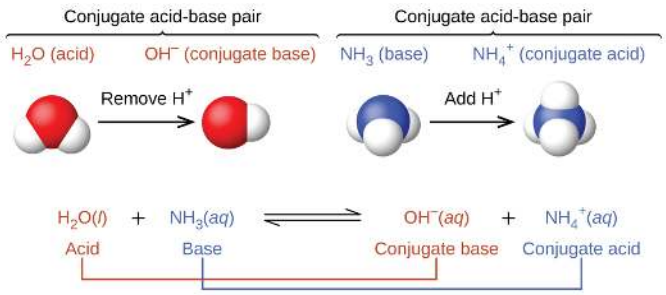
$$NH_3 + H^+ \rightleftharpoons NH_4^+ \tag{12.1.11}$$

$$S^{2-} + H^+ \rightleftharpoons HS^- \tag{12.1.12}$$

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^- \tag{12.1.13}$$

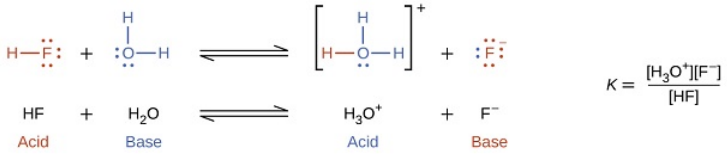
$$F^- + H^+ \rightleftharpoons HF \tag{12.1.14}$$

In these two sets of equations, the behaviors of acids as proton donors and bases as proton acceptors are represented in isolation. In reality, all acid-base reactions involve the transfer of protons between acids and bases. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water. A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water, OH^-, and the conjugate acid of ammonia, NH_4^+:



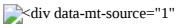
This figure has three parts in two rows. In the first row, two diagrams of acid-base pairs are shown. On the left, a space filling model of H subscript 2 O is shown with a red O atom at the center and two smaller white H atoms attached in a bent shape. Above this model is the label “H subscript 2 O (acid)” in purple. An arrow points right, which is labeled “Remove H superscript plus.” To the right is another space filling model with a single red O atom to which a single smaller white H atom is attached. The label in purple above this model reads, “O H superscript negative (conjugate base).” Above both of these red and white models is an upward pointing bracket that is labeled “Conjugate acid-base pair.” To the right is a space filling model with a central blue N atom to which three smaller white H atoms are attached in a triangular pyramid arrangement. A label in green above reads “N H subscript 3 (base).” An arrow labeled “Add H superscript plus” points right. To the right of the arrow is another space filling model with a blue central N atom and four smaller white H atoms in a tetrahedral arrangement. The green label above reads “N H subscript 3 superscript plus (conjugate acid).” Above both of these blue and white models is an upward pointing bracket that is labeled “Conjugate acid-base pair.” The second row of the figure shows the chemical reaction, H subscript 2 O (l) is shown in purple, and is labeled below in purple as “acid,” plus N H subscript 3 (a q) in green, labeled below in green as “base,” followed by a double sided arrow arrow and O H superscript negative (a q) in purple, labeled in purple as “conjugate base,” plus N H subscript 4 superscript plus (a q)” in green, which is labeled in green as “conjugate acid.” The acid on the left side of the equation is connected to the conjugate base on the right with a purple line. Similarly, the base on the left is connected to the conjugate acid on the right side.

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 and fluoride ions:

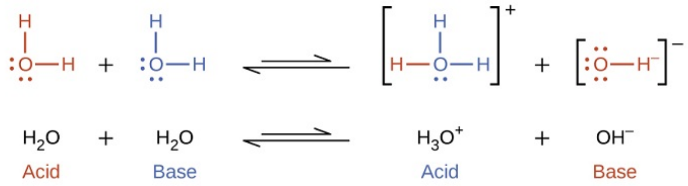


This figure has two rows. In both rows, a chemical reaction is shown. In the first, structural formulas are provided. In this model, in purple, an H atom is connected to an F atom with a single bond. The F atom has pairs of electron dots at the top, right, and bottom. This is followed by a plus sign, which is followed in green by an O atom which has H atoms singly bonded above and to the right. The O atom has pairs of electron dots on its left and lower sides. A double arrow follows. To the right, in brackets is a structure with a central O atom in green, with green H atoms singly bonded above and to the right. A pair of green electron dots is on the lower side of the O atom. To the left of the green O atom, a purple H atom is singly bonded. This is followed by a plus sign and an F atom in purple with pairs of electron dots above, right, below, and to the left. This atom also has a superscript negative sign. The reaction is written in symbolic form below. H F is labeled in purple below as “Acid subscript 1.” This is followed by plus H subscript 2 O, which is labeled in green below as “Base subscript 2.” A double sided arrow follows. To the right is H subscript 3 O superscript plus, which is labeled in green as below in as “Acid subscript 2.” This is followed by plus and F surrounded by 4 pairs of dots and superscript negative. The label below in purple reads, “Base subscript 1.” To the right of the reactions is the formula, K subscript a equals left bracket H subscript 3 O superscript plus right bracket left bracket F superscript negative right bracket all over left bracket H F right bracket.

When we add a base to water, a base ionization reaction occurs in which protons are transferred from water molecules to base molecules. For example, adding pyridine to water yields hydroxide ions and pyridinium ions:



Notice that both these ionization reactions are represented as equilibrium processes. The relative extent to which these acid and base ionization reactions proceed is an important topic treated in a later section of this chapter. In the preceding paragraphs we saw that water can function as either an acid or a base, depending on the nature of the solute dissolved in it. In fact, in pure water or in any aqueous solution, water acts both as an acid and a base. A very small fraction of water molecules donate protons to other water molecules to form hydronium ions and hydroxide ions:



This figure has two rows. In both rows, a chemical reaction is shown. In the first, structural formulas are provided. In this model, in purple, O atom which has H atoms singly bonded above and to the right. The O atom has pairs of electron dots on its left and lower sides. This is followed by a plus sign, which is followed in green by an O atom which has H atoms singly bonded above and to the right. The O atom has pairs of electron dots on its left and lower sides. A double arrow follows. To the right, in brackets is a structure with a central O atom in green, with green H atoms singly bonded above and to the right. A pair of green electron dots is on the lower side of the O atom. To the left of the green O atom, a purple H atom is singly bonded. Outside the brackets to the right is a superscript plus. This is followed by a plus sign and an O atom in purple with pairs of electron dots above, left, and below. An H atom is singly bonded to the right. This atom has a superscript negative sign. The reaction is written in symbolic form below. H subscript 2 O is labeled in purple below as “Acid subscript 1.” This is followed by plus H subscript 2 O, which is labeled in green below as “Base subscript 2.” A double sided arrow follows. To the right is H subscript 3 O superscript plus, which is labeled in green as below in as “Acid subscript 2.” This is followed by plus and O with pairs of dots above, below, and to the left with a singly bonded H on the right with a superscript negative. The label below in purple reads, “ Base subscript 1.”

This type of reaction, in which a substance ionizes when one molecule of the substance reacts with another molecule of the same substance, is referred to as **autoionization**. Pure water undergoes autoionization to a very slight extent. Only about two out of every 10^9 molecules in a sample of pure water are ionized at 25 °C. The equilibrium constant for the ionization of water is called the ion-product constant for water (K_w):

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)} \quad K_w = [H_3O^+][OH^-] \tag{12.1.15}$$

The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C, Kw 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 approximately 5.1×10^{-13}, roughly 50-times larger than the value at 25 °C.

Example 12.1.1: 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, $[H_3O^+] = [OH^-]$. At 25 °C:

$$K_w = [H_3O^+][OH^-] = [H_3O^+]^2 = [OH^-]^2 = 1.0 \times 10^{-14}$$

So:

$$[H_3O^+] = [OH^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}\ M$$

The hydronium ion concentration and the hydroxide ion concentration are the same, and we find that both equal $1.0 \times 10^{-7}\ M$.

Exercise 12.1.1

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

$[H_3O^+] = [OH^-] = 4.9 \times 10^{-7}\ M$

It is important to realize that the autoionization equilibrium for water is established in all aqueous solutions. Adding an acid or base to water will not change the position of the equilibrium. Example 14.12 demonstrates the quantitative aspects of this relation between hydronium and hydroxide ion concentrations.

Example 12.1.2: The Inverse Proportionality of $[H_3O^+]$ and $[OH^-]$

The Inverse Proportionality of $[H_3O^+]$ and $[OH^-]$ A solution of carbon dioxide 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

We know the value of the ion-product constant for water at 25 °C:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

Thus, we can calculate the missing equilibrium concentration.

Rearrangement of the K_w expression yields that $[OH^-]$ is directly proportional to the inverse of $[H_3O^+]$:

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9}$$

The hydroxide ion concentration in water is reduced to $5.0 \times 10^{-9}\ M$ as the hydrogen ion concentration increases to $2.0 \times 10^{-6}\ M$. This is expected from Le Chatelier's principle; the autoionization reaction shifts to the left to reduce the stress of the increased hydronium ion concentration and the $[OH^-]$ is reduced relative to that in pure water.

A check of these concentrations confirms that our arithmetic is correct:

$$\begin{aligned} K_w &= [H_3O^+][OH^-] \\ &= (2.0 \times 10^{-6})(5.0 \times 10^{-9}) \\ &= 1.0 \times 10^{-14} \end{aligned}$$

? Exercise 12.1.2

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 M at 25 °C?

Answer

$$[H_3O^+] = 1 \times 10^{-11} M$$

Amphiprotic Species

Like water, many molecules and ions may either gain or lose a proton under the appropriate conditions. Such species are said to be amphiprotic. Another term used to describe such species is amphoteric, which is a more general term for a species that may act either as an acid or a base by any definition (not just the Brønsted-Lowry one). Consider for example the bicarbonate ion, which may either donate or accept a proton as shown here:

$$HCO^-{}_{3(aq)} + H_2O_{(l)} \rightleftharpoons CO^{2-}{}_{3(aq)} + H_3O^+{}_{(aq)} \tag{12.1.16}$$

$$HCO^-{}_{3(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)} + OH^-{}_{(aq)} \tag{12.1.17}$$

✓ Example 12.1.3: The Acid-Base Behavior of an Amphoteric Substance

Write separate equations representing the reaction of HSO_3^-

a. as an acid with OH^-
b. as a base with HI

Solution

a. $HSO_3^-(aq) + OH^-(aq) \rightleftharpoons SO_3{}^{2-}(aq) + H_2O_{(l)}$
b. $HSO_3^-(aq) + HI(aq) \rightleftharpoons H_2SO_3(aq) + I^-(aq)$

? Exercise 12.1.3

Write separate equations representing the reaction of $H_2PO_4^-$

a. as a base with HBr
b. as an acid with OH^-

Answer a

$H_2PO_4^-(aq) + HBr(aq) \rightleftharpoons H_3PO_4(aq) + Br^-(aq)$

Answer b

$H_2PO_4^-(aq) + OH^-(aq) \rightleftharpoons HPO_4{}^{2-}(aq) + H_2O_{(l)}$

Summary

A compound that can donate a proton (a hydrogen ion) to another compound is called a Brønsted-Lowry acid. The compound that accepts the proton is called a Brønsted-Lowry base. The species remaining after a Brønsted-Lowry acid has lost a proton is the conjugate base of the acid. The species formed when a Brønsted-Lowry base gains a proton is the conjugate acid of the base. Thus, an acid-base reaction occurs when a proton is transferred from an acid to a base, with formation of the conjugate base of the reactant acid and formation of the conjugate acid of the reactant base. Amphiprotic species can act as both proton donors and

proton acceptors. Water is the most important amphiprotic species. It can form both the hydronium ion, H_3O^+, and the hydroxide ion, OH^- when it undergoes autoionization:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

The ion product of water, K_w is the equilibrium constant for the autoionization reaction:

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25°C$$

Key Equations

- $$K_w = [H_3O^+][OH^-\,] = 1.0 \times 10^{-14} \text{ (at 25 °C)}$$

Glossary

acid ionization
reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

amphiprotic
species that may either gain or lose a proton in a reaction

amphoteric
species that can act as either an acid or a base

autoionization
reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

base ionization
reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

Brønsted-Lowry acid
proton donor

Brønsted-Lowry base
proton acceptor

conjugate acid
substance formed when a base gains a proton

conjugate base
substance formed when an acid loses a proton

ion-product constant for water (K_w)
equilibrium constant for the autoionization of water

This page titled 12.1: Brønsted-Lowry Acids and Bases is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

- **14.1: Brønsted-Lowry Acids and Bases** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

12.2: pH and pOH

Learning Objectives

- 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

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, the values of which may span many orders of magnitude, is to use a logarithmic scale. One such scale that is very popular for chemical concentrations and equilibrium constants is based on the p-function, defined as shown where "X" is the quantity of interest and "log" is the base-10 logarithm:

$$\mathrm{pX} = -\log \mathrm{X} \tag{12.2.1}$$

The pH of a solution is therefore defined as shown here, where $[H_3O^+]$ is the molar concentration of hydronium ion in the solution:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] \tag{12.2.2}$$

Rearranging this equation to isolate the hydronium ion molarity yields the equivalent expression:

$$[\mathrm{H_3O^+}] = 10^{-\mathrm{pH}} \tag{12.2.3}$$

Likewise, the hydroxide ion molarity may be expressed as a p-function, or pOH:

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] \tag{12.2.4}$$

or

$$[\mathrm{OH^-}] = 10^{-\mathrm{pOH}} \tag{12.2.5}$$

Finally, the relation between these two ion concentration expressed as p-functions is easily derived from the K_w expression:

$$K_\mathrm{w} = [\mathrm{H_3O^+}][\mathrm{OH^-}] \tag{12.2.6}$$

$$-\log K_\mathrm{w} = -\log([\mathrm{H_3O^+}][\mathrm{OH^-}]) = -\log[\mathrm{H_3O^+}] + -\log[\mathrm{OH^-}] \tag{12.2.7}$$

$$\mathrm{p}K_\mathrm{w} = \mathrm{pH} + \mathrm{pOH} \tag{12.2.8}$$

At 25 °C, the value of K_w is 1.0×10^{-14}, and so:

$$14.00 = \mathrm{pH} + \mathrm{pOH} \tag{12.2.9}$$

The hydronium ion molarity in pure water (or any neutral solution) is $1.0 \times 10^{-7}\ M$ at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{12.2.10}$$

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{12.2.11}$$

And so, at this temperature, acidic solutions are those with hydronium ion molarities greater than $1.0 \times 10^{-7}\ M$ and hydroxide ion molarities less than $1.0 \times 10^{-7}\ M$ (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 $1.0 \times 10^{-7}\ M$ and hydroxide ion molarities greater than $1.0 \times 10^{-7}\ M$ (corresponding to pH values greater than 7.00 and pOH values less than 7.00).

When $pH = 7$ Solutions are not Neutral

Since the autoionization constant K_w is temperature dependent, these correlations between pH values and the acidic/neutral/basic adjectives will be different at temperatures other than 25 °C. For example, the hydronium molarity of pure water at 80 °C is 4.9×10^{-7} *M*, which corresponds to pH and pOH values of:

$$\begin{aligned} pH &= -\log[H_3O^+] \\ &= -\log(4.9 \times 10^{-7}) \\ &= 6.31 \end{aligned}$$

$$\begin{aligned} pOH &= -\log[OH^-] \\ &= -\log(4.9 \times 10^{-7}) \\ &= 6.31 \end{aligned}$$

At this temperature, then, neutral solutions exhibit pH = pOH = 6.31, acidic solutions exhibit pH less than 6.31 and pOH greater than 6.31, whereas basic solutions exhibit pH greater than 6.31 and pOH less than 6.31. This distinction can be important when studying certain processes that occur at nonstandard temperatures, such as enzyme reactions in warm-blooded organisms. Unless otherwise noted, references to pH values are presumed to be those at standard temperature (25 °C) (Table **12.2.1**).

Table **12.2.1**: Summary of Relations for Acidic, Basic and Neutral Solutions

Classification	Relative Ion Concentrations	pH at 25 °C
acidic	$[H_3O^+] > [OH^-]$	pH < 7
neutral	$[H_3O^+] = [OH^-]$	pH = 7
basic	$[H_3O^+] < [OH^-]$	pH > 7

Figure **12.2.1** shows the relationships between $[H_3O^+]$, $[OH^-]$, pH, and pOH, and gives values for these properties at standard temperatures for some common substances.

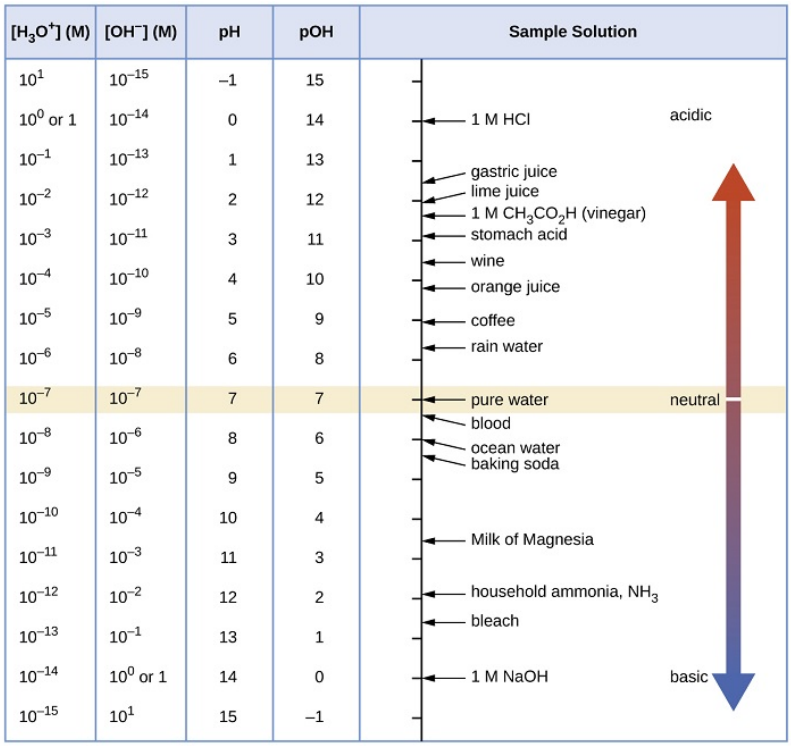


Figure 12.2.1: The pH and pOH scales represent concentrations of $[H_3O^+]$ and OH^-, respectively. The pH and pOH values of some common substances at standard temperature (25 °C) are shown in this chart.

A table is provided with 5 columns. The first column is labeled “left bracket H subscript 3 O superscript plus right bracket (M).” Powers of ten are listed in the column beginning at 10 superscript 1, including 10 superscript 0 or 1, 10 superscript negative 1, decreasing by single powers of 10 to 10 superscript negative 15. The second column is labeled “left bracket O H superscript negative right bracket (M).” Powers of ten are listed in the column beginning at 10 superscript negative 15, increasing by single powers of 10 to including 10 superscript 0 or 1, and 10 superscript 1. The third column is labeled “p H.” Values listed in this column are integers beginning at negative 1, increasing by ones up to 14. The fourth column is labeled “p O H.” Values in this column are integers beginning at 15, decreasing by ones up to negative 1. The fifth column is labeled “Sample Solution.” A vertical line at the left of the column has tick marks corresponding to each p H level in the table. Substances are listed next to this line segment with line segments connecting them to the line to show approximate p H and p O H values. 1 M H C l is listed at a p H of 0. Gastric juices are listed at a p H of about 1.5. Lime juice is listed at a p H of about 2, followed by 1 M C H subscript 3 C O subscript 2 H, followed by stomach acid at a p H value of nearly 3. Wine is listed around 3.5. Coffee is listed just past 5. Pure water is listed at a p H of 7. Pure blood is just beyond 7. Milk of Magnesia is listed just past a p H of 10.5. Household ammonia is listed just before a pH of 12. 1 M N a O H is listed at a p H of 0. To the right of this labeled arrow is an arrow that points up and down through the height of the column. A beige strip passes through the table and to this double headed arrow at p H 7. To the left of the double headed arrow in this beige strip is the label “neutral.” A narrow beige strip runs through the arrow. Just above and below this region, the arrow is purple. It gradually turns to a bright red as it extends upward. At the top of the arrow, near the head of the arrow is the label “acidic.” Similarly, the lower region changes color from purple to blue moving to the bottom of the column. The head at this end of the arrow is labeled “basic.”

Example 12.2.1: Calculation of pH from $[H_3O^+]$

What is the pH of stomach acid, a solution of HCl with a hydronium ion concentration of $1.2 \times 10^{-3}\ M$?

Solution

$$\begin{aligned} pH &= -\log[H_3O^+] \\ &= -\log(1.2 \times 10^{-3}) \\ &= -(-2.92) \\ &= 2.92 \end{aligned}$$

Exercise 12.2.1

Water exposed to air contains carbonic acid, H_2CO_3, due to the reaction between carbon dioxide and water:

$$\mathrm{CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq)}$$

Air-saturated water has a hydronium ion concentration caused by the dissolved $\mathrm{CO_2}$ of $2.0 \times 10^{-6}\ M$, about 20-times larger than that of pure water. Calculate the pH of the solution at 25 °C.

Answer

5.70

Example 12.2.2: Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of blood, the pH of which is 7.3 (slightly alkaline).

Solution

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = 7.3$$

$$\log[\mathrm{H_3O^+}] = -7.3$$

$$[\mathrm{H_3O^+}] = 10^{-7.3}$$

or

$$[\mathrm{H_3O^+}] = \text{antilog of} - 7.3$$

$$[\mathrm{H_3O^+}] = 5 \times 10^{-8}\ M$$

(On a calculator take the antilog, or the "inverse" log, of −7.3, or calculate $10^{-7.3}$.)

Exercise 12.2.2

Calculate the hydronium ion concentration of a solution with a pH of −1.07.

Answer

12 M

Environmental Science

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved CO_2 which forms carbonic acid:

$$\mathrm{H_2O\,(l) + CO_2\,(g) \longrightarrow H_2CO_3\,(aq)} \tag{12.2.12}$$

$$\mathrm{H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq)} \tag{12.2.13}$$

Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including CO_2, SO_2, SO_3, NO, and NO_2 being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:

$$\mathrm{H_2O\,(l) + SO_3\,(g) \longrightarrow H_2SO_4\,(aq)} \tag{12.2.14}$$

$$\mathrm{H_2SO_4\,(aq) \longrightarrow H^+\,(aq) + HSO_4^-\,(aq)} \tag{12.2.15}$$

Carbon dioxide is naturally present in the atmosphere because we and most other organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or when we burn wood or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also stems from burning fossil fuels, which have traces of sulfur, and from the process of "roasting" ores of metal sulfides in metal-refining processes. Oxides of nitrogen are

formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (Figure 12.2.2). 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.



Figure 12.2.2: (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)

Two photos are shown. Photograph a on the left shows the upper portion of trees against a bright blue sky. The tops of several trees at the center of the photograph have bare branches and appear to be dead. Image b shows a statue of a man that appears to from the revolutionary war era in either marble or limestone.

Example 12.2.3: Calculation of pOH

What are the pOH and the pH of a 0.0125-M solution of potassium hydroxide, KOH?

Solution

Potassium hydroxide is a highly soluble ionic compound and completely dissociates when dissolved in dilute solution, yielding $[OH^-] = 0.0125$ M:

$$\mathrm{pOH} = -\log[\mathrm{OH}^-] = -\log 0.0125$$

$$= -(-1.903) = 1.903$$

The pH can be found from the pOH:

$$\mathrm{pH} + \mathrm{pOH} = 14.00$$

$$\mathrm{pH} = 14.00 - \mathrm{pOH} = 14.00 - 1.903 = 12.10$$

Exercise 12.2.3

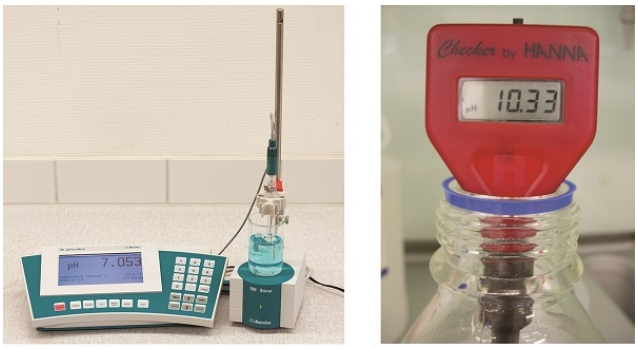
The hydronium ion concentration of vinegar is approximately $4 \times 10^{-3}\ M$. What are the corresponding values of pOH and pH?

Answer

pOH = 11.6,

pH = 14.00 - pOH = 2.4

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 12.2.3).



(a) (b)

Figure **12.2.3**: (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)

This figure contains two images. The first, image a, is of an analytical digital p H meter on a laboratory counter. The second, image b, is of a portable hand held digital p H meter.

The pH of a solution may also be visually estimated using colored indicators (Figure **12.2.3**).



(a) (b)

Figure **12.2.4**: (a) A universal indicator assumes a different color in solutions of different pH values. Thus, it can be added to a solution to determine the pH of the solution. The eight vials each contain a universal indicator and 0.1-M solutions of progressively weaker acids: HCl (pH = l), CH_3CO_2H (pH = 3), and NH_4Cl (pH = 5), deionized water, a neutral substance (pH = 7); and 0.1-M solutions of the progressively stronger bases: KCl (pH = 7), aniline, $C_6H_5NH_2$ (pH = 9), NH_3 (pH = 11), and NaOH (pH = 13). (b) pH paper contains a mixture of indicators that give different colors in solutions of differing pH values. (credit: modification of work by Sahar Atwa).

This figure contains two images. The first shows a variety of colors of solutions in labeled beakers. A red solution in a beaker is labeled “0.10 M H C l.” An orange solution is labeled “0.10 M C H subscript 3 C O O H.” A yellow-orange solution is labeled “0.1 M N H subscript 4 C l.” A yellow solution is labeled “deionized water.” A second solution beaker is labeled “0.10 M K C l.” A green solution is labeled “0.10 M aniline.” A blue solution is labeled “0.10 M N H subscript 4 C l (a q).” A final beaker containing a dark blue solution is labeled “0.10 M N a O H.” Image b shows pHydrion paper that is used for measuring pH in the range of p H from 1 to 12. The color scale for identifying p H based on color is shown along with several of the test strips used to evaluate p H.

Summary

The concentration of hydronium ion in a solution of an acid in water is greater than $1.0 \times 10^{-7}\ M$ at 25 °C. The concentration of hydroxide ion in a solution of a base in water is greater than $1.0 \times 10^{-7}\ M$ at 25 °C. The concentration of H_3O^+ in a solution can be expressed as the pH of the solution; $\mathbf{pH = -\log H_3O^+}$. The concentration of OH^- can be expressed as the pOH of the solution: $\mathbf{pOH = -\log[OH^-]}$. In pure water, pH = 7.00 and pOH = 7.00

Key Equations

- $\mathbf{pH = -\log[H_3O^+]}$
- $\mathbf{pOH = -\log[OH^-]}$
- $[H_3O^+] = 10^{-\text{pH}}$
- $[OH^-] = 10^{-\text{pOH}}$
- pH + pOH = pK_w = 14.00 at 25 °C

Glossary

acidic

describes a solution in which $[H_3O^+] > [OH^-]$

basic

describes a solution in which $[H_3O^+] < [OH^-]$

neutral

describes a solution in which $[H_3O^+] = [OH^-]$

pH

logarithmic measure of the concentration of hydronium ions in a solution

pOH

logarithmic measure of the concentration of hydroxide ions in a solution

---

This page titled 12.2: pH and pOH is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

- **14.2: pH and pOH** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

12.3: Relative Strengths of Acids and Bases

Learning Objectives

- 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

We can rank the strengths of acids by the extent to which they ionize in aqueous solution. The reaction of an acid with water is given by the general expression:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq)$$

Water is the base that reacts with the acid HA, $\mathrm{A^-}$ is the conjugate base of the acid HA, and the hydronium ion is the conjugate acid of water. A strong acid yields 100% (or very nearly so) of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$ when the acid ionizes in water; Figure 12.3.1 lists several strong acids. A weak acid gives small amounts of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$.

Figure 12.3.1: Some of the common strong acids and bases are listed here.

Six Strong Acids		Six Strong Bases	
$\mathrm{HClO_4}$	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$\mathrm{Ca(OH)_2}$	calcium hydroxide
$\mathrm{HNO_3}$	nitric acid	$\mathrm{Sr(OH)_2}$	strontium hydroxide
$\mathrm{H_2SO_4}$	sulfuric acid	$\mathrm{Ba(OH)_2}$	barium hydroxide

The relative strengths of acids may be determined 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:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq)$$

we write the equation for the ionization constant as:

$$K_a = \frac{[H3O+][A-]}{[HA]}$$

where the concentrations are those at equilibrium. As noted in the section on equilibrium constants, although water is a reactant in the reaction, it is the solvent as well, so its activity has a value of 1, which does not change the value of K_a.

Note

It is a common error to claim that the molar concentration of the solvent is in some way involved in the equilibrium law. This error is a result of a misunderstanding of solution thermodynamics. For example, it is often claimed that $K_a = K_{eq}[H_2O]$ for aqueous solutions. This equation is incorrect because it is an erroneous interpretation of the correct equation $K_a = K_{eq}(a_{H_2O})$. Because $a_{H_2O} = 1$ for a dilute solution, $K_a = K_{eq}(1)$, or $K_a = K_{eq}$.

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. Thus a stronger acid has a larger ionization constant than does a weaker acid. The ionization constants increase as the strengths of the acids increase.

The following data on acid-ionization constants indicate the order of acid strength: $CH_3CO_2H < HNO_2 < HSO_4^-$

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq) \qquad K_a = 1.8 \times 10^{-5}$$
$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq) \qquad K_a = 4.6 \times 10^{-4}$$
$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq) \qquad K_a = 1.2 \times 10^{-2}$$

Another measure of the strength of an acid is its *percent ionization*. The percent ionization of a weak acid is the ratio of the concentration of the ionized acid to the initial acid concentration, times 100:

$$\%\ \text{ionization} = \frac{[H3O+]_{eq}}{[HA]_0} \times 100\% \tag{12.3.1}$$

Because the ratio includes the initial concentration, the percent ionization for a solution of a given weak acid varies depending on the original concentration of the acid, and actually decreases with increasing acid concentration.

Example 12.3.1: Calculation of Percent Ionization from pH

Calculate the percent ionization of a 0.125-*M* solution of nitrous acid (a weak acid), with a pH of 2.09.

Solution

The percent ionization for an acid is:

$$\frac{[H3O+]_{eq}}{[HNO2]_0} \times 100$$

The chemical equation for the dissociation of the nitrous acid is:

$$HNO_2(aq) + H_2O(l) \rightleftharpoons NO_2^-(aq) + H_3O^+(aq).$$

Since $10^{-pH} = [H_3O^+]$, we find that $10^{-2.09} = 8.1 \times 10^{-3}\ M$, so that percent ionization (Equation 12.3.1) is:

$$\frac{8.1 \times 10^{-3}}{0.125} \times 100 = 6.5\%$$

Remember, the logarithm 2.09 indicates a hydronium ion concentration with only two significant figures.

Exercise 12.3.1

Calculate the percent ionization of a 0.10 *M* solution of acetic acid with a pH of 2.89.

Answer

1.3% ionized

We can rank the strengths of bases by their tendency to form hydroxide ions in aqueous solution. The reaction of a Brønsted-Lowry base with water is given by:

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$$

Water is the acid that reacts with the base, HB^+ is the conjugate acid of the base B, and the hydroxide ion is the conjugate base of water. A strong base yields 100% (or very nearly so) of OH^- and HB^+ when it reacts with water; Figure 12.3.1 lists several strong bases. A weak base yields a small proportion of hydroxide ions. Soluble ionic hydroxides such as NaOH are considered strong bases because they dissociate completely when dissolved in water.

As we did with acids, we can measure the relative strengths of bases by measuring their base-ionization constant (K_b) in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, **B**:

$$\mathrm{B}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HB^+}(aq) + \mathrm{OH^-}(aq),$$

we write the equation for the ionization constant as:

$$K_b = \frac{[HB+][OH-]}{[B]}$$

where the concentrations are those at equilibrium. Again, we do not see water in the equation because water is the solvent and has an activity of 1. The chemical reactions and ionization constants of the three bases shown are:

$$\mathrm{NO_2^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HNO_2}(aq) + \mathrm{OH^-}(aq) \qquad K_b = 2.17 \times 10^{-11}$$
$$\mathrm{CH_3CO_2^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{CH_3CO_2H}(aq) + \mathrm{OH^-}(aq) \qquad K_b = 5.6 \times 10^{-10}$$
$$\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq) \qquad K_b = 1.8 \times 10^{-5}$$

A table of ionization constants of weak bases appears in Table E2. As with acids, percent ionization can be measured for basic solutions, but will vary depending on the base ionization constant and the initial concentration of the solution.

Consider the ionization reactions for a conjugate acid-base pair, $\mathrm{HA - A^-}$:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq)$$

with $K_a = \frac{[H3O+][A-]}{[HA]}$.

$$\mathrm{A^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{OH^-}(aq) + \mathrm{HA}(aq)$$

with $K_b = \frac{[HA][OH]}{[A-]}$.

Adding these two chemical equations yields the equation for the autoionization for water:

$$\cancel{\mathrm{HA}(aq)} + \mathrm{H_2O}(l) + \cancel{\mathrm{A^-}(aq)} + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \cancel{\mathrm{A^-}(aq)} + \mathrm{OH^-}(aq) + \cancel{\mathrm{HA}(aq)}$$
$$2\,\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{OH^-}(aq)$$

As shown in the previous chapter on equilibrium, the K expression for a chemical equation derived from adding two or more other equations is the mathematical product of the other equations' K expressions. Multiplying the mass-action expressions together and cancelling common terms, we see that:

$$K_a \times K_b = \frac{[H3O+][A-]}{[HA]} \times \frac{[HA][OH-]}{[A-]} = [\mathrm{H_3O^+}][\mathrm{OH^-}] = K_w$$

For example, the acid ionization constant of acetic acid (CH_3COOH) is 1.8×10^{-5}, and the base ionization constant of its conjugate base, acetate ion ($\mathrm{CH_3COO^-}$), is 5.6×10^{-10}. The product of these two constants is indeed equal to K_w:

$$K_a \times K_b = (1.8 \times 10^{-5}) \times (5.6 \times 10^{-10}) = 1.0 \times 10^{-14} = K_w$$

The extent to which an acid, **HA**, donates protons to water molecules depends on the strength of the conjugate base, $\mathrm{A^-}$, of the acid. If $\mathrm{A^-}$ is a strong base, any protons that are donated to water molecules are recaptured by $\mathrm{A^-}$. Thus there is relatively little $\mathrm{A^-}$ and $\mathrm{H_3O^+}$ in solution, and the acid, **HA**, is weak. If $\mathrm{A^-}$ is a weak base, water binds the protons more strongly, and the solution contains primarily $\mathrm{A^-}$ and $\mathrm{H_3O^+}$—the acid is strong. Strong acids form very weak conjugate bases, and weak acids form stronger conjugate bases (Figure **12.3.2**).

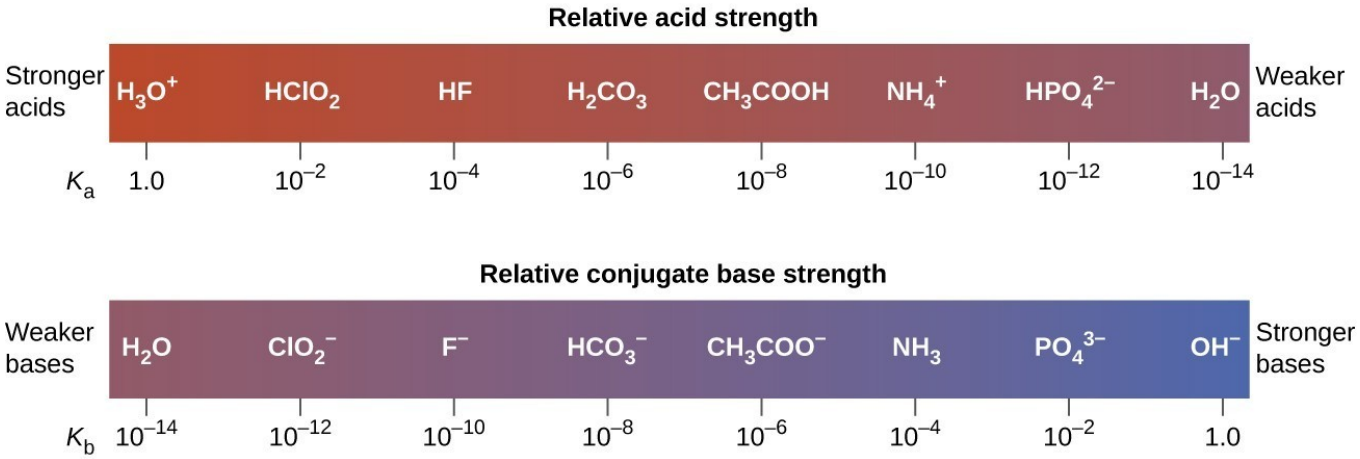


Figure **12.3.2**: This diagram shows the relative strengths of conjugate acid-base pairs, as indicated by their ionization constants in aqueous solution.

Figure **12.3.3** lists a series of acids and bases in order of the decreasing strengths of the acids and the corresponding increasing strengths of the bases. The acid and base in a given row are conjugate to each other.

The first six acids in Figure **12.3.3** are the most common strong acids. These acids are completely dissociated in aqueous solution. The conjugate bases of these acids are weaker bases than water. When one of these acids dissolves in water, their protons are completely transferred to water, the stronger base.

Those acids that lie between the hydronium ion and water in Figure **12.3.3** form conjugate bases that can compete with water for possession of a proton. Both hydronium ions and nonionized acid molecules are present in equilibrium in a solution of one of these acids. Compounds that are weaker acids than water (those found below water in the column of acids) in Figure **12.3.3** exhibit no observable acidic behavior when dissolved in water. Their conjugate bases are stronger than the hydroxide ion, and if any conjugate base were formed, it would react with water to re-form the acid.

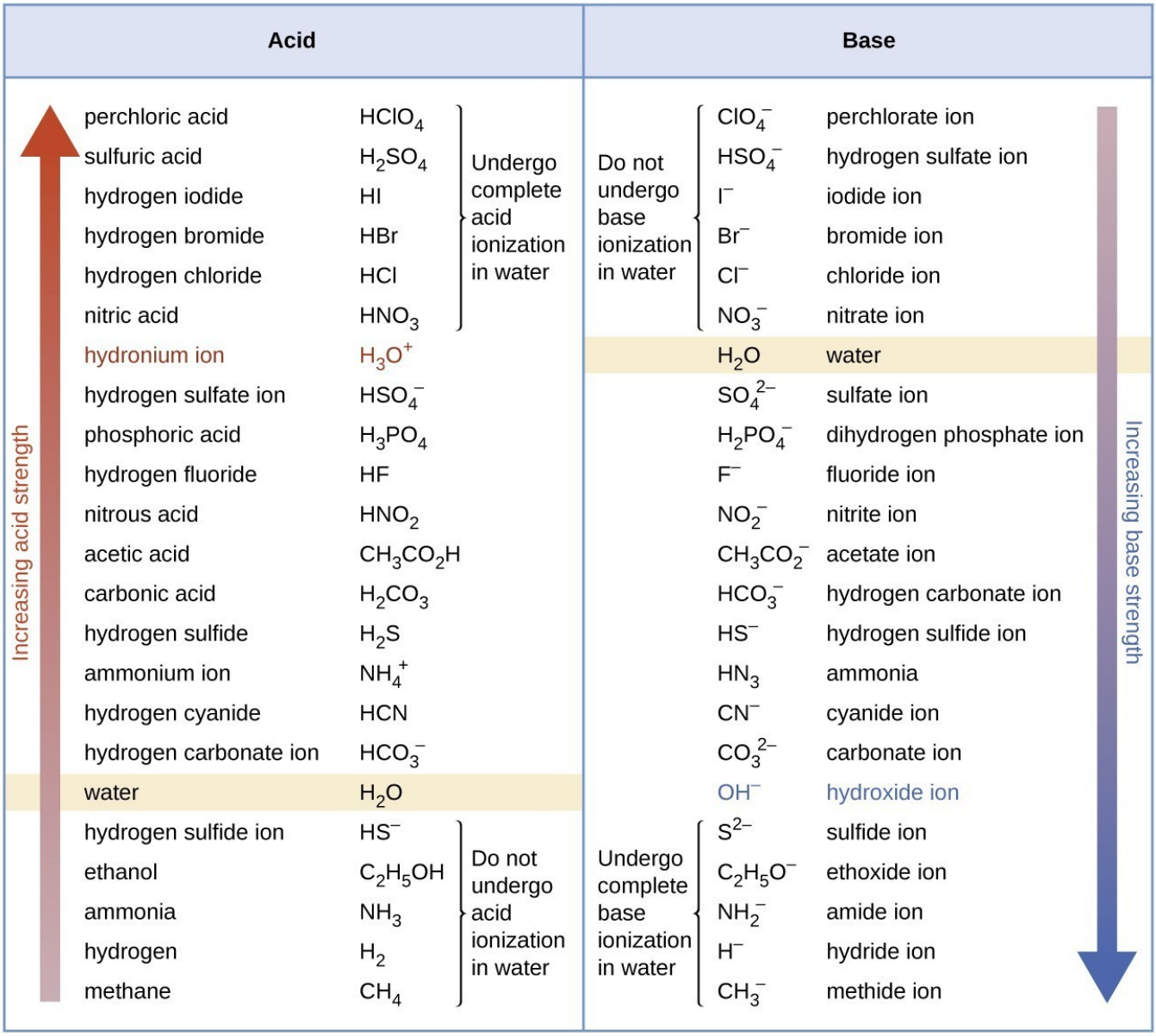


Figure **12.3.3**: The chart shows the relative strengths of conjugate acid-base pairs.

The extent to which a base forms hydroxide ion in aqueous solution depends on the strength of the base relative to that of the hydroxide ion, as shown in the last column in Figure **12.3.3**. A strong base, such as one of those lying below hydroxide ion, accepts protons from water to yield 100% of the conjugate acid and hydroxide ion. Those bases lying between water and hydroxide ion accept protons from water, but a mixture of the hydroxide ion and the base results. Bases that are weaker than water (those that lie above water in the column of bases) show no observable basic behavior in aqueous solution.

✔ Example **12.3.2**: The Product $K_a \times K_b = K_w$

Use the K_b for the nitrite ion, NO_2^-, to calculate the K_a for its conjugate acid.

Solution

K_b for NO_2^- is given in this section as 2.17×10^{-11}. The conjugate acid of NO_2^- is HNO_2; K_a for HNO_2 can be calculated using the relationship:

$$K_a \times K_b = 1.0 \times 10^{-14} = K_w$$

Solving for K_a, we get:

$$K_a = \frac{K_w}{K_b}$$
$$= \frac{1.0 \times 10^{-14}}{2.17 \times 10^{-11}}$$
$$= 4.6 \times 10^{-4}$$

This answer can be verified by finding the K_a for HNO_2 in Table E1

? Exercise 12.3.2

We can determine the relative acid strengths of NH_4^+ and HCN by comparing their ionization constants. The ionization constant of HCN is given in Table E1 as 4.9×10^{-10}. The ionization constant of NH_4^+ is not listed, but the ionization constant of its conjugate base, NH_3, is listed as 1.8×10^{-5}. Determine the ionization constant of NH_4^+, and decide which is the stronger acid, HCN or NH_4^+.

Answer

NH_4^+ is the slightly stronger acid (K_a for $NH_4^+ = 5.6 \times 10^{-10}$).

The Ionization of Weak Acids and Weak Bases

Many acids and bases are weak; that is, they do not ionize fully in aqueous solution. A solution of a weak acid in water is a mixture of the nonionized acid, hydronium ion, and the conjugate base of the acid, with the nonionized acid present in the greatest concentration. Thus, a weak acid increases the hydronium ion concentration in an aqueous solution (but not as much as the same amount of a strong acid).

Acetic acid (CH_3CO_2H) is a weak acid. When we add acetic acid to water, it ionizes to a small extent according to the equation:

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

giving an equilibrium mixture with most of the acid present in the nonionized (molecular) form. This equilibrium, like other equilibria, is dynamic; acetic acid molecules donate hydrogen ions to water molecules and form hydronium ions and acetate ions at the same rate that hydronium ions donate hydrogen ions to acetate ions to reform acetic acid molecules and water molecules. We can tell by measuring the pH of an aqueous solution of known concentration that only a fraction of the weak acid is ionized at any moment (Figure 12.3.4). The remaining weak acid is present in the nonionized form.

For acetic acid, at equilibrium:

$$K_a = \frac{[H3O+][CH3CO2-]}{[CH3CO2H]} = 1.8 \times 10^{-5}$$



Figure **12.3.4**: pH paper indicates that a 0.l-M solution of **HCl** (beaker on left) has a pH of 1. The acid is fully ionized and $[H_3O^+]$ = 0.1 M. A 0.1-M solution of CH_3CO_2H (beaker on right) has a pH of 3 ($[H_3O^+]$ = 0.001 M) because the weak acid CH_3CO_2H is only partially ionized. In this solution, $[H_3O^+] < [CH_3CO_2H]$. (credit: modification of work by Sahar Atwa)

This image shows two bottles containing clear colorless solutions. Each bottle contains a single p H indicator strip. The strip in the bottle on the left is red, and a similar red strip is placed on a filter paper circle in front of the bottle on surface on which the bottles are resting. Similarly, the second bottle on the right contains and orange strip and an orange strip is placed in front of it on a filter paper circle. Between the two bottles is a pack of p Hydrion papers with a p H color scale on its cover.

Table **12.3.1**: Ionization Constants of Some Weak Acids

Ionization Reaction	K_a at 25 °C
$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$	1.2×10^{-2}
$HF + H_2O \rightleftharpoons H_3O^+ + F^-$	3.5×10^{-4}
$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$	4.6×10^{-4}
$HNCO + H_2O \rightleftharpoons H_3O^+ + NCO^-$	2×10^{-4}
$HCO_2H + H_2O \rightleftharpoons H_3O^+ + HCO_2^-$	1.8×10^{-4}
$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$	1.8×10^{-5}
$HClO + H_2O \rightleftharpoons H_3O^+ + ClO^-$	2.9×10^{-8}
$HBrO + H_2O \rightleftharpoons H_3O^+ + BrO^-$	2.8×10^{-9}
$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$	4.9×10^{-10}

Table **12.3.1** gives the ionization constants for several weak acids; additional ionization constants can be found in Table E1.

At equilibrium, a solution of a weak base in water is a mixture of the nonionized base, the conjugate acid of the weak base, and hydroxide ion with the nonionized base present in the greatest concentration. Thus, a weak base increases the hydroxide ion concentration in an aqueous solution (but not as much as the same amount of a strong base).

For example, a solution of the weak base trimethylamine, $(CH_3)_3N$, in water reacts according to the equation:

$$(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons (CH_3)_3NH^+(aq) + OH^-(aq)$$

This gives an equilibrium mixture with most of the base present as the nonionized amine. This equilibrium is analogous to that described for weak acids.

We can confirm by measuring the pH of an aqueous solution of a weak base of known concentration that only a fraction of the base reacts with water (Figure 14.4.5). The remaining weak base is present as the unreacted form. The equilibrium constant for the ionization of a weak base, K_b, is called the **ionization constant** of the weak base, and is equal to the reaction quotient when the reaction is at equilibrium. For trimethylamine, at equilibrium:

$$K_b = \frac{[(CH3)3NH+][OH-]}{[(CH3)3N]}$$



Figure 12.3.5: pH paper indicates that a 0.1-M solution of NH_3 (left) is weakly basic. The solution has a pOH of 3 ($[OH^-]$ = 0.001 M) because the weak base NH_3 only partially reacts with water. A 0.1-M solution of NaOH (right) has a pOH of 1 because NaOH is a strong base (credit: modification of work by Sahar Atwa).

The ionization constants of several weak bases are given in Table 12.3.2 and Table E2.

Table 12.3.2: Ionization Constants of Some Weak Bases

Ionization Reaction	K_b at 25 °C
$(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2^+ + OH^-$	5.9×10^{-4}
$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$	4.4×10^{-4}
$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$	6.3×10^{-5}
$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}
$C_6H_5NH_2 + H_2O \rightleftharpoons C_6N_5NH_3^+ + OH^-$	4.3×10^{-10}

Example 12.3.3: Determination of K_a from Equilibrium Concentrations

Acetic acid is the principal ingredient in vinegar; that's why it tastes sour. At equilibrium, a solution contains $[CH_3CO_2H]$ = 0.0787 *M* and $[H_3O^+] = [CH_3CO_2^-] = 0.00118\ M$. What is the value of K_a for acetic acid?



Vinegar is a solution of acetic acid, a weak acid. (credit: modification of work by “HomeSpot HQ”/Flickr)

Solution

We are asked to calculate an equilibrium constant from equilibrium concentrations. At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

$$K_a = \frac{[H3O+][CH3CO2-]}{[CH3CO2H]}$$

$$= \frac{(0.00118)(0.00118)}{0.0787}$$

$$= 1.77 \times 10^{-5}$$

Exercise 12.3.3

What is the equilibrium constant for the ionization of the HSO_4^- ion, the weak acid used in some household cleansers:

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$$

In one mixture of $NaHSO_4$ and Na_2SO_4 at equilibrium, $[H_3O^+]$ = 0.027 *M*; $[HSO_4^-] = 0.29\ M$; and $[SO_4^{2-}] = 0.13\ M$.

Answer

K_a for $HSO_4^- = 1.2 \times \times 10^{-2}$

Example 12.3.4: Determination of K_b from Equilibrium Concentrations

Caffeine, $C_8H_{10}N_4O_2$ is a weak base. What is the value of K_b for caffeine if a solution at equilibrium has $[C_8H_{10}N_4O_2]$ = 0.050 *M*, $[C_8H_{10}N_4O_2H^+]$ = 5.0 × 10^{-3} *M*, and $[OH^-]$ = 2.5 × 10^{-3} *M*?

Solution

At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:

$$C_8H_{10}N_4O_2(aq) + H_2O(l) \rightleftharpoons C_8H_{10}N_4O_2H^+(aq) + OH^-(aq)$$

so

$$K_b = \frac{[C8H10N4O2H+][OH-]}{[C8H10N4O2]} = \frac{(5.0 \times 10^{-3})(2.5 \times 10^{-3})}{0.050} = 2.5 \times 10^{-4}$$

Exercise 12.3.4

What is the equilibrium constant for the ionization of the HPO_4^{2-} ion, a weak base:

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + OH^-(aq)$$

In a solution containing a mixture of NaH_2PO_4 and Na_2HPO_4 at equilibrium with:

- $[OH^-] = 1.3 \times 10^{-6} M$
- $[H_2PO_4^-]$=0.042 M and
- $[HPO_4^{2-}]$=0.341 M.

Answer

K_b for $HPO_4^{2-} = 1.6 \times 10^{-7}$

Example 12.3.5: Determination of K_a or K_b from pH

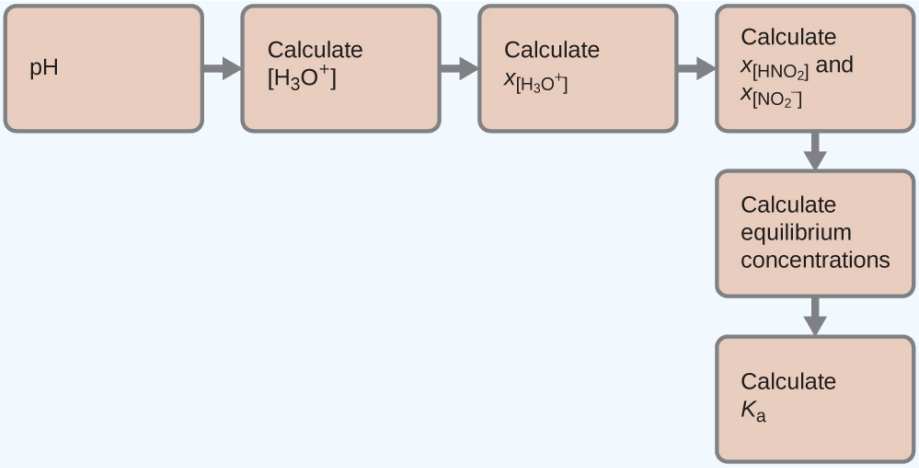
The pH of a 0.0516-*M* solution of nitrous acid, HNO_2, is 2.34. What is its K_a?

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$$

Solution

We determine an equilibrium constant starting with the initial concentrations of HNO_2, H_3O^+, and NO_2^- as well as one of the final concentrations, the concentration of hydronium ion at equilibrium. (Remember that pH is simply another way to express the concentration of hydronium ion.)

We can solve this problem with the following steps in which *x* is a change in concentration of a species in the reaction:



We can summarize the various concentrations and changes as shown here. Because water is the solvent, it has a fixed activity equal to 1. Any small amount of water produced or used up during the reaction will not change water's role as the solvent, so the value of its activity remains equal to 1 throughout the reaction.

	HNO_2 + H_2O ⇌ H_3O^+ + NO_2^-			
Initial concentration (*M*)	0.0516		~0	0
Change (*M*)	$-x$	+	x	x
Equilibrium concentration (*M*)	$[HNO_2]_i + (-x) = 0.0516 + (-x)$		$[H_3O]^+ + x[NO_2]^- + x \sim 0 + x$	0.0046

To get the various values in the ICE (Initial, Change, Equilibrium) table, we first calculate $[H_3O^+]$, the equilibrium concentration of H_3O^+, from the pH:

$$[H_3O^+] = 10^{-2.34} = 0.0046\ M$$

The change in concentration of H_3O^+, $x_{[H_3O^+]}$, is the difference between the equilibrium concentration of H_3O^+, which we determined from the pH, and the initial concentration, $[H_3O^+]_i$. The initial concentration of H_3O^+ is its concentration in pure water, which is so much less than the final concentration that we approximate it as zero (~0).

The change in concentration of NO_2^- is equal to the change in concentration of $[H_3O^+]$. For each 1 mol of H_3O^+ that forms, 1 mol of NO_2^- forms. The equilibrium concentration of HNO_2 is equal to its initial concentration plus the change in its concentration.

Now we can fill in the ICE table with the concentrations at equilibrium, as shown here:

	HNO_2 + H_2O ⇌ H_3O^+ + NO_2^-			
Initial concentration (*M*)	0.0516		~0	0
Change (*M*)	$-x$	+	$x = 0.0046$	$x = 0.0046$
Equilibrium concentration (*M*)	0.0470		0.0046	0.0046

Finally, we calculate the value of the equilibrium constant using the data in the table:

$$K_a = \frac{[H3O+][NO2-]}{[HNO2]} = \frac{(0.0046)(0.0046)}{(0.0470)} = 4.5 \times 10^{-4}$$

Exercise 12.3.5

The pH of a solution of household ammonia, a 0.950-*M* solution of NH_3, is 11.612. What is K_b for NH_3.

Answer

$K_b = 1.8 \times 10^{-5}$

Example 12.3.6: Equilibrium Concentrations in a Solution of a Weak Acid

Formic acid, HCO_2H, is the irritant that causes the body's reaction to ant stings.



The pain of an ant's sting is caused by formic acid. (credit: John Tann)

What is the concentration of hydronium ion and the pH in a 0.534-*M* solution of formic acid?

$$\mathrm{HCO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_2^-}(aq) \quad K_a = 1.8 \times 10^{-4}$$

Solution

1. Determine x and equilibrium concentrations. The equilibrium expression is:

$$\mathrm{HCO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_2^-}(aq)$$

Because water is the solvent, it has a fixed activity equal to 1. Any small amount of water produced or used up during the reaction will not change water's role as the solvent, so the value of its activity remains equal to 1 throughout the reaction so we do not need to consider it when setting up the ICE table.

The table shows initial concentrations (concentrations before the acid ionizes), changes in concentration, and equilibrium concentrations follows (the data given in the problem appear in color):

	HCO_2H +	H_2O ⇌	H_3O^+
Initial concentration (*M*)	0.534	~0	0
Change (*M*)	−*x*	*x*	*x*
Equilibrium concentration (*M*)	0.534 + (−*x*)	0 + *x* = *x*	0 + *x* = *x*

2. Solve for x and the equilibrium concentrations. At equilibrium:

$$K_a = 1.8 \times 10^{-4} = \frac{[H3O+][HCO2-]}{[HCO2H]}$$

$$= \frac{(x)(x)}{0.534 - x} = 1.8 \times 10^{-4}$$

Now solve for x. Because the initial concentration of acid is reasonably large and K_a is very small, we assume that $x << 0.534$, which *permits* us to simplify the denominator term as $(0.534 - x) = 0.534$. This gives:

$$K_a = 1.8 \times 10^{-4} = \frac{x^2}{0.534}$$

Solve for x as follows:

$$x^2 = 0.534 \times (1.8 \times 10^{-4})$$
$$= 9.6 \times 10^{-5}$$
$$x = \sqrt{9.6 \times 10^{-5}}$$
$$= 9.8 \times 10^{-3}$$

To check the assumption that x is small compared to 0.534, we calculate:

$$\frac{x}{0.534} = \frac{9.8 \times 10^{-3}}{0.534}$$
$$= 1.8 \times 10^{-2}\,(1.8$$

x is less than 5% of the initial concentration; the assumption is valid.

We find the equilibrium concentration of hydronium ion in this formic acid solution from its initial concentration and the change in that concentration as indicated in the last line of the table:

$$[H_3O^+] = \ 0 + x = 0 + 9.8 \times 10^{-3}\ M.$$
$$= 9.8 \times 10^{-3}\ M$$

The pH of the solution can be found by taking the negative log of the $[H_3O^+]$, so:

$$pH = -\log(9.8 \times 10^{-3}) = 2.01$$

? Exercise 12.3.6: acetic acid

Only a small fraction of a weak acid ionizes in aqueous solution. What is the percent ionization of acetic acid in a 0.100-*M* solution of acetic acid, CH_3CO_2H?

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2{}^-(aq) \quad K_a = 1.8 \times 10^{-5}$$

Hint

Determine $[CH_3CO_2{}^-]$ at equilibrium.) Recall that the percent ionization is the fraction of acetic acid that is ionized × 100, or $\frac{[CH3CO2-]}{[CH3CO2H]_{initial}} \times 100$.

Answer

percent ionization = 1.3%

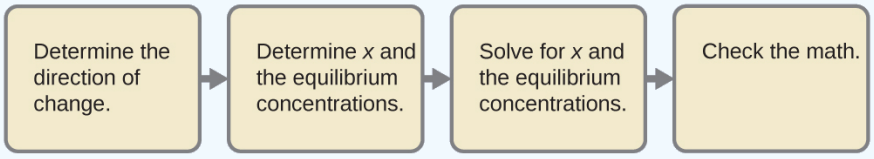
The following example shows that the concentration of products produced by the ionization of a weak base can be determined by the same series of steps used with a weak acid.

✓ Example 12.3.7: Equilibrium Concentrations in a Solution of a Weak Base

Find the concentration of hydroxide ion in a 0.25-*M* solution of trimethylamine, a weak base:

$$(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons (CH_3)_3NH^+(aq) + OH^-(aq) \quad K_b = 6.3 \times 10^{-5}$$

Solution This problem requires that we calculate an equilibrium concentration by determining concentration changes as the ionization of a base goes to equilibrium. The solution is approached in the same way as that for the ionization of formic acid in Example 12.3.6. The reactants and products will be different and the numbers will be different, but the logic will be the same:



1. Determine x and equilibrium concentrations. The table shows the changes and concentrations:

	$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$			
Initial concentration (*M*)	0.25		0	~0
Change (*M*)	$-x$		x	x
Equilibrium concentration (*M*)	$0.25 + (-x)$		$0 + x$	$\sim 0 + x$

2. Solve for x and the equilibrium concentrations. At equilibrium:

$$K_b = \frac{[(CH3)3NH+][OH-]}{[(CH3)3N]} = \frac{(x)(x)}{0.25 - x =} 6.3 \times 10^{-5}$$

If we assume that x is small relative to 0.25, then we can replace $(0.25 - x)$ in the preceding equation with 0.25. Solving the simplified equation gives:

$$x = 4.0 \times 10^{-3}$$

This change is less than 5% of the initial concentration (0.25), so the assumption is justified.

Recall that, for this computation, x is equal to the equilibrium concentration of *hydroxide ion* in the solution (see earlier tabulation):

$$([OH^-] = 0 + x = x = 4.0 \times 10^{-3}\ M$$
$$= 4.0 \times 10^{-3}\ M$$

Then calculate pOH as follows:

$$\text{pOH} = -\log(4.3 \times 10^{-3}) = 2.40$$

Using the relation introduced in the previous section of this chapter:

$$\text{pH} + \text{pOH} = \text{p}K_w = 14.00$$

permits the computation of pH:

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.37 = 11.60$$

Check the work. A check of our arithmetic shows that $K_b = 6.3 \times 10^{-5}$.

? Exercise 12.3.7

a. Show that the calculation in Step 2 of this example gives an x of 4.3×10^{-3} and the calculation in Step 3 shows $K_b = 6.3 \times 10^{-5}$.

b. Find the concentration of hydroxide ion in a 0.0325-*M* solution of ammonia, a weak base with a K_b of 1.76×10^{-5}.

Calculate the percent ionization of ammonia, the fraction ionized × 100, or $\frac{[NH4+]}{[NH3]} \times 100\%$

Answer a

$7.56 \times 10^{-4}\ M$, 2.33%

Answer b

2.33%

Some weak acids and weak bases ionize to such an extent that the simplifying assumption that x is small relative to the initial concentration of the acid or base is inappropriate. As we solve for the equilibrium concentrations in such cases, we will see that we cannot neglect the change in the initial concentration of the acid or base, and we must solve the equilibrium equations by using the quadratic equation.

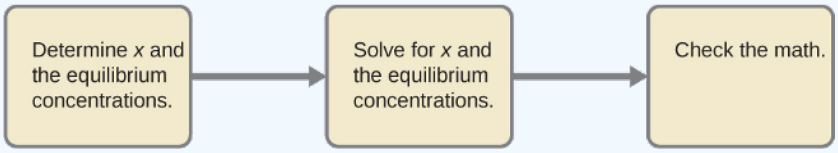
Example 12.3.8: Equilibrium Concentrations in a Solution of a Weak Acid

Sodium bisulfate, $NaHSO_4$, is used in some household cleansers because it contains the HSO_4^- ion, a weak acid. What is the pH of a 0.50-*M* solution of HSO_4^-?

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq) \quad K_a = 1.2 \times 10^{-2}$$

Solution

We need to determine the equilibrium concentration of the hydronium ion that results from the ionization of HSO_4^- so that we can use $[H_3O^+]$ to determine the pH. As in the previous examples, we can approach the solution by the following steps:



1. Determine x and equilibrium concentrations. This table shows the changes and concentrations:

	HSO_4^- + H_2O $\rightleftharpoons$	H_3O^+	SO_4^{2-}
Initial concentration (*M*)	0.50	~0	0
Change (*M*)	$-x$	x	x
Equilibrium concentration (*M*)	$0.50 + (-x) = 0.50 - x$	$0 + x = x$	$0 + x = x$

2. Solve for x and the concentrations.

As we begin solving for x, we will find this is more complicated than in previous examples. As we discuss these complications we should not lose track of the fact that it is still the purpose of this step to determine the value of x.

At equilibrium:

$$K_a = 1.2 \times 10^{-2} = \frac{[H3O+][SO4^{2-}]}{[HSO4-]} = \frac{(x)(x)}{0.50 - x}$$

If we assume that x is small and approximate $(0.50 - x)$ as 0.50, we find:

$$x = 7.7 \times 10^{-2}$$

When we check the assumption, we confirm:

$$\frac{x}{[HSO_4^-]_i} \overset{?}{\leq} 0.05$$

which for this system is

$$\frac{x}{0.50} = \frac{7.7 \times 10^{-2}}{0.50} = 0.15(15\%)$$

The value of x is not less than 5% of 0.50, so the assumption is not valid. We need the quadratic formula to find x.

The equation:

$$K_a = 1.2 \times 10^{-2} = \frac{(x)(x)}{0.50 - x}$$

gives

$$6.0 \times 10^{-3} - 1.2 \times 10^{-2}x = x^{2+}$$

or

$$x^{2+} + 1.2 \times 10^{-2}x - 6.0 \times 10^{-3} = 0$$

This equation can be solved using the quadratic formula. For an equation of the form

$$ax^{2+} + bx + c = 0,$$

x is given by the quadratic equation:

$$x = \frac{-b \pm \sqrt{b^{2+} - 4ac}}{2a}$$

In this problem, $a = 1$, $b = 1.2 \times 10^{-3}$, and $c = -6.0 \times 10^{-3}$.

Solving for x gives a negative root (which cannot be correct since concentration cannot be negative) and a positive root:

$$x = 7.2 \times 10^{-2}$$

Now determine the hydronium ion concentration and the pH:

$$\begin{aligned}[\mathrm{H_3O^+}] = \ & 0 + x = 0 + 7.2 \times 10^{-2}\ M \\ & = 7.2 \times 10^{-2}\ M\end{aligned}$$

The pH of this solution is:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log 7.2 \times 10^{-2} = 1.14$$

? Exercise 12.3.8

a. Show that the quadratic formula gives $x = 7.2 \times 10^{-2}$.

b. Calculate the pH in a 0.010-*M* solution of caffeine, a weak base:

$$\mathrm{C_8H_{10}N_4O_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{C_8H_{10}N_4O_2H^+}(aq) + \mathrm{OH^-}(aq) \quad K_\mathrm{b} = 2.5 \times 10^{-4}$$

Hint

It will be necessary to convert [OH^-] to [H_3O^+] or pOH to pH toward the end of the calculation.

Answer

pH 11.16

The Relative Strengths of Strong Acids and Bases

Strong acids, such as **HCl**, **HBr**, and **HI**, all exhibit the same strength in water. The water molecule is such a strong base compared to the conjugate bases Cl^-, Br^-, and I^- that ionization of these strong acids is essentially complete in aqueous solutions. In solvents less basic than water, we find **HCl**, **HBr**, and **HI** differ markedly in their tendency to give up a proton to the solvent. For example, when dissolved in ethanol (a weaker base than water), the extent of ionization increases in the order **HCl < HBr < HI**, and so **HI** is demonstrated to be the strongest of these acids. The inability to discern differences in strength among strong acids dissolved in water is known as the leveling effect of water.

Water also exerts a leveling effect on the strengths of strong bases. For example, the oxide ion, O^{2-}, and the amide ion, $\mathbf{NH_2^-}$, are such strong bases that they react completely with water:

$$\mathrm{O^{2-}}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{OH^-}(aq) + \mathrm{OH^-}(aq)$$

$$\mathrm{NH_2^-}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{NH_3}(aq) + \mathrm{OH^-}(aq)$$

Thus, O^{2-} and $\mathbf{NH_2^-}$ appear to have the same base strength in water; they both give a 100% yield of hydroxide ion.

In the absence of any leveling effect, 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**.

Likewise, for group 16, the order of increasing acid strength is $H_2O < H_2S < H_2Se < H_2Te$. 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 $\mathbf{CH_4 < NH_3 < H_2O < HF}$; across the third row, it is $\mathbf{SiH_4 < PH_3 < H_2S < HCl}$ (see Figure **12.3.6**).

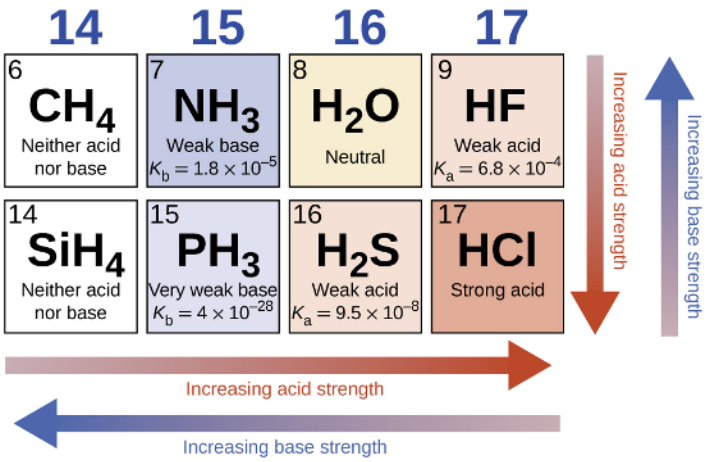
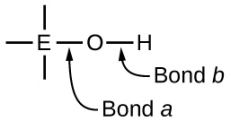


Figure **12.3.6**: As you move from left to right and down the periodic table, the acid strength increases. As you move from right to left and up, the base strength increases.

This diagram has two rows and four columns. Red arrows point left across the bottom of the figure and down at the right side and are labeled “Increasing acid strength.” Blue arrows point left across the bottom and up at the right side of the figure and are labeled “Increasing base strength.” The first column is labeled 14 at the top and two white squares are beneath it. The first has the number 6 in the upper left corner and the formula C H subscript 4 in the center along with designation Neither acid nor base. The second square contains the number 14 in the upper left corner, the formula C H subscript 4 at the center and the designation Neither acid nor base. The second column is labeled 15 at the top and two blue squares are beneath it. The first has the number 7 in the upper left corner and the formula N H subscript 3 in the center along with the designation Weak base and K subscript b equals 1.8 times 10 superscript negative 5. The second square contains the number 15 in the upper left corner, the formula P H subscript 3 at the center and the designation Very weak base and K subscript b equals 4 times 10 superscript negative 28. The third column is labeled 16 at the top and two squares are beneath it. The first is shaded tan and has the number 8 in the upper left corner and the formula H subscript 2 O in the center along with the designation neutral. The second square is shaded pink, contains the number 16 in the upper left corner, the formula H subscript 2 S at the center and the designation Weak acid and K subscript a equals 9.5 times 10 superscript negative 8. The fourth column is labeled 17 at the top and two squares are beneath it. The first is shaded pink, has the number 9 in the upper left corner and the formula H F in the center along with the designation Weak acid and K subscript a equals 6.8 times 10 superscript negative 4. The second square is shaded a deeper pink, contains the number 17 in the upper left corner, the formula H C l at the center, and the designation Strong acid.

Compounds containing oxygen and one or more hydroxyl (OH) groups can be acidic, basic, or amphoteric, depending on the position in the periodic table of the central atom E, the atom bonded to the hydroxyl group. Such compounds have the general formula $O_nE(OH)_m$, and include sulfuric acid, $\mathbf{O_2S(OH)_2}$, sulfurous acid, $\mathbf{OS(OH)_2}$, nitric acid, $\mathbf{O_2NOH}$, perchloric acid, $\mathbf{O_3ClOH}$, aluminum hydroxide, $\mathbf{Al(OH)_3}$, calcium hydroxide, $\mathbf{Ca(OH)_2}$, and potassium hydroxide, $\mathbf{KOH}$:



A diagram is shown that includes a central atom designated with the letter E. Single bonds extend above, below, left, and right of the E. An O atom is bonded to the right of the E, and an arrow points to the bond labeling it, “Bond a.” An H atom is single bonded to the right of the O atom. An arrow pointing to this bond connects it to the label, “Bond b.”

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 **12.3.7**).

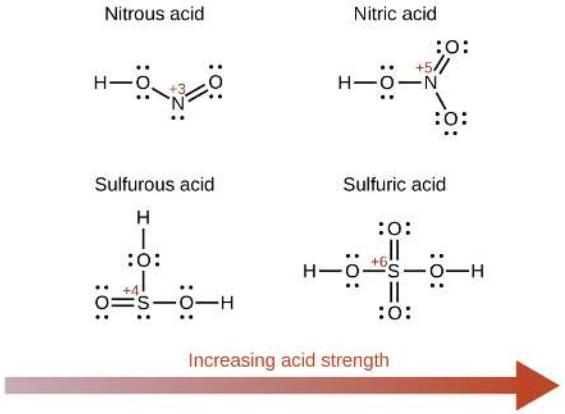


Figure **12.3.7**: As the oxidation number of the central atom E increases, the acidity also increases.

A diagram is shown that includes four structural formulas for acids. A red, right pointing arrow is placed beneath the structures which is labeled “Increasing acid strength.” At the top left, the structure of Nitrous acid is provided. It includes an H atom to which an O atom with two unshared electron pairs is connected with a single bond to the right. A single bond extends to the right and slightly below to a N atom with one unshared electron pair. A double bond extends up and to the right from this N atom to an O atom which has two unshared electron pairs. To the upper right is a structure for Nitric acid. This structure differs from the previous structure in that the N atom is directly to the right of the first O atom and a second O atom with three unshared electron pairs is connected with a single bond below and to the right of the N atom which has no unshared electron pairs. At the lower left, an O atom with two unshared electron pairs is double bonded to its right to an S atom with a single unshared electron pair. An O atom with two unshared electron pairs is bonded above and an H atom is single bonded to this O atom. To the right of the S atom is a single bond to another O atom with two unshared electron pairs to which an H atom is single bonded. This structure is labeled “Sulfurous acid.” A similar structure which is labeled “Sulfuric acid” is placed in the lower right region of the figure. This structure differs in that an H atom is single bonded to the left of the first O atom, leaving it with two unshared electron pairs and a fourth O atom with two unshared electron pairs is double bonded beneath the S atom, leaving it with no unshared electron pairs.

Hydroxy compounds of elements with intermediate electronegativities and relatively high oxidation numbers (for example, elements near the diagonal line separating the metals from the nonmetals in the periodic table) are usually amphoteric. This means that the hydroxy compounds act as acids when they react with strong bases and as bases when they react with strong acids. The amphoterism of aluminum hydroxide, which commonly exists as the hydrate $\mathbf{Al(H_2O)_3(OH)_3}$, is reflected in its solubility in both strong acids and strong bases. In strong bases, the relatively insoluble hydrated aluminum hydroxide, $\mathbf{Al(H_2O)_3(OH)_3}$, is converted into the soluble ion, $\mathbf{[Al(H_2O)_2(OH)_4]^-}$, by reaction with hydroxide ion:

$$\mathbf{[Al(H_2O)_3(OH)_3](aq) + OH^-(aq) \rightleftharpoons H_2O(\mathit{l}) + [Al(H_2O)_2(OH)_4]^-(aq)}$$

In this reaction, a proton is transferred from one of the aluminum-bound H_2O molecules to a hydroxide ion in solution. The $\mathbf{Al(H_2O)_3(OH)_3}$ compound thus acts as an acid under these conditions. On the other hand, when dissolved in strong acids, it is converted to the soluble ion $\mathbf{[Al(H_2O)_6]^{3+}}$ by reaction with hydronium ion:

$$\mathbf{3\,H_3O^+(aq) + Al(H_2O)_3(OH)_3(aq) \rightleftharpoons Al(H_2O)_6{}^{3+}(aq) + 3\,H_2O(\mathit{l})}$$

In this case, protons are transferred from hydronium ions in solution to $\mathbf{Al(H_2O)_3(OH)_3}$, and the compound functions as a base.

Summary

The strengths of Brønsted-Lowry acids and bases in aqueous solutions can be determined by their acid or base ionization constants. Stronger acids form weaker conjugate bases, and weaker acids form stronger conjugate bases. Thus strong acids are completely ionized in aqueous solution because their conjugate bases are weaker bases than water. Weak acids are only partially ionized because their conjugate bases are strong enough to compete successfully with water for possession of protons. Strong bases react with water to quantitatively form hydroxide ions. Weak bases give only small amounts of hydroxide ion. The strengths of the binary acids increase from left to right across a period of the periodic table ($CH_4 < NH_3 < H_2O < HF$), and they increase down a group ($HF < HCl < HBr < HI$). The strengths of oxyacids that contain the same central element increase as the oxidation number of the element increases ($H_2SO_3 < H_2SO_4$). The strengths of oxyacids also increase as the electronegativity of the central element increases [$H_2SeO_4 < H_2SO_4$].

Key Equations

- $K_a = \frac{[H3O+][A-]}{[HA]}$
- $K_b = \frac{[HB+][OH-]}{[B]}$
- $K_a \times K_b = 1.0 \times 10^{-14} = K_w \text{ (at room temperature)}$
- $\text{Percent ionization} = \frac{[H3O+]_{eq}}{[HA]_0} \times 100$

Glossary

acid ionization constant (K_a)
equilibrium constant for the ionization of a weak acid

base ionization constant (K_b)
equilibrium constant for the ionization of a weak base

leveling effect of water
any acid stronger than H_3O^+, or any base stronger than OH^- will react with water to form H_3O^+, or OH^-, respectively; water acts as a base to make all strong acids appear equally strong, and it acts as an acid to make all strong bases appear equally strong

oxyacid
compound containing a nonmetal and one or more hydroxyl groups

percent ionization
ratio of the concentration of the ionized acid to the initial acid concentration, times 100

This page titled 12.3: Relative Strengths of Acids and Bases is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

- **14.3: Relative Strengths of Acids and Bases** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

12.4: Polyprotic Acids

Learning Objectives

- Extend previously introduced equilibrium concepts to acids and bases that may donate or accept more than one proton

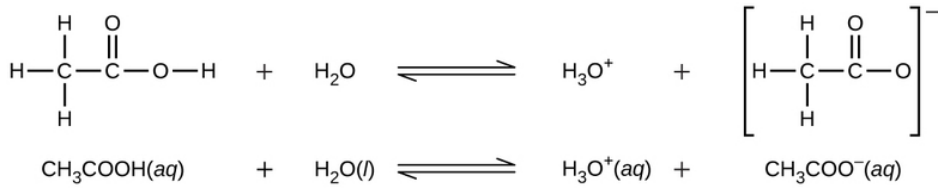
We can classify acids by the number of protons per molecule that they can give up in a reaction. Acids such as $\mathbf{HCl}$, $\mathbf{HNO_3}$, and $\mathbf{HCN}$ that contain one ionizable hydrogen atom in each molecule are called monoprotic acids. Their reactions with water are:

$$\mathbf{HCl}(aq) + \mathbf{H_2O}(l) \longrightarrow \mathbf{H_3O^+}(aq) + \mathbf{Cl^-}(aq)$$

$$\mathbf{HNO_3}(aq) + \mathbf{H_2O}(l) \longrightarrow \mathbf{H_3O^+}(aq) + \mathbf{NO_3^-}(aq)$$

$$\mathbf{HCN}(aq) + \mathbf{H_2O}(l) \longrightarrow \mathbf{H_3O^+}(aq) + \mathbf{CN^-}(aq)$$

Even though it contains four hydrogen atoms, acetic acid, $\mathbf{CH_3CO_2H}$, is also monoprotic because only the hydrogen atom from the carboxyl group ($\mathbf{-COOH}$) reacts with bases:



This image contains two equilibrium reactions. The first shows a C atom bonded to three H atoms and another C atom. The second C atom is double bonded to an O atom and also forms a single bond to another O atom. The second O atom is bonded to an H atom. There is a plus sign and then the molecular formula H subscript 2 O. An equilibrium arrow follows the H subscript 2 O. To the right of the arrow is H subscript 3 O superscript positive sign. There is a plus sign. The final structure shows a C atom bonded the three H atoms and another C atom. This second C atom is double bonded to an O atom and single bonded to another O atom. The entire structure is in brackets and a superscript negative sign appears outside the brackets. The second reaction shows C H subscript 3 C O O H (a q) plus H subscript 2 O (l) equilibrium arrow H subscript 3 O (a q) plus C H subscript 3 C O O superscript negative sign (a q).

Similarly, monoprotic bases are bases that will accept a single proton.

Diprotic Acids

Diprotic acids contain two ionizable hydrogen atoms per molecule; ionization of such acids occurs in two steps. The first ionization always takes place to a greater extent than the second ionization. For example, sulfuric acid, a strong acid, ionizes as follows:

- **The first ionization is**

$$\mathbf{H_2SO_4}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{H_3O^+}(aq) + \mathbf{HSO_4^-}(aq)$$

with $K_{a1} > 10^2$; *complete dissociation*.

- **The second ionization is**

$$\mathbf{HSO_4^-}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{H_3O^+}(aq) + \mathbf{SO_4^{2-}}(aq)$$

with $K_{a2} = 1.2 \times 10^{-2}$.

This stepwise ionization process occurs for all polyprotic acids. When we make a solution of a weak diprotic acid, we get a solution that contains a mixture of acids. Carbonic acid, $\mathbf{H_2CO_3}$, is an example of a weak diprotic acid. The first ionization of carbonic acid yields hydronium ions and bicarbonate ions in small amounts.

- **First Ionization**

$$\mathbf{H_2CO_3}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{H_3O^+}(aq) + \mathbf{HCO_3^-}(aq)$$

with

$$K_{H_2CO_3} = \frac{[H3O+][HCO3-]}{[H2CO3]} = 4.3 \times 10^{-7}$$

The bicarbonate ion can also act as an acid. It ionizes and forms hydronium ions and carbonate ions in even smaller quantities.

- **Second Ionization**

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

with

$$K_{HCO_3^-} = \frac{[H3O+][CO3^2-]}{[HCO3-]} = 4.7 \times 10^{-11}$$

$K_{H_2CO_3}$ is larger than $K_{HCO_3^-}$ by a factor of 10^4, so H_2CO_3 is the dominant producer of hydronium ion in the solution. This means that little of the HCO_3^- formed by the ionization of H_2CO_3 ionizes to give hydronium ions (and carbonate ions), and the concentrations of H_3O^+ and HCO_3^- are practically equal in a pure aqueous solution of H_2CO_3.

If the first ionization constant of a weak diprotic acid is larger than the second by a factor of at least 20, it is appropriate to treat the first ionization separately and calculate concentrations resulting from it before calculating concentrations of species resulting from subsequent ionization. This can simplify our work considerably because we can determine the concentration of H_3O^+ and the conjugate base from the first ionization, then determine the concentration of the conjugate base of the second ionization in a solution with concentrations determined by the first ionization.

Example 12.4.1: Ionization of a Diprotic Acid

When we buy soda water (carbonated water), we are buying a solution of carbon dioxide in water. The solution is acidic because CO_2 reacts with water to form carbonic acid, H_2CO_3. What are $[H_3O^+]$, $[HCO_3^-]$, and $[CO_3^{2-}]$ in a saturated solution of CO_2 with an initial $[H_2CO_3] = 0.033\ M$?

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \quad K_{a1} = 4.3 \times 10^{-7} \qquad \text{(equilibrium step 1)}$$

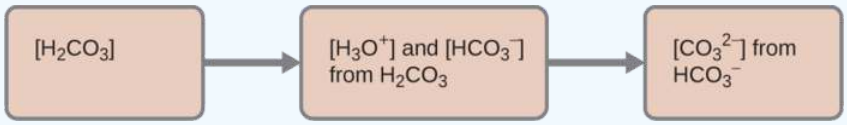
$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq) \quad K_{a2} = 4.7 \times 10^{-11} \qquad \text{(equilibrium step 2)}$$

Solution

As indicated by the ionization constants, H_2CO_3 is a much stronger acid than HCO_3^-, so H_2CO_3 is the dominant producer of hydronium ion in solution. Thus there are two parts in the solution of this problem:

1. Using the customary four steps, we determine the concentration of H_3O^+ and HCO_3^- produced by ionization of H_2CO_3.
2. Then we determine the concentration of CO_3^{2-} in a solution with the concentration of H_3O^+ and HCO_3^- determined in (1).

To summarize:



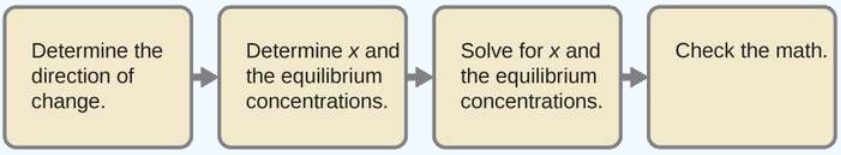
Four tan rectangles are shown that are connected with right pointing arrows. The first is labeled “left bracket H subscript 2 C O subscript 3 right bracket.” The second is labeled “left bracket H subscript 3 O superscript plus right bracket and left bracket H C O subscript 3 superscript negative right bracket from H subscript 2 C O subscript 3.” The third is labeled “left bracket C O subscript 3 superscript 2 negative right bracket from H C O subscript 3 superscript negative.”

1. First Ionization: Determine the concentrations of H_3O^+ *and* HCO_3^-.

Since equilibrium step 1 is has a much bigger $K_{a1} = 4.3 \times 10^{-7}$ than $K_{a2} = 4.7 \times 10^{-11}$ for equilibrium step 2, we can safely ignore the second ionization step and focus only on the first step (but address it in next part of problem).

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \quad K_{a1} = 4.3 \times 10^{-7}$$

As for the ionization of any other weak acid:



Four tan rectangles are shown that are connected with right pointing arrows. The first is labeled “Determine the direction of change.” The second is labeled “Determine x and the equilibrium concentrations.” The third is labeled “Solve for x and the equilibrium concentrations.” The fourth is labeled “Check the math.”

An abbreviated table of changes and concentrations shows:

Abbreviated table of changes and concentrations

ICE Table	$H_2CO_3(aq)$	$H_2O(l)$	$H_3O^+(aq)$	$HCO_3^-(aq)$
Initial (M)	$0.033\ M$	-	0	0
Change (M)	$-x$	-	$+x$	$+x$
Equilibrium (M)	$0.033\ M - x$	-	x	x

Substituting the equilibrium concentrations into the equilibrium constant gives us:

$$K_{H_2CO_3} = \frac{[H3O+][HCO3-]}{[H2CO3]} = \frac{(x)(x)}{0.033 - x} = 4.3 \times 10^{-7}$$

Solving the preceding equation making our standard assumptions gives:

$$x = 1.2 \times 10^{-4}$$

Thus:

$$[H_2CO_3] = 0.033\ M$$

$$[H_3O^+] = [HCO_3^-] = 1.2 \times 10^{-4}\ M$$

2. Second Ionization: Determine the concentration of CO_3^{2-} in a solution at equilibrium.

Since the equilibrium step 1 is has a much bigger K_a than equilibrium step 2, we can the equilibrium conditions calculated from first part of example as the initial conditions for an ICER Table for the equilibrium step 2:

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

ICER Table for the equilibrium step 2:

ICE Table	$HCO_3^-(aq)$	$H_2O(l)$	$H_3O^+(aq)$	$CO_3^{2-}(aq)$
Initial (M)	$1.2 \times 10^{-4}\ M$	-	$1.2 \times 10^{-4}\ M$	0
Change (M)	$-y$	-	$+y$	$+y$
Equilibrium (M)	$1.2 \times 10^{-4}\ M - y$	-	$1.2 \times 10^{-4}\ M + y$	y

$$K_{HCO_3^-} = \frac{[H3O+][CO3^2-]}{[HCO3-]} = \frac{(1.2 \times 10^{-4}\ M + y)(y)}{(1.2 \times 10^{-4}\ M - y)}$$

To avoid solving a quadratic equation, we can assume $y \ll 1.2 \times 10^{-4}\ M$ so

$$K_{HCO_3^-} = 4.7 \times 10^{-11} \approx \frac{(1.2 \times 10^{-4}\ M)(y)}{(1.2 \times 10^{-4}\ M)}$$

Rearranging to solve for y

$$y \approx \frac{(4.7 \times 10^{-11})(1.2 \times 10^{-4}\ M)}{1.2 \times 10^{-4}\ M}$$

$$[CO_3^{2-}] = y \approx 4.7 \times 10^{-11}$$

To summarize:

In part 1 of this example, we found that the H_2CO_3 in a 0.033-M solution ionizes slightly and at equilibrium $[H_2CO_3] = 0.033\ M$, $[H_3O^+] = 1.2 \times 10^{-4}$, and $[HCO_3^-] = 1.2 \times 10^{-4}\ M$. In part 2, we determined that $[CO_3^{2-}] = 5.6 \times 10^{-11}\ M$.

? Exercise 12.4.2: Hydrogen Sulfide

The concentration of H_2S in a saturated aqueous solution at room temperature is approximately 0.1 M. Calculate $[H_3O^+]$, $[HS^-]$, and $[S^{2-}]$ in the solution:

$$H_2S(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HS^-(aq) \quad K_{a1} = 8.9 \times 10^{-8}$$

$$HS^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + S^{2-}(aq) \quad K_{a2} = 1.0 \times 10^{-19}$$

Answer

$[H_2S] = 0.1M$, $[H_3O^+] = [HS^-] = 0.0001\ M$, $[S^{2-}] = 1 \times 10^{-19}\ M$

We note that the concentration of the sulfide ion is the same as K_{a2}. This is due to the fact that each subsequent dissociation occurs to a lesser degree (as acid gets weaker).

Triprotic Acids

A triprotic acid is an acid that has three dissociable protons that undergo stepwise ionization: Phosphoric acid is a typical example:

- **The first ionization is**

$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq)$$

with $K_{a1} = 7.5 \times 10^{-3}$.

- **The second ionization is**

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$$

with $K_{a2} = 6.2 \times 10^{-8}$.

- **The third ionization is**

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq)$$

with $K_{a3} = 4.2 \times 10^{-13}$.

As with the diprotic acids, the differences in the ionization constants of these reactions tell us that in each successive step the degree of ionization is significantly weaker. This is a general characteristic of polyprotic acids and successive ionization constants often differ by a factor of about 10^5 to 10^6. This set of three dissociation reactions may appear to make calculations of equilibrium concentrations in a solution of H_3PO_4 complicated. However, because the successive ionization constants differ by a factor of 10^5 to 10^6, the calculations can be broken down into a series of parts similar to those for diprotic acids.

Polyprotic bases can accept more than one hydrogen ion in solution. The carbonate ion is an example of a diprotic base, since it can accept up to two protons. Solutions of alkali metal carbonates are quite alkaline, due to the reactions:

$$H_2O(l) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

and

$$\mathrm{H_2O}(l) + \mathrm{HCO_3^-}(aq) \rightleftharpoons \mathrm{H_2CO_3}(aq) + \mathrm{OH^-}(aq)$$

Summary

An acid that contains more than one ionizable proton is a polyprotic acid. The protons of these acids ionize in steps. The differences in the acid ionization constants for the successive ionizations of the protons in a polyprotic acid usually vary by roughly five orders of magnitude. As long as the difference between the successive values of K_a of the acid is greater than about a factor of 20, it is appropriate to break down the calculations of the concentrations of the ions in solution into a series of steps.

Glossary

diprotic acid

acid containing two ionizable hydrogen atoms per molecule. A diprotic acid ionizes in two steps

diprotic base

base capable of accepting two protons. The protons are accepted in two steps

monoprotic acid

acid containing one ionizable hydrogen atom per molecule

stepwise ionization

process in which an acid is ionized by losing protons sequentially

triprotic acid

acid that contains three ionizable hydrogen atoms per molecule; ionization of triprotic acids occurs in three steps

---

This page titled 12.4: Polyprotic Acids is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

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

12.5: Buffers

Learning Objectives

- 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 mixture of a weak acid and its conjugate base (or a mixture of a weak base and its conjugate acid) 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 12.5.1). A solution of acetic acid (CH_3COOH and sodium acetate 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 ($NH_3\,(aq)$) and ammonium chloride ($NH_4Cl\,(aq)$).



Figure 12.5.1: (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)

How Buffers Work

A mixture of acetic acid and sodium acetate is acidic because the K_a of acetic acid is greater than the K_b of its conjugate base acetate. It is a buffer because it contains both the weak acid and its salt. Hence, it acts to keep the hydronium ion concentration (and the pH) almost constant by the addition of either a small amount of a strong acid or a strong base. If we add a base such as sodium hydroxide, the hydroxide ions react with the few hydronium ions present. Then more of the acetic acid reacts with water, restoring the hydronium ion concentration almost to its original value:

$$CH_3CO_2H(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + CH_3CO_2{}^-(aq)$$

The pH changes very little. If we add an acid such as hydrochloric acid, most of the hydronium ions from the hydrochloric acid combine with acetate ions, forming acetic acid molecules:

$$H_3O^+(aq) + CH_3CO_2{}^-(aq) \longrightarrow CH_3CO_2H(aq) + H_2O(l)$$

Thus, there is very little increase in the concentration of the hydronium ion, and the pH remains practically unchanged (Figure 12.5.2).

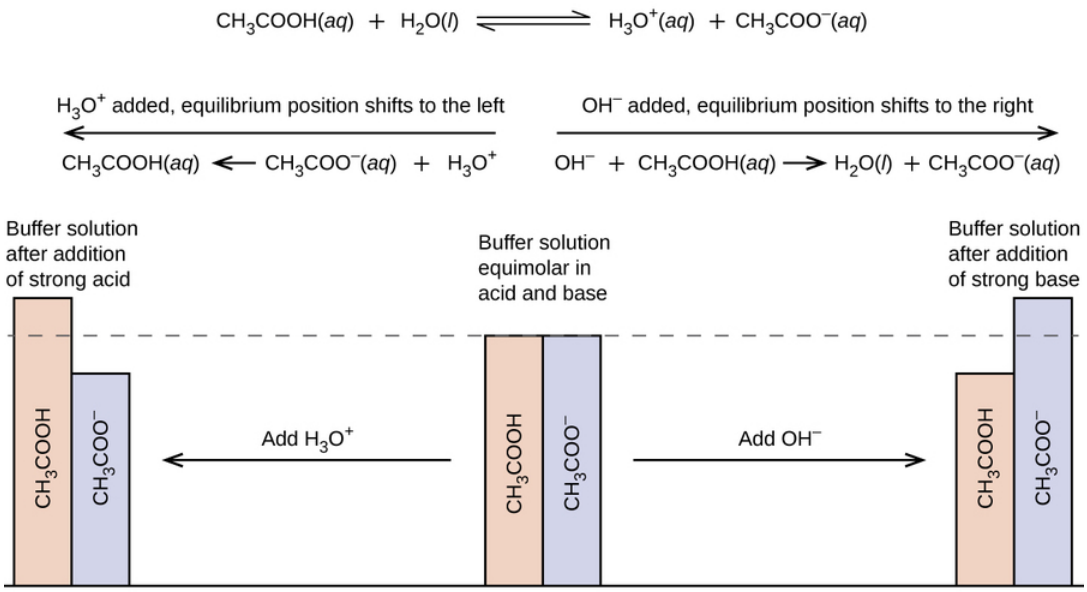


Figure **12.5.2**: This diagram shows the buffer action of these reactions.

A mixture of ammonia and ammonium chloride is basic because the K_b for ammonia is greater than the K_a for the ammonium ion. It is a buffer because it also contains the salt of the weak base. If we add a base (hydroxide ions), ammonium ions in the buffer react with the hydroxide ions to form ammonia and water and reduce the hydroxide ion concentration almost to its original value:

$$\mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq) \longrightarrow \mathrm{NH_3}(aq) + \mathrm{H_2O}(l)$$

If we add an acid (hydronium ions), ammonia molecules in the buffer mixture react with the hydronium ions to form ammonium ions and reduce the hydronium ion concentration almost to its original value:

$$\mathrm{H_3O^+}(aq) + \mathrm{NH_3}(aq) \longrightarrow \mathrm{NH_4^+}(aq) + \mathrm{H_2O}(l)$$

The three parts of the following example illustrate the change in pH that accompanies the addition of base to a buffered solution of a weak acid and to an unbuffered solution of a strong acid.

Example 12.5.1: pH Changes in Buffered and Unbuffered Solutions

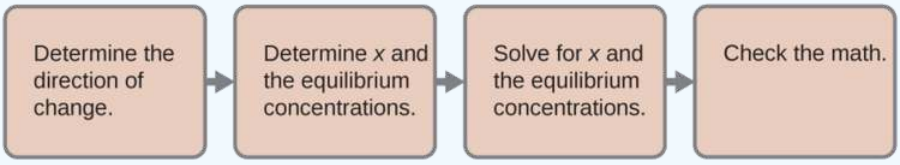
Acetate buffers are used in biochemical studies of enzymes and other chemical components of cells to prevent pH changes that might change the biochemical activity of these compounds.

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 1.0 mL of 0.10 *M* NaOH is added to 100 mL of this buffer, giving a solution with a volume of 101 mL.

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.

To determine the pH of the buffer solution we use a typical equilibrium calculation (as illustrated in earlier Examples):



1. *Determine the direction of change.* The equilibrium in a mixture of H_3O^+, $\mathrm{CH_3CO_2^-}$, and CH_3CO_2H is:

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq)$$

The equilibrium constant for CH_3CO_2H is not given, so we look it up in Table E1: $K_a = 1.8 \times 10^{-5}$. With $[CH_3CO_2H] = [CH_3CO_2^-] = 0.10\ M$ and $[H_3O^+] = \sim 0\ M$, the reaction shifts to the right to form H_3O^+.

2. *Determine* x *and equilibrium concentrations*. A table of changes and concentrations follows:

	$[CH_3CO_2H] + [H_2O] \rightleftharpoons H_3O^+ + [CH_3CO_2^-]$		
Initial concentration (*M*)	0.10	~0	0.10
Change (*M*)	$-x$	x	x
Equilibrium constant (*M*)	$0.10 - x$	x	$0.10 + x$

- *Solve for x and the equilibrium concentrations.* We find:

$$x = 1.8 \times 10^{-5}\ M$$

- and

$$[H_3O^+] = 0 + x = 1.8 \times 10^{-5}\ M$$

Thus:

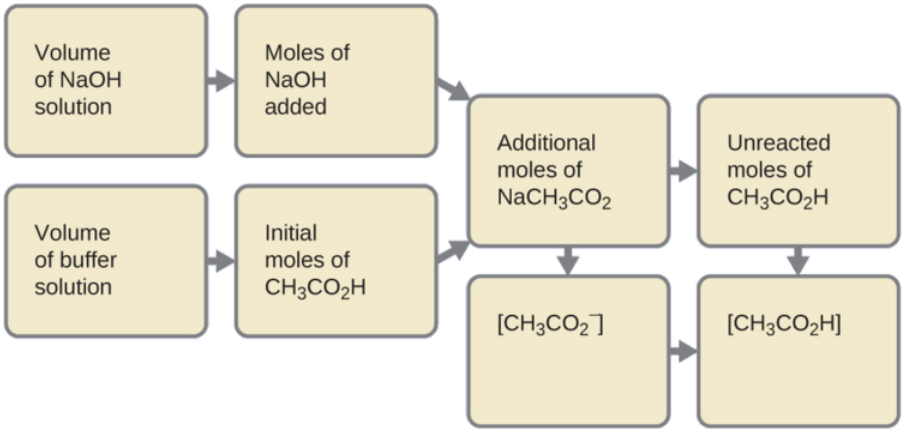
$$pH = -\log[H_3O^+] = -\log(1.8 \times 10^{-5})$$

$$= 4.74$$

4. *Check the work*. If we calculate all calculated equilibrium concentrations, we find that the equilibrium value of the reaction coefficient, $Q = K_a$.

(b) Calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of this buffer, giving a solution with a volume of 101 mL.

First, we calculate the concentrations of an intermediate mixture resulting from the complete reaction between the acid in the buffer and the added base. Then we determine the concentrations of the mixture at the new equilibrium:



1. *Determine the moles of NaOH*. One milliliter (0.0010 L) of 0.10 *M* NaOH contains:

$$0.0010\,\cancel{L} \times \left(\frac{0.10\ \text{mol NaOH}}{1\,\cancel{L}}\right) = 1.0 \times 10^{-4}\ \text{mol NaOH}$$

2. *Determine the moles of CH_2CO_2H*. Before reaction, 0.100 L of the buffer solution contains:

$$0.100\,\cancel{L} \times \left(\frac{0.100\ \text{mol } CH_3CO_2H}{1\,\cancel{L}}\right) = 1.00 \times 10^{-2}\ \text{mol } CH_3CO_2H$$

3. *Solve for the amount of $NaCH_3CO_2$ produced.* The 1.0×10^{-4} mol of NaOH neutralizes 1.0×10^{-4} mol of CH_3CO_2H, leaving:

$$(1.0 \times 10^{-2}) - (0.01 \times 10^{-2}) = 0.99 \times 10^{-2} \text{ mol } CH_3CO_2H$$

and producing 1.0×10^{-4} mol of $NaCH_3CO_2$. This makes a total of:

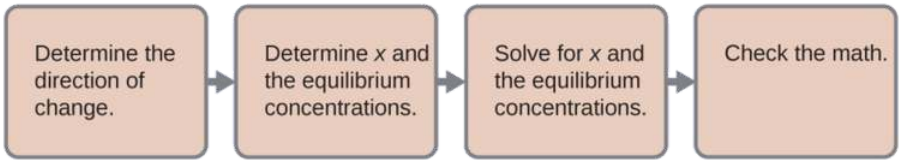
[\mathrm{(1.0×10^{−2})+(0.01×10^{−2})=1.01×10^{−2}\:mol\:NaCH_3CO_2} \nonumber \]

4. *Find the molarity of the products.* After reaction, CH_3CO_2H and $NaCH_3CO_2$ are contained in 101 mL of the intermediate solution, so:

$$[CH_3CO_2H] = \frac{9.9 \times 10^{-3} \text{ mol}}{0.101 \text{ L}} = 0.098\ M$$

$$[NaCH_3CO_2] = \frac{1.01 \times 10^{-2} \text{ mol}}{0.101 \text{ L}} = 0.100\ M$$

Now we calculate the pH after the intermediate solution, which is 0.098 *M* in CH_3CO_2H and 0.100 *M* in $NaCH_3CO_2$, comes to equilibrium. The calculation is very similar to that in part (a) of this example:



This series of calculations gives a pH = 4.75. Thus the addition of the base barely changes the pH of the solution.

(c) For comparison, calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of a solution of an unbuffered solution with a pH of 4.74 (a 1.8×10^{-5}-*M* solution of HCl). The volume of the final solution is 101 mL.

Solution

This 1.8×10^{-5}-*M* solution of HCl has the same hydronium ion concentration as the 0.10-*M* solution of acetic acid-sodium acetate buffer described in part (a) of this example. The solution contains:

$$0.100 \text{ L} \times \left(\frac{1.8 \times 10^{-5} \text{ mol HCl}}{1 \text{ L}} \right) = 1.8 \times 10^{-6} \text{ mol HCl}$$

As shown in part (b), 1 mL of 0.10 *M* NaOH contains 1.0×10^{-4} mol of NaOH. When the NaOH and HCl solutions are mixed, the HCl is the limiting reagent in the reaction. All of the HCl reacts, and the amount of NaOH that remains is:

$$(1.0 \times 10^{-4}) - (1.8 \times 10^{-6}) = 9.8 \times 10^{-5}\ M$$

The concentration of NaOH is:

$$\frac{9.8 \times 10^{-5}\ M \text{ NaOH}}{0.101 \text{ L}} = 9.7 \times 10^{-4}\ M$$

The pOH of this solution is:

$$\text{pOH} = -\log[OH^-] = -\log(9.7 \times 10^{-4}) = 3.01$$

The pH is:

$$\text{pH} = 14.00 - \text{pOH} = 10.99$$

The pH changes from 4.74 to 10.99 in this unbuffered solution. This compares to the change of 4.74 to 4.75 that occurred when the same amount of NaOH was added to the buffered solution described in part (b).

? Exercise 12.5.1

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.

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^+ 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:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log\left(\frac{\text{total moles H}_3\text{O}^+}{\text{total volume}}\right) = -\log\left(\frac{1.0 \times 10^{-4}\ \text{mol} + 1.8 \times 10^{-6}\ \text{mol}}{101\ \text{mL}\left(\frac{1\ \text{L}}{1000\ \text{mL}}\right)}\right) = 3.00$$

Buffer Capacity

Buffer solutions do not have an unlimited capacity to keep the pH relatively constant (Figure **12.5.3**). If we add so much base to a buffer that the weak acid is exhausted, no more buffering action toward the base is possible. On the other hand, if we add an excess of acid, the weak base would be exhausted, and no more buffering action toward any additional acid would be possible. In fact, we do not even need to exhaust all of the acid or base in a buffer to overwhelm it; its buffering action will diminish rapidly as a given component nears depletion.



Figure **12.5.3**: 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.

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 **12.5.4** shows 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.

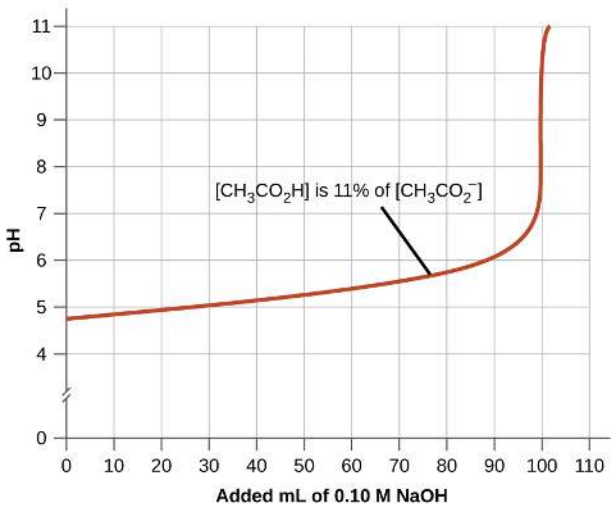


Figure **12.5.4**: The graph, an illustration of buffering action, shows change of pH as an increasing amount of a 0.10-M NaOH solution is added to 100 mL of a buffer solution in which, initially, $[CH_3CO_2H] = 0.10\ M$ and $[CH_3CO_2^-] = 0.10\ M$.

2. Weak acids and their salts are better as buffers for pHs less than 7; weak bases and their salts are better as buffers for pHs 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 an excess of hydrogen ion enters the blood stream, it is removed primarily by the reaction:

$$H_3O^+(aq) + HCO_3^-(aq) \longrightarrow H_2CO_3(aq) + H_2O(l)$$

When an excess of the hydroxide ion is present, it is removed by the reaction:

$$OH^-(aq) + H_2CO_3(aq) \longrightarrow HCO_3^-(aq) + H_2O(l)$$

The pH of human blood thus remains very near 7.35, that is, slightly basic. Variations are usually less than 0.1 of a pH unit. A change of 0.4 of a pH unit is likely to be fatal.

The Henderson-Hasselbalch Approximation

The ionization-constant expression for a solution of a weak acid can be written as:

$$K_a = \frac{[H3O+][A-]}{[HA]}$$

Rearranging to solve for $[H_3O^+]$, we get:

$$[H_3O^+] = K_a \times \frac{[HA]}{[A-]}$$

Taking the negative logarithm of both sides of this equation, we arrive at:

$$-\log[H_3O^+] = -\log K_a - \log\frac{[HA]}{[A^-]}$$

which can be written as

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

where pK_a is the negative of the common 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 acid and its salt in a buffered solution. Scientists often use this expression, called the Henderson-Hasselbalch approximation, 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.

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.

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, H_2CO_3 is approximately 0.0012 *M*, and the concentration of the hydrogen carbonate ion, $\mathbf{HCO_3^-}$, is around 0.024 *M*. Using the Henderson-Hasselbalch equation and the pK_a of carbonic acid at body temperature, we can calculate the pH of blood:

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\text{base}]}{[\text{acid}]} = 6.1 + \log\frac{0.024}{0.0012} = 7.4$$

The fact that the H_2CO_3 concentration is significantly lower than that of the $\mathbf{HCO_3^-}$ ion may seem unusual, but this imbalance is due to the fact that most of the by-products of our metabolism that enter our bloodstream are acidic. Therefore, there must be a larger proportion of base than acid, so that the capacity of the buffer will not be exceeded.

Lactic acid is produced in our muscles when we exercise. As the lactic acid enters the bloodstream, it is neutralized by the $\mathbf{HCO_3^-}$ ion, producing H_2CO_3. An enzyme then accelerates the breakdown of the excess carbonic acid to carbon dioxide and water, which can be eliminated by breathing. In fact, in addition to the regulating effects of the carbonate buffering system on the pH of blood, the body uses breathing to regulate blood pH. If the pH of the blood decreases too far, an increase in breathing removes CO_2 from the blood through the lungs driving the equilibrium reaction such that $[H_3O^+]$ is lowered. If the blood is too alkaline, a lower breath rate increases CO_2 concentration in the blood, driving the equilibrium reaction the other way, increasing $[H^+]$ and restoring an appropriate pH.

Summary

A solution containing a mixture of an acid and its conjugate base, or of a base and its conjugate acid, is called a buffer solution. Unlike in the case of an acid, base, or salt solution, the hydronium ion concentration of a buffer solution does not change greatly when a small amount of acid or base is added to the buffer solution. The base (or acid) in the buffer reacts with the added acid (or base).

Key Equations

- $pK_a = -\log K_a$
- $pK_b = -\log K_b$
- $\mathrm{pH} = pK_a + \log \frac{[A^-]}{[HA]}$

Glossary

buffer capacity

amount of an acid or base that can be added to a volume of a buffer solution before its pH changes significantly (usually by one pH unit)

buffer

mixture of a weak acid or a weak base and the salt of its conjugate; the pH of a buffer resists change when small amounts of acid or base are added

Henderson-Hasselbalch equation

equation used to calculate the pH of buffer solutions

This page titled 12.5: Buffers is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

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

12.6: Acid-Base Titrations

Learning Objectives

- Interpret titration curves for strong and weak acid-base systems
- Compute sample pH at important stages of a titration
- Explain the function of acid-base indicators

As seen in the chapter on the stoichiometry of chemical reactions, titrations can be used to quantitatively analyze solutions for their acid or base concentrations. In this section, we will explore the changes in the concentrations of the acidic and basic species present in a solution during the process of a titration.

Titration Curves

Previously, when we studied acid-base reactions in solution, we focused only on the point at which the acid and base were stoichiometrically equivalent. No consideration was given to the pH of the solution before, during, or after the neutralization.

Example 12.6.1: Calculating pH for Titration Solutions: Strong Acid/Strong Base

A titration is carried out for 25.00 mL of 0.100 *M* HCl (strong acid) with 0.100 *M* of a strong base NaOH the titration curve is shown in Figure **12.6.1**. Calculate the pH at these volumes of added base solution:

a. 0.00 mL
b. 12.50 mL
c. 25.00 mL
d. 37.50 mL

Solution

Since HCl is a strong acid, we can assume that all of it dissociates. The initial concentration of H_3O^+ is $[\mathbf{H_3O^+}]_0 = 0.100\ M$. When the base solution is added, it also dissociates completely, providing OH^- ions. The H_3O^+ and OH^- ions neutralize each other, so only those of the two that were in excess remain, and their concentration determines the pH. Thus, the solution is initially acidic (pH < 7), but eventually all the hydronium ions present from the original acid are neutralized, and the solution becomes neutral. As more base is added, the solution turns basic.

The total initial amount of the hydronium ions is:

$$\mathbf{n(H^+)_0 = [H_3O^+]_0 \times 0.02500\ L = 0.002500\ mol}$$

Once X mL of the 0.100-*M* base solution is added, the number of moles of the OH^- ions introduced is:

$$\mathbf{n(OH^-)_0} = 0.100\ M \times \mathbf{X\ mL} \times \left(\frac{\mathbf{1\ L}}{\mathbf{1000\ mL}}\right)$$

The total volume becomes:

$$V = (\mathbf{25.00\ mL + X\ mL})\left(\frac{\mathbf{1\ L}}{\mathbf{1000\ mL}}\right)$$

The number of moles of H_3O^+ becomes:

$$\mathbf{n(H^+) = n(H^+)_0 - n(OH^-)_0 = 0.002500\ mol} - 0.100\ M \times \mathbf{X\ mL} \times \left(\frac{\mathbf{1\ L}}{\mathbf{1000\ mL}}\right)$$

The concentration of H_3O^+ is:

$$[\mathbf{H_3O^+}] = \frac{\mathbf{n(H^+)}}{\mathbf{V}} = \frac{\mathbf{0.002500\ mol} - 0.100\ M \times \mathbf{X\ mL} \times \left(\frac{\mathbf{1\ L}}{\mathbf{1000\ mL}}\right)}{(\mathbf{25.00\ mL + X\ mL})\left(\frac{\mathbf{1\ L}}{\mathbf{1000\ mL}}\right)}$$

$$= \frac{0.002500\ \text{mol} \times \left(\frac{1000\ \text{mL}}{1\ \text{L}}\right) - 0.100\ M \times \text{X mL}}{25.00\ \text{mL} + \text{X mL}}$$

with the definition of $\mathbf{pH}$:

$$\text{pH} = -\log([\text{H}_3\text{O}^+]) \tag{12.6.1}$$

The preceding calculations work if $\mathbf{n(H^+)_0 - n(OH^-)_0 > 0}$ and so n(H^+) > 0. When $\mathbf{n(H^+)_0 = n(OH^-)_0}$, the H_3O^+ ions from the acid and the OH^- ions from the base mutually neutralize. At this point, the only hydronium ions left are those from the autoionization of water, and there are no OH^- particles to neutralize them. Therefore, in this case:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-\ ],\ [\text{H}_3\text{O}^+] = K_w = 1.0 \times 10^{-14};\ [\text{H}_3\text{O}^+] = 1.0 \times 10^{-7}$$

$$\text{pH} = -\log(1.0 \times 10^{-7}) = 7.00$$

Finally, when $\mathbf{n(OH^-)_0 > n(H^+)_0}$, there are not enough H_3O^+ ions to neutralize all the OH^- ions, and instead of $\mathbf{n(H^+) = n(H^+)_0 - n(OH^-)_0}$, we calculate: $\mathbf{n(OH^-) = n(OH^-)_0 - n(H^+)_0}$

In this case:

$$[\text{OH}^-] = \frac{\text{n(OH}^-)}{V} = \frac{0.100\ M \times \text{X mL} \times \left(\frac{1\ \text{L}}{1000\ \text{mL}}\right) - 0.002500\ \text{mol}}{(25.00\ \text{mL} + \text{X mL})\left(\frac{1\ \text{L}}{1000\ \text{mL}}\right)}$$

$$= \frac{0.100\ M \times \text{X mL} - 0.002500\ \text{mol} \times \left(\frac{1000\ \text{mL}}{1\ \text{L}}\right)}{25.00\ \text{mL} + \text{X mL}}$$

then using the definition of $\boldsymbol{pOH}$ and its relationship to $\boldsymbol{pH}$ in room temperature aqueous solutios (Equation 12.6.1):

$$\begin{aligned} pH &= 14 - pOH \\ &= 14 + \log([OH^-]) \end{aligned}$$

Let us now consider the four specific cases presented in this problem:

(a) X = 0 mL

$$[\text{H}_3\text{O}^+] = \frac{\text{n(H}^+)}{V} = \frac{0.002500\ \text{mol} \times \left(\frac{1000\ \text{mL}}{1\ \text{L}}\right)}{25.00\ \text{mL}} = 0.1\ M$$

then using the definition of $\boldsymbol{pH}$ (Equation 12.6.1):

$$\begin{aligned} pH &= -\log(0.100) \\ &= 1.000 \end{aligned}$$

(b) X = 12.50 mL

$$[\text{H}_3\text{O}^+] = \frac{\text{n(H}^+)}{V} = \frac{0.002500\ \text{mol} \times \left(\frac{1000\ \text{mL}}{1\ \text{L}}\right) - 0.100\ M \times 12.50\ \text{mL}}{25.00\ \text{mL} + 12.50\ \text{mL}} = 0.0333\ M$$

then using the definition of $\boldsymbol{pH}$ (Equation 12.6.1):

$$\begin{aligned} pH &= -\log(0.0333) \\ &= 1.477 \end{aligned}$$

(c) X = 25.00 mL

Since the volumes and concentrations of the acid and base solutions are the same:

$$\mathbf{n(H^+)_0 = n(OH^-)_0}$$

and

$$pH = 7.000$$

as described earlier.

(d) X = 37.50 mL

In this case:

$$\mathrm{n(OH^-)_0 > n(H^+)_0}$$

$$[\mathrm{OH^-}] = \frac{\mathrm{n(OH^-)}}{V} = \frac{0.100\ M \times 35.70\ \mathrm{mL} - 0.002500\ \mathrm{mol} \times \left(\frac{1000\ \mathrm{mL}}{1\ \mathrm{L}}\right)}{25.00\ \mathrm{mL} + 37.50\ \mathrm{mL}} = 0.0200\ M$$

then using the definition of pH (Equation 12.6.1):

$$\begin{aligned}[pH &= 14 - pOH \\ &= 14 + \log([OH^-]) \\ &= 14 + \log(0.0200) \\ &= 12.30\end{aligned}$$

Exercise 12.6.1

Calculate the pH for the strong acid/strong base titration between 50.0 mL of 0.100 *M* $HNO_3(aq)$ and 0.200 *M* NaOH (titrant) at the listed volumes of added base:

a. 0.00 mL,
b. 15.0 mL,
c. 25.0 mL, and
d. 40.0 mL.

Answer a

0.00: 1.000

Answer b

15.0: 1.5111

Answer c

25.0: 7e. Do not delete this text first.

Answer d

40.0: 12.523

In Example **12.6.1**, we calculated pH at four points during a titration. Table **12.6.1** shows a detailed sequence of changes in the pH of a strong acid and a weak acid in a titration with NaOH.

Table **12.6.1**: pH Values in the Titrations of a Strong Acid with a Strong Base and of a Weak Acid with a Strong Base

Volume of 0.100 M NaOH Added (mL)	Moles of NaOH Added	pH Values 0.100 M HCl[1]	pH Values 0.100 M CH_3CO_2H[2]
0.0	0.0	1.00	2.87
5.0	0.00050	1.18	4.14
10.0	0.00100	1.37	4.57
15.0	0.00150	1.60	4.92
20.0	0.00200	1.95	5.35
22.0	0.00220	2.20	5.61
24.0	0.00240	2.69	6.13
24.5	0.00245	3.00	6.44
24.9	0.00249	3.70	7.14
25.0	0.00250	7.00	8.72
25.1	0.00251	10.30	10.30
25.5	0.00255	11.00	11.00
26.0	0.00260	11.29	11.29
28.0	0.00280	11.75	11.75
30.0	0.00300	11.96	11.96
35.0	0.00350	12.22	12.22
40.0	0.00400	12.36	12.36
45.0	0.00450	12.46	12.46
50.0	0.00500	12.52	12.52

1. Titration of 25.00 mL of 0.100 *M* HCl (0.00250 mol of HCI) with 0.100 *M* NaOH.
2. Titration of 25.00 mL of 0.100 *M* CH_3CO_2H (0.00250 mol of CH_3CO_2H) with 0.100 *M* NaOH.

The simplest acid-base reactions are those of a strong acid with a strong base. Table **12.6.1** shows data for the titration of a 25.0-mL sample of 0.100 *M* hydrochloric acid with 0.100 *M* sodium hydroxide. The values of the pH measured after successive additions of small amounts of NaOH are listed in the first column of this table, and are graphed in Figure **12.6.1**, in a form that is called a titration curve. The pH increases slowly at first, increases rapidly in the middle portion of the curve, and then increases slowly again. The point of inflection (located at the midpoint of the vertical part of the curve) is the equivalence point for the titration. It indicates when equivalent quantities of acid and base are present. For the titration of a strong acid with a strong base, the equivalence point occurs at a pH of 7.00 and the points on the titration curve can be calculated using solution stoichiometry (Table **12.6.1** and Figure **12.6.1**).

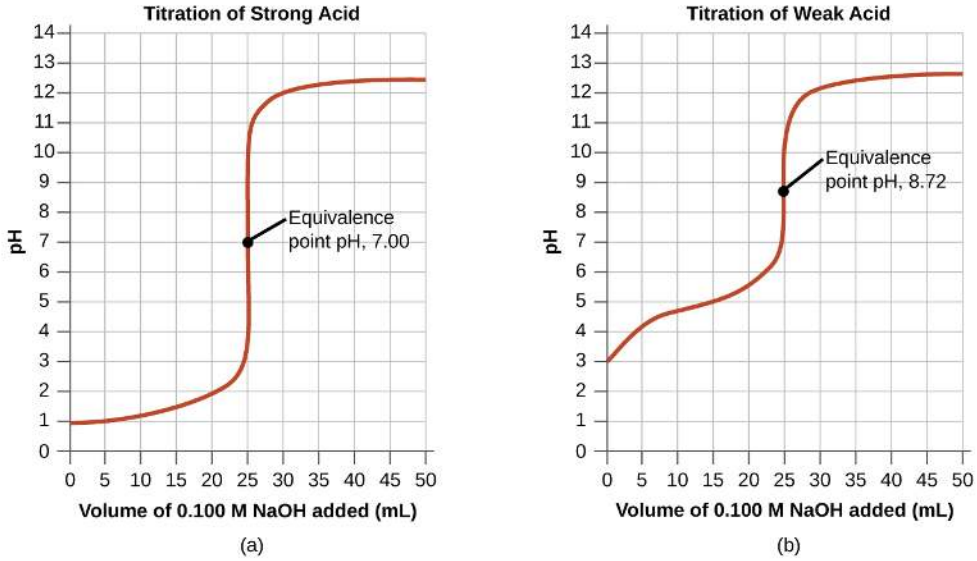


Figure **12.6.1**: (a) The titration curve for the titration of 25.00 mL of 0.100 M HCl (strong acid) with 0.100 M NaOH (strong base) has an equivalence point of 7.00 pH. (b) The titration curve for the titration of 25.00 mL of 0.100 M CH_3CO_2H (weak acid) with 0.100 M NaOH (strong base) has an equivalence point of 8.72 pH.

Two graphs are shown. The first graph on the left is titled “Titration of Weak Acid.” The horizontal axis is labeled “Volume of 0.100 M N a O H added (m L).” Markings and vertical gridlines are provided every 5 units from 0 to 50. The vertical axis is labeled “p H” and is marked every 1 unis beginning at 0 extending to 14. A red curve is drawn on the graph which increases steadily from the point (0, 3) up to about (20, 5.5) after which the graph has a vertical section from (25, 7) up to (25, 11). The graph then levels off to a value of about 12.5 from about 40 m L up to 50 m L. The midpoint of the vertical segment of the curve is labeled “Equivalence point p H, 8.72.” The second graph on the right is titled “Titration of Strong Acid.” The horizontal axis is labeled “Volume of 0.100 M N a O H added (m L).” Markings and vertical gridlines are provided every 5 units from 0 to 50. The vertical axis is labeled “p H” and is marked every 1 units beginning at 0 extending to 14. A red curve is drawn on the graph which increases gradually from the point (0, 1) up to about (22.5, 2.2) after which the graph has a vertical section from (25, 4) up to nearly (25, 11). The graph then levels off to a value of about 12.4 from about 40 m L up to 50 m L. The midpoint of the vertical segment of the curve is labeled “Equivalence point p H, 7.00.”

The titration of a weak acid with a strong base (or of a weak base with a strong acid) is somewhat more complicated than that just discussed, but it follows the same general principles. Let us consider the titration of 25.0 mL of 0.100 *M* acetic acid (a weak acid) with 0.100 *M* sodium hydroxide and compare the titration curve with that of the strong acid. Table **12.6.1** gives the pH values during the titration, Figure **12.6.1***b* shows the titration curve.

Although the initial volume and molarity of the acids are the same, there are important differences between the two titration curves. The titration curve for the weak acid begins at a higher value (less acidic) and maintains higher pH values up to the equivalence point. This is because acetic acid is a weak acid, which is only partially ionized. The pH at the equivalence point is also higher (8.72 rather than 7.00) due to the hydrolysis of acetate, a weak base that raises the pH:

$$\mathrm{CH_3CO_2^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{CH_3CO_2H}(l) + \mathrm{OH^-}(aq)$$

After the equivalence point, the two curves are identical because the pH is dependent on the excess of hydroxide ion in both cases.

Example **12.6.2**: Titration of a Weak Acid with a Strong Base

The titration curve shown in Figure **12.6.1***b* is for the titration of 25.00 mL of 0.100 *M* CH_3CO_2H with 0.100 *M* NaOH. The reaction can be represented as:

$$\mathrm{CH_3CO_2H + OH^- \longrightarrow CH_3CO_2^- + H_2O}$$

a. What is the initial pH before any amount of the NaOH solution has been added? $K_a = 1.8 \times 10^{-5}$ for CH_3CO_2H.
b. Find the pH after 25.00 mL of the NaOH solution have been added.
c. Find the pH after 12.50 mL of the NaOH solution has been added.
d. Find the pH after 37.50 mL of the NaOH solution has been added.

Solution

(a) Assuming that the dissociated amount is small compared to 0.100 *M*, we find that:

$$K_a = \frac{[H3O+][CH3CO2-]}{[CH3CO2H]} \approx \frac{[H3O+]^2}{[CH3CO2H]_0}$$

and

$$[H_3O^+] = \sqrt{K_a \times [CH_3CO_2H]} = \sqrt{1.8 \times 10^{-5} \times 0.100} = 1.3 \times 10^{-3}$$

$$pH = -\log(1.3 \times 10^{-3}) = 2.87$$

(b) After 25.00 mL of NaOH are added, the number of moles of NaOH and CH_3CO_2H are equal because the amounts of the solutions and their concentrations are the same. All of the CH_3CO_2H has been converted to $CH_3CO_2^-$. The concentration of the $CH_3CO_2^-$ ion is:

$$\frac{0.00250\ \text{mol}}{0.0500\ \text{L}} = 0.0500\ \text{M} CH_3CO_2^-$$

The equilibrium that must be focused on now is the basicity equilibrium for $CH_3CO_2^-$:

$$CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq)$$

so we must determine K_b for the base by using the ion product constant for water:

$$K_b = \frac{[CH3CO2H][OH-]}{[CH3CO2-]}$$

$$K_a = \frac{[CH3CO2-][H+]}{[CH3CO2H]}, \text{ so } \frac{[CH3CO2H]}{[CH3CO2-]} = \frac{[H^+]}{K_a}.$$

Since $K_w = [H^+][OH^-]$:

$$K_b = \frac{[H^+][OH^-]}{K_a} \tag{12.6.2}$$

$$= \frac{K_w}{K_a} \tag{12.6.3}$$

$$= \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} \tag{12.6.4}$$

$$= 5.6 \times 10^{-10} \tag{12.6.5}$$

Let us denote the concentration of each of the products of this reaction, CH_3CO_2H and OH^-, as *x*. Using the assumption that *x* is small compared to 0.0500 *M*, $K_b = \frac{x^2}{0.0500\ M}$, and then:

$$x = [OH^-] = 5.3 \times 10^{-6}$$

$$pOH = -\log(5.3 \times 10^{-6}) = 5.28$$

$$pH = 14.00 - 5.28 = 8.72$$

Note that the pH at the equivalence point of this titration is significantly greater than 7.

(c) In (a), 25.00 mL of the NaOH solution was added, and so practically all the CH_3CO_2H was converted into $CH_3CO_2^-$. In this case, only 12.50 mL of the base solution has been introduced, and so only half of all the CH_3CO_2H is converted into $CH_3CO_2^-$. The total initial number of moles of CH_3CO_2H is 0.02500L × 0.100 $\underline{M}$ = 0.00250 mol, and so after adding the NaOH, the numbers of moles of CH_3CO_2H and $CH_3CO_2^-$ are both approximately equal to $\frac{0.00250\ \text{mol}}{2} = 0.00125\ \text{mol}$, and their concentrations are the same.

Since the amount of the added base is smaller than the original amount of the acid, the equivalence point has not been reached, the solution remains a buffer, and we can use the Henderson-Hasselbalch equation:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[Base]}{[Acid]} = -\log(K_\mathrm{a}) + \log\frac{[CH3CO2-]}{[CH3CO2H]} = -\log(1.8\times10^{-5}) + \log(1)$$

(as the concentrations of $\mathbf{CH_3CO_2^-}$ and CH_3CO_2H are the same)

Thus:

$$\mathrm{pH} = -\log(1.8\times10^{-5}) = 4.74$$

(the pH = the pK_a at the halfway point in a titration of a weak acid)

(d) After 37.50 mL of NaOH is added, the amount of NaOH is 0.03750 L × 0.100 *M* = 0.003750 mol NaOH. Since this is past the equivalence point, the excess hydroxide ions will make the solution basic, and we can again use stoichiometric calculations to determine the pH:

$$[\mathrm{OH^-}] = \frac{(0.003750\ \mathrm{mol} - 0.00250\ \mathrm{mol})}{0.06250\ \mathrm{L}} = 2.00\times10^{-2}\ M$$

So:

$$\mathrm{pOH} = -\log(2.00\times10^{-2}) = 1.70,\ \text{and}\ \mathrm{pH} = 14.00 - 1.70 = 12.30$$

Note that this result is the same as for the strong acid-strong base titration example provided, since the amount of the strong base added moves the solution past the equivalence point.

? Exercise 12.6.2

Calculate the pH for the weak acid/strong base titration between 50.0 mL of 0.100 *M* HCOOH(*aq*) (formic acid) and 0.200 *M* NaOH (titrant) at the listed volumes of added base:

a. 0.00 mL,
b. 15.0 mL,
c. 25.0 mL, and
d. 30.0 mL.

Answer a

0.00 mL: 2.37

Answer b

15.0 mL: 3.92

Answer c

25.00 mL: 8.29

Answer d

30.0 mL: 12.097

Acid-Base Indicators

Certain organic substances change color in dilute solution when the hydronium ion concentration reaches a particular value. For example, phenolphthalein is a colorless substance in any aqueous solution with a hydronium ion concentration greater than 5.0×10^{-9} *M* (pH < 8.3). In more basic solutions where the hydronium ion concentration is less than 5.0×10^{-9} *M* (pH > 8.3), it is red or pink. Substances such as phenolphthalein, which can be used to determine the pH of a solution, are called acid-base indicators. Acid-base indicators are either weak organic acids or weak organic bases.

The equilibrium in a solution of the acid-base indicator methyl orange, a weak acid, can be represented by an equation in which we use **HIn** as a simple representation for the complex methyl orange molecule:

$$\underbrace{\mathrm{HIn\,(aq)}}_{\text{red}} + \mathrm{H_2O\,(l)} \rightleftharpoons \mathrm{H_3O^+\,(aq)} + \underbrace{\mathrm{In^-\,(aq)}}_{\text{yellow}}$$

$$K_a = \frac{[H3O+][In-]}{[HIn]} = 4.0 \times 10^{-4}$$

The anion of methyl orange, $\mathbf{In^-}$, is yellow, and the nonionized form, **HIn**, is red. When we add acid to a solution of methyl orange, the increased hydronium ion concentration shifts the equilibrium toward the nonionized red form, in accordance with Le Chatelier's principle. If we add base, we shift the equilibrium towards the yellow form. This behavior is completely analogous to the action of buffers.

An indicator's color is the visible result of the ratio of the concentrations of the two species In^- and **HIn**. If most of the indicator (typically about 60−90% or more) is present as $\mathbf{In^-}$, then we see the color of the $\mathbf{In^-}$ ion, which would be yellow for methyl orange. If most is present as **HIn**, then we see the color of the **HIn** molecule: red for methyl orange. For methyl orange, we can rearrange the equation for K_a and write:

$$\frac{[\mathrm{In^-}]}{[\mathrm{HIn}]} = \frac{[\text{substance with yellow color}]}{[\text{substance with red color}]} = \frac{K_a}{[\mathrm{H_3O^+}]} \tag{12.6.6}$$

Equation 12.6.6 shows us how the ratio of $\frac{[In-]}{[HIn]}$ varies with the concentration of hydronium ion. The above expression describing the indicator equilibrium can be rearranged:

$$\frac{[H_3O^+]}{K_a} = \frac{[HIn]}{[In^-]} \tag{12.6.7}$$

$$\log\left(\frac{[H_3O^+]}{K_a}\right) = \log\left(\frac{[HIn]}{[In^-]}\right) \tag{12.6.8}$$

$$\log([H_3O^+]) - \log(K_a) = -\log\left(\frac{[In^-]}{[HIn]}\right) \tag{12.6.9}$$

$$-pH + pK_a = -\log\left(\frac{[In^-]}{[HIn]}\right) \tag{12.6.10}$$

$$pH = pK_a + \log\left(\frac{[In^-]}{[HIn]}\right) \tag{12.6.11}$$

or in general terms

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) \tag{12.6.12}$$

Equation 12.6.12 is the same as the *Henderson-Hasselbalch equation*, which can be used to describe the equilibrium of indicators.

When $[H_3O^+]$ has the same numerical value as K_a, the ratio of $[In^-]$ to [HIn] is equal to 1, meaning that 50% of the indicator is present in the red form (HIn) and 50% is in the yellow ionic form (In^-), and the solution appears orange in color. When the hydronium ion concentration increases to 8×10^{-4} *M* (a pH of 3.1), the solution turns red. No change in color is visible for any further increase in the hydronium ion concentration (decrease in pH). At a hydronium ion concentration of 4×10^{-5} *M* (a pH of 4.4), most of the indicator is in the yellow ionic form, and a further decrease in the hydronium ion concentration (increase in pH) does not produce a visible color change. The pH range between 3.1 (red) and 4.4 (yellow) is the color-change interval of methyl orange; the pronounced color change takes place between these pH values.

There are many different acid-base indicators that cover a wide range of pH values and can be used to determine the approximate pH of an unknown solution by a process of elimination. Universal indicators and pH paper contain a mixture of indicators and exhibit different colors at different pHs. Figure **12.6.2** presents several indicators, their colors, and their color-change intervals.

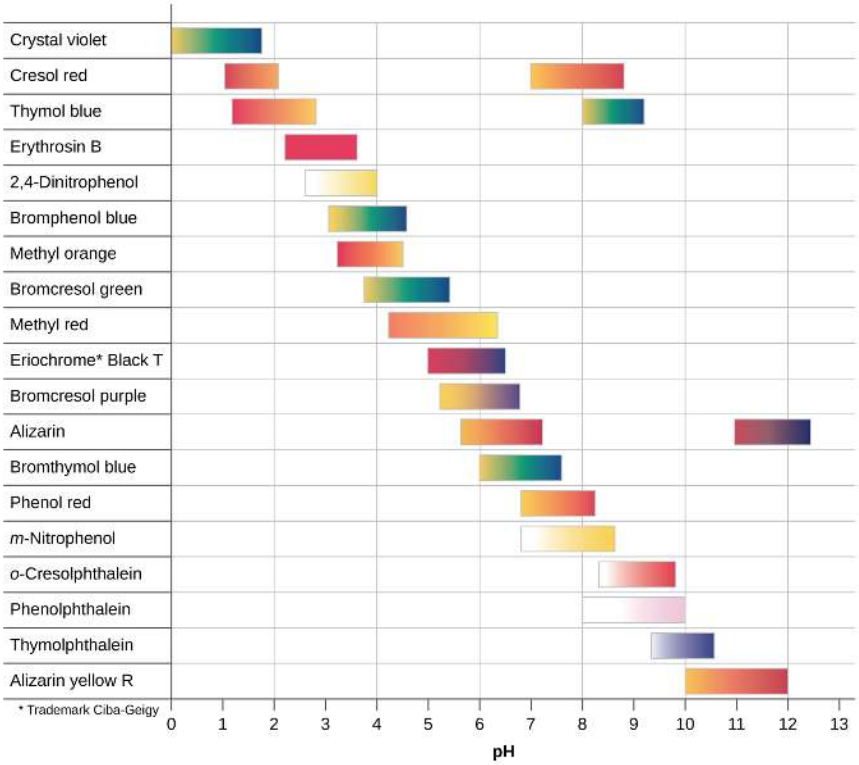


Figure **12.6.2**: This chart illustrates the ranges of color change for several acid-base indicators.

Titration curves help us pick an indicator that will provide a sharp color change at the equivalence point. The best selection would be an indicator that has a color change interval that brackets the pH at the equivalence point of the titration.

The color change intervals of three indicators are shown in Figure **12.6.3**. The equivalence points of both the titration of the strong acid and of the weak acid are located in the color-change interval of phenolphthalein. We can use it for titrations of either strong acid with strong base or weak acid with strong base.

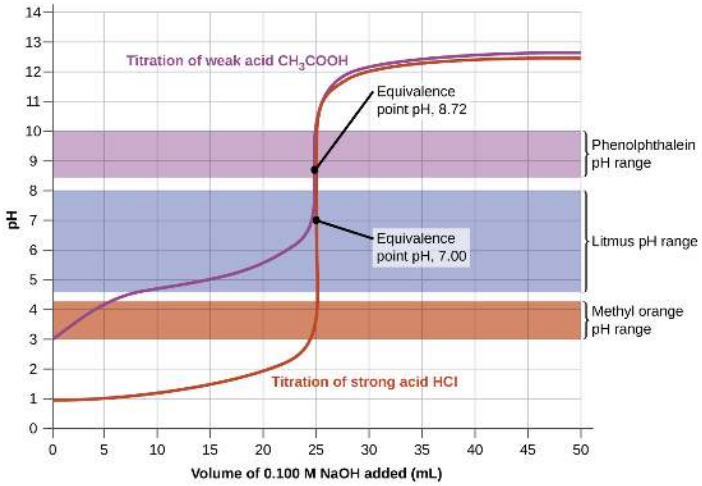


Figure **12.6.3**: The graph shows a titration curve for the titration of 25.00 mL of 0.100 M CH_3CO_2H (weak acid) with 0.100 M NaOH (strong base) and the titration curve for the titration of HCl (strong acid) with NaOH (strong base). The pH ranges for the color change of phenolphthalein, litmus, and methyl orange are indicated by the shaded areas.

A graph is shown which is titled “Titration of Weak Acid.” The horizontal axis is labeled “Volume of 0.100 M N a O H added (m L)” and begins at 0 with markings every 5 units up to 50. The vertical axis is labeled “p H” and begins at 0 and increases by single units up to 14. A red curve is drawn on the graph. The curve begins at (0, 3) and passes through the points (5, 4.1), (10, 4.7), (15, 5), (20, 5.5), and (22.5, 6), after which it rapidly increases, forming a vertical section centered at the point (25, 8.7). The rapid increase of the curve then levels off and the curve passes through the points (30, 12), (35, 12.4), (40, 12.5), (45, 12.6), and (50, 12.6). A brown rectangle extends horizontally across the graph covering the p H of 3 to 4.2 range. To the right, this rectangle is labeled “Methyl orange p H range.” A blue rectangle extends horizontally across the graph covering the p H of 4.6 to 8 range. To the right, this rectangle is labeled “Litmus p H range.” A purple rectangle extends horizontally across the graph covering the p H of 8.4 to 10 range. To the right, this rectangle is labeled “Phenolphthalein p H range.” The midpoint of the vertical segment of the curve is labeled “Equivalence point p H, 8.72.”

Litmus is a suitable indicator for the HCl titration because its color change brackets the equivalence point. However, we should not use litmus for the CH_3CO_2H titration because the pH is within the color-change interval of litmus when only about 12 mL of NaOH has been added, and it does not leave the range until 25 mL has been added. The color change would be very gradual, taking place during the addition of 13 mL of NaOH, making litmus useless as an indicator of the equivalence point.

We could use methyl orange for the HCl titration, but it would not give very accurate results: (1) It completes its color change slightly before the equivalence point is reached (but very close to it, so this is not too serious); (2) it changes color, as Figure **12.6.2** demonstrates, during the addition of nearly 0.5 mL of NaOH, which is not so sharp a color change as that of litmus or phenolphthalein; and (3) it goes from yellow to orange to red, making detection of a precise endpoint much more challenging than the colorless to pink change of phenolphthalein. Figure **12.6.2** shows us that methyl orange would be completely useless as an indicator for the CH_3CO_2H titration. Its color change begins after about 1 mL of NaOH has been added and ends when about 8 mL has been added. The color change is completed long before the equivalence point (which occurs when 25.0 mL of NaOH has been added) is reached and hence provides no indication of the equivalence point.

We base our choice of indicator on a calculated pH, the pH at the equivalence point. At the equivalence point, equimolar amounts of acid and base have been mixed, and the calculation becomes that of the pH of a solution of the salt resulting from the titration.

Summary

A titration curve is a graph that relates the change in pH of an acidic or basic solution to the volume of added titrant. The characteristics of the titration curve are dependent on the specific solutions being titrated. The pH of the solution at the equivalence point may be greater than, equal to, or less than 7.00. The choice of an indicator for a given titration depends on the expected pH at the equivalence point of the titration, and the range of the color change of the indicator.

Glossary

acid-base indicator

organic acid or base whose color changes depending on the pH of the solution it is in

color-change interval

range in pH over which the color change of an indicator takes place

titration curve

plot of the pH of a solution of acid or base versus the volume of base or acid added during a titration

---

This page titled 12.6: Acid-Base Titrations is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

- **14.7: Acid-Base Titrations** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

CHAPTER OVERVIEW

13: Nuclear Chemistry and Other Topics

13.1: Nuclear Chemistry Introduction

13.2: The Effects of Radiation on Life

13.3: Radioactivity in Medicine and Other Applications

13: Nuclear Chemistry and Other Topics is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

13.1: Nuclear Chemistry Introduction

Nuclear Chemistry is purely the chemistry of the nucleus, and it is incredibly important to health and wellness. In addition to the readings in the course, the rest of this chapter provides examples and information on how nuclear chemistry and radiation affect human beings.

13.1: Nuclear Chemistry Introduction is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

13.2: The Effects of Radiation on Life

Learning Objectives

- To know the differences between ionizing and nonionizing radiation and their effects on matter.
- To identify natural and artificial sources of radiation.

Because nuclear reactions do not typically affect the valence electrons of the atom (although electron capture draws an electron from an orbital of the lowest energy level), they do not directly cause chemical changes. Nonetheless, the particles and the photons emitted during nuclear decay are very energetic, and they can indirectly produce chemical changes in the matter surrounding the nucleus that has decayed. For instance, an α particle is an ionized helium nucleus (He^{2+}) that can act as a powerful oxidant. In this section, we describe how radiation interacts with matter and the some of the chemical and biological effects of radiation.

Ionizing versus Nonionizing Radiation

The effects of radiation on matter are determined primarily by the energy of the radiation, which depends on the nuclear decay reaction that produced it. **Nonionizing radiation** is relatively low in energy; when it collides with an atom in a molecule or an ion, most or all of its energy can be absorbed without causing a structural or a chemical change. Instead, the kinetic energy of the radiation is transferred to the atom or molecule with which it collides, causing it to rotate, vibrate, or move more rapidly. Because this energy can be transferred to adjacent molecules or ions in the form of heat, many radioactive substances are warm to the touch. Highly radioactive elements such as polonium, for example, have been used as heat sources in the US space program. As long as the intensity of the nonionizing radiation is not great enough to cause overheating, it is relatively harmless, and its effects can be neutralized by cooling.

In contrast, **ionizing radiation** is higher in energy, and some of its energy can be transferred to one or more atoms with which it collides as it passes through matter. If enough energy is transferred, electrons can be excited to very high energy levels, resulting in the formation of positively charged ions:

$$\text{atom} + \text{ionizing radiation} \rightarrow \text{ion}^+ + \text{e}^- \tag{13.2.1}$$

Molecules that have been ionized in this way are often highly reactive, and they can decompose or undergo other chemical changes that create a cascade of reactive molecules that can damage biological tissues and other materials (Figure 13.2.1). Because the energy of ionizing radiation is very high, we often report its energy in units such as megaelectronvolts (MeV) per particle:

$$1\ \text{MeV/particle} = 96\ \text{billion J/mol.}$$



Figure 13.2.1: Radiation Damage. When high-energy particles emitted by radioactive decay interact with matter, they can break bonds or ionize molecules, resulting in changes in physical properties such as ductility or color. The glass electrical insulator on the left has not been exposed to radiation, but the insulator on the right has received intense radiation doses over a long period of time. Radiation damage changed the chemical structure of the glass, causing it to become bright blue. (CC BY-SA-NC; anonymous)

The Effects of Ionizing Radiation on Matter

The effects of ionizing radiation depend on four factors:

1. The type of radiation, which dictates how far it can penetrate into matter
2. The energy of the individual particles or photons
3. The number of particles or photons that strike a given area per unit time

4. The chemical nature of the substance exposed to the radiation

The relative abilities of the various forms of ionizing radiation to penetrate biological tissues are illustrated in Figure **13.2.2**. Because of its high charge and mass, α radiation interacts strongly with matter. Consequently, it does not penetrate deeply into an object, and it can be stopped by a piece of paper, clothing, or skin. In contrast, γ rays, with no charge and essentially no mass, do not interact strongly with matter and penetrate deeply into most objects, including the human body. Several inches of lead or more than 12 inches of special concrete are needed to completely stop γ rays. Because β particles are intermediate in mass and charge between α particles and γ rays, their interaction with matter is also intermediate. Beta particles readily penetrate paper or skin, but they can be stopped by a piece of wood or a relatively thin sheet of metal.

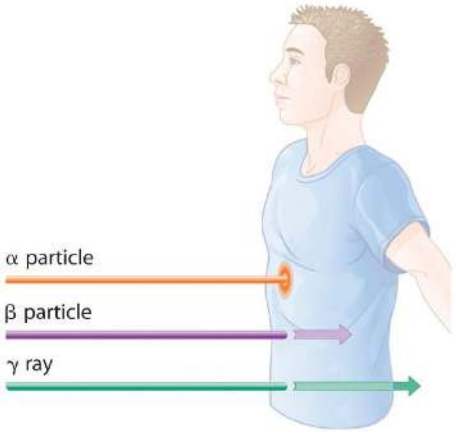


Figure **13.2.2**: Depth of Penetration of Ionizing Radiation. The depth of penetration of alpha, beta, and gamma radiation varies with the particle. Because α particles interact strongly with matter, they do not penetrate deeply into the human body. In contrast, β particles do not interact as strongly with matter and penetrate more deeply. Gamma rays, which have no charge, are stopped by only very dense materials and can pass right through the human body without being absorbed. (CC BY-SA-NC; anonymous)

Because of their great penetrating ability, γ rays are by far the most dangerous type of radiation when they come from a source *outside* the body. Alpha particles, however, are the most damaging if their source is *inside* the body because internal tissues absorb all of their energy. Thus danger from radiation depends strongly on the type of radiation emitted and the extent of exposure, which allows scientists to safely handle many radioactive materials if they take precautions to avoid, for example, inhaling fine particulate dust that contains alpha emitters. Some properties of ionizing radiation are summarized in Table **13.2.1**.

Table **13.2.1**: Some Properties of Ionizing Radiation

Type	Energy Range (MeV)	Penetration Distance in Water*	Penetration Distance in Air*
α particles	3–9	< 0.05 mm	< 10 cm
β particles	≤ 3	< 4 mm	1 m
x-rays	$<10^{-2}$	< 1 cm	< 3 m
γ rays	10^{-2}–10^{1}	< 20 cm	> 3 m

*Distance at which half of the radiation has been absorbed.

There are many different ways to measure radiation exposure, or the dose. The **roentgen (R)**, which measures the amount of energy absorbed by dry air, can be used to describe quantitative exposure.Named after the German physicist Wilhelm Röntgen (1845–1923; Nobel Prize in Physics, 1901), who discovered x-rays. The roentgen is actually defined as the amount of radiation needed to produce an electrical charge of 2.58×10^{-4} C in 1 kg of dry air. Damage to biological tissues, however, is proportional to the amount of energy absorbed by tissues, not air. The most common unit used to measure the effects of radiation on biological tissue is the **rad (radiation absorbed dose)**; the SI equivalent is the gray (Gy). The rad is defined as the amount of radiation that causes 0.01 J of energy to be absorbed by 1 kg of matter, and the gray is defined as the amount of radiation that causes 1 J of energy to be absorbed per kilogram:

$$1\ \text{rad} = 0.010\ \text{J/kg} \qquad 1\ \text{Gy} = 1\ \text{J/kg} \tag{13.2.2}$$

Thus a 70 kg human who receives a dose of 1.0 rad over his or her entire body absorbs 0.010 J/70 kg = 1.4×10^{-4} J, or 0.14 mJ. To put this in perspective, 0.14 mJ is the amount of energy transferred to your skin by a 3.8×10^{-5} g droplet of boiling water. Because the energy of the droplet of water is transferred to a relatively large area of tissue, it is harmless. A radioactive particle, however, transfers its energy to a single molecule, which makes it the atomic equivalent of a bullet fired from a high-powered rifle.

Because α particles have a much higher mass and charge than β particles or γ rays, the difference in mass between α and β particles is analogous to being hit by a bowling ball instead of a table tennis ball traveling at the same speed. Thus the amount of tissue damage caused by 1 rad of α particles is much greater than the damage caused by 1 rad of β particles or γ rays. Thus a unit called the **rem (roentgen equivalent in man)** was devised to describe the actual amount of tissue damage caused by a given amount of radiation. The number of rems of radiation is equal to the number of rads multiplied by the RBE (relative biological effectiveness) factor, which is 1 for β particles, γ rays, and x-rays and about 20 for α particles. Because actual radiation doses tend to be very small, most measurements are reported in millirems (1 mrem = 10^{-3} rem).

Wilhelm Röntgen

Born in the Lower Rhine Province of Germany, Röntgen was the only child of a cloth manufacturer and merchant. His family moved to the Netherlands where he showed no particular aptitude in school, but where he was fond of roaming the countryside. Röntgen was expelled from technical school in Utrecht after being unjustly accused of drawing a caricature of one of the teachers. He began studying mechanical engineering in Zurich, which he could enter without having the credentials of a regular student, and received a PhD at the University of Zurich in 1869. In 1876 he became professor of physics.

Natural Sources of Radiation

We are continuously exposed to measurable background radiation from a variety of natural sources, which, on average, is equal to about 150–600 mrem/yr (Figure **13.2.3**). One component of background radiation is *cosmic rays*, high-energy particles and γ rays emitted by the sun and other stars, which bombard Earth continuously. Because cosmic rays are partially absorbed by the atmosphere before they reach Earth's surface, the exposure of people living at sea level (about 30 mrem/yr) is significantly less than the exposure of people living at higher altitudes (about 50 mrem/yr in Denver, Colorado). Every 4 hours spent in an airplane at greater than 30,000 ft adds about 1 mrem to a person's annual radiation exposure.

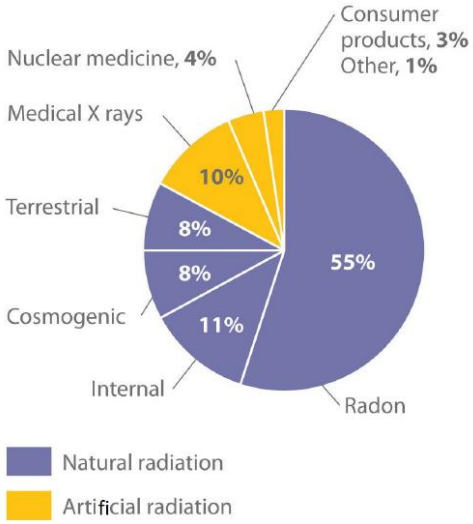


Figure **13.2.3**: The Radiation Exposure of a Typical Adult in the United States. The average radiation dose from natural sources for an adult in the United States is about 150–600 mrem/yr. Radon accounts for more than half of an adult's total radiation exposure, whereas background radiation (terrestrial and cosmogenic) and exposure from medical sources account for about 15% each. Data source: Office of Civilian Radioactive Waste Management (CC BY-SA-NC; anonymous)

A second component of background radiation is *cosmogenic radiation*, produced by the interaction of cosmic rays with gases in the upper atmosphere. When high-energy cosmic rays collide with oxygen and nitrogen atoms, neutrons and protons are released. These, in turn, react with other atoms to produce radioactive isotopes, such as ^{14}C:

$$^{14}_{7}\mathrm{N} + {}_{0}^{1}\mathrm{n} \rightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{p} \tag{13.2.3}$$

The carbon atoms react with oxygen atoms to form CO_2, which is eventually washed to Earth's surface in rain and taken up by plants. About 1 atom in 1×10^{12} of the carbon atoms in our bodies is radioactive ^{14}C, which decays by beta emission. About 5000 ^{14}C nuclei disintegrate in your body during the 15 s or so that it takes you to read this paragraph. Tritium (^{3}H) is also produced in the upper atmosphere and falls to Earth in precipitation. The total radiation dose attributable to ^{14}C is estimated to be 1 mrem/yr, while that due to ^{3}H is about 1000 times less.

The third major component of background radiation is *terrestrial radiation*, which is due to the remnants of radioactive elements that were present on primordial Earth and their decay products. For example, many rocks and minerals in the soil contain small amounts of radioactive isotopes, such as $^{232}\mathrm{Th}$ and $^{238}\mathrm{U}$ as well as radioactive daughter isotopes, such as $^{226}\mathrm{Ra}$. The amount of background radiation from these sources is about the same as that from cosmic rays (approximately 30 mrem/yr). These isotopes are also found in small amounts in building materials derived from rocks and minerals, which significantly increases the radiation exposure for people who live in brick or concrete-block houses (60–160 mrem/yr) instead of houses made of wood (10–20 mrem/yr). Our tissues also absorb radiation (about 40 mrem/yr) from naturally occurring radioactive elements that are present in our bodies. For example, the average adult contains about 140 g of potassium as the K^+ ion. Naturally occurring potassium contains 0.0117% $^{40}\mathrm{K}$, which decays by emitting both a β particle and a (\gamma\) ray. In the last 20 seconds, about the time it took you to read this paragraph, approximately 40,000 $^{40}\mathrm{K}$ nuclei disintegrated in your body.

By far the most important source of background radiation is radon, the heaviest of the noble gases (group 18). Radon-222 is produced during the decay of ^{238}U, and other isotopes of radon are produced by the decay of other heavy elements. Even though radon is chemically inert, all its isotopes are radioactive. For example, ^{222}Rn undergoes two successive alpha-decay events to give ^{214}Pb:

$$^{222}_{86}\mathrm{Rn} \rightarrow {}^{4}_{2}\alpha^{+} + {}^{218}_{84}\mathrm{Po} + {}^{4}_{2}\alpha^{+} + {}^{214}_{82}\mathrm{Pb} \tag{13.2.4}$$

Because radon is a dense gas, it tends to accumulate in enclosed spaces such as basements, especially in locations where the soil contains greater-than-average amounts of naturally occurring uranium minerals. Under most conditions, radioactive decay of radon poses no problems because of the very short range of the emitted α particle. If an atom of radon happens to be in your lungs when it decays, however, the chemically reactive daughter isotope polonium-218 can become irreversibly bound to molecules in the lung tissue. Subsequent decay of $^{218}\mathrm{Po}$ releases an α particle directly into one of the cells lining the lung, and the resulting damage can eventually cause lung cancer. The $^{218}\mathrm{Po}$ isotope is also readily absorbed by particles in cigarette smoke, which adhere to the surface of the lungs and can hold the radioactive isotope in place. Recent estimates suggest that radon exposure is a contributing factor in about 15% of the deaths due to lung cancer. Because of the potential health problem radon poses, many states require houses to be tested for radon before they can be sold. By current estimates, radon accounts for more than half of the radiation exposure of a typical adult in the United States.

Artificial Sources of Radiation

In addition to naturally occurring background radiation, humans are exposed to small amounts of radiation from a variety of artificial sources. The most important of these are the x-rays used for diagnostic purposes in medicine and dentistry, which are photons with much lower energy than γ rays. A single chest x-ray provides a radiation dose of about 10 mrem, and a dental x-ray about 2–3 mrem. Other minor sources include television screens and computer monitors with cathode-ray tubes, which also produce x-rays. Luminescent paints for watch dials originally used radium, a highly toxic alpha emitter if ingested by those painting the dials. Radium was replaced by tritium (^{3}H) and promethium (^{147}Pr), which emit low-energy β particles that are absorbed by the watch crystal or the glass covering the instrument. Radiation exposure from television screens, monitors, and luminescent dials totals about 2 mrem/yr. Residual fallout from previous atmospheric nuclear-weapons testing is estimated to account for about twice this amount, and the nuclear power industry accounts for less than 1 mrem/yr (about the same as a single 4 h jet flight).

Example 13.2.1

Calculate the annual radiation dose in rads a typical 70 kg chemistry student receives from the naturally occurring ^{40}K in his or her body, which contains about 140 g of potassium (as the K^+ ion). The natural abundance of ^{40}K is 0.0117%. Each 1.00 mol of ^{40}K undergoes 1.05×10^7 decays/s, and each decay event is accompanied by the emission of a 1.32 MeV β particle.

Given: mass of student, mass of isotope, natural abundance, rate of decay, and energy of particle

Asked for: annual radiation dose in rads

Strategy:

A. Calculate the number of moles of ^{40}K present using its mass, molar mass, and natural abundance.
B. Determine the number of decays per year for this amount of ^{40}K.
C. Multiply the number of decays per year by the energy associated with each decay event. To obtain the annual radiation dose, use the mass of the student to convert this value to rads.

Solution

A The number of moles of ^{40}K present in the body is the total number of potassium atoms times the natural abundance of potassium atoms present as ^{40}K divided by the atomic mass of ^{40}K:

$$\text{moles } ^{40}\text{K} = 140 \text{ g K} \times \frac{0.0117 \text{ mol } ^{40}\text{K}}{100 \text{ mol K}} \times \frac{1 \text{ mol K}}{40.0 \text{ g K}} = 4.10 \times 10^{-4} \text{ mol } ^{40}\text{K}$$

B We are given the number of atoms of ^{40}K that decay per second in 1.00 mol of ^{40}K, so the number of decays per year is as follows:

$$\frac{\text{decays}}{\text{year}} = 4.10 \times 10^{-4} \text{ mol}^{40}\text{ K} \times \frac{1.05 \times 10^7 \text{ decays/s}}{1.00 \text{ mol } ^{40}\text{K}} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{60 \text{ min}}{1 \text{ h}} \times \frac{24 \text{ h}}{1 \text{ day}} \times \frac{365 \text{ days}}{1 \text{ yr}}$$

C The total energy the body receives per year from the decay of ^{40}K is equal to the total number of decays per year multiplied by the energy associated with each decay event:

$$\begin{aligned}\text{total energy per year} &= \frac{1.36 \times 10^{11} \text{ decays}}{\text{yr}} \times \frac{1.32 \text{ MeV}}{\text{decays}} \times \frac{10^6 \text{ eV}}{\text{MeV}} \times \frac{1.602 \times 10^{-19} \text{ J}}{\text{eV}} \\ &= 2.87 \times 10^{-2} \text{ J/yr}\end{aligned}$$

We use the definition of the rad (1 rad = 10^{-2} J/kg of tissue) to convert this figure to a radiation dose in rads. If we assume the dose is equally distributed throughout the body, then the radiation dose per year is as follows:

$$\begin{aligned}\text{radiation dose per year} &= \frac{2.87 \times 10^{-2} \text{ J/yr}}{70.0 \text{ kg}} \times \frac{1 \text{ rad}}{1 \times 10^{-2} \text{ J/kg}} \\ &= 4.10 \times 10^{-2} \text{ rad/yr} = 41 \text{ mrad/yr}\end{aligned}$$

This corresponds to almost half of the normal background radiation most people experience.

Exercise 13.2.1

Because strontium is chemically similar to calcium, small amounts of the Sr^{2+} ion are taken up by the body and deposited in calcium-rich tissues such as bone, using the same mechanism that is responsible for the absorption of Ca^{2+}. Consequently, the radioactive strontium (^{90}Sr) found in fission waste and released by atmospheric nuclear-weapons testing is a major health concern. A normal 70 kg human body has about 280 mg of strontium, and each mole of ^{90}Sr undergoes 4.55×10^{14} decays/s by the emission of a 0.546 MeV β particle. What would be the annual radiation dose in rads for a 70 kg person if 0.10% of the strontium ingested were ^{90}Sr?

Answer

5.7×10^3 rad/yr (which is 10 times the fatal dose)

Assessing the Impact of Radiation Exposure

One of the more controversial public policy issues debated today is whether the radiation exposure from artificial sources, when combined with exposure from natural sources, poses a significant risk to human health. The effects of single radiation doses of different magnitudes on humans are listed in Table **13.2.2**. Because of the many factors involved in radiation exposure (length of exposure, intensity of the source, and energy and type of particle), it is difficult to quantify the specific dangers of one radioisotope versus another. Nonetheless, some general conclusions regarding the effects of radiation exposure are generally accepted as valid.

Table **13.2.2**: The Effects of a Single Radiation Dose on a 70 kg Human

Dose (rem)	Symptoms/Effects
< 5	no observable effect
5–20	possible chromosomal damage
20–100	temporary reduction in white blood cell count
50–100	temporary sterility in men (up to a year)
100–200	mild radiation sickness, vomiting, diarrhea, fatigue; immune system suppressed; bone growth in children retarded
> 300	permanent sterility in women
> 500	fatal to 50% within 30 days; destruction of bone marrow and intestine
> 3000	fatal within hours

Radiation doses of 600 rem and higher are invariably fatal, while a dose of 500 rem kills half the exposed subjects within 30 days. Smaller doses (≤ 50 rem) appear to cause only limited health effects, even though they correspond to tens of years of natural radiation. This does not, however, mean that such doses have no ill effects; they may cause long-term health problems, such as cancer or genetic changes that affect offspring. The possible detrimental effects of the much smaller doses attributable to artificial sources (< 100 mrem/yr) are more difficult to assess.

The tissues most affected by large, whole-body exposures are bone marrow, intestinal tissue, hair follicles, and reproductive organs, all of which contain rapidly dividing cells. The susceptibility of rapidly dividing cells to radiation exposure explains why cancers are often treated by radiation. Because cancer cells divide faster than normal cells, they are destroyed preferentially by radiation. Long-term radiation-exposure studies on fruit flies show a linear relationship between the number of genetic defects and both the magnitude of the dose and the exposure time. In contrast, similar studies on mice show a much lower number of defects when a given dose of radiation is spread out over a long period of time rather than received all at once. Both patterns are plotted in Figure **13.2.4**, but which of the two is applicable to humans? According to one hypothesis, mice have very low risk from low doses because their bodies have ways of dealing with the damage caused by natural radiation. At much higher doses, however, their natural repair mechanisms are overwhelmed, leading to irreversible damage. Because mice are biochemically much more similar to humans than are fruit flies, many scientists believe that this model also applies to humans. In contrast, the linear model assumes that all exposure to radiation is intrinsically damaging and suggests that stringent regulation of low-level radiation exposure is necessary. Which view is more accurate? The answer—while yet unknown—has extremely important consequences for regulating radiation exposure.

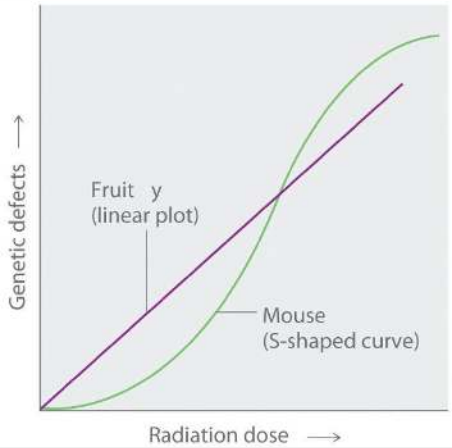


Figure **13.2.4**: Two Possible Relationships between the Number of Genetic Defects and Radiation Exposure. Studies on fruit flies show a linear relationship between the number of genetic defects and the magnitude of the radiation dose and exposure time, which is consistent with a cumulative effect of radiation. In contrast, studies on mice show an S-shaped curve, which suggests that the number of defects is lower when radiation exposure occurs over a longer time. Which of these relationships is more applicable to humans is a matter of considerable debate. (CC BY-SA-NC; anonymous)

Graph of genetic defects against radiation dose. Fruit is graphed in purple and has a linear plot. Mouse is graphed in green and has a S shaped curve.

Summary

Nonionizing radiation is relatively low in energy and can be used as a heat source, whereas ionizing radiation, which is higher in energy, can penetrate biological tissues and is highly reactive. The effects of radiation on matter depend on the energy of the radiation. Nonionizing radiation is relatively low in energy, and the energy is transferred to matter in the form of heat. Ionizing radiation is relatively high in energy, and when it collides with an atom, it can completely remove an electron to form a positively charged ion that can damage biological tissues. Alpha particles do not penetrate very far into matter, whereas γ rays penetrate more deeply. Common units of radiation exposure, or dose, are the roentgen (R), the amount of energy absorbed by dry air, and the rad (radiation absorbed dose), the amount of radiation that produces 0.01 J of energy in 1 kg of matter. The rem (roentgen equivalent in man) measures the actual amount of tissue damage caused by a given amount of radiation. Natural sources of radiation include cosmic radiation, consisting of high-energy particles and γ rays emitted by the sun and other stars; cosmogenic radiation, which is produced by the interaction of cosmic rays with gases in the upper atmosphere; and terrestrial radiation, from radioactive elements present on primordial Earth and their decay products. The risks of ionizing radiation depend on the intensity of the radiation, the mode of exposure, and the duration of the exposure.

13.2: The Effects of Radiation on Life is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **21.8: Biological Effects of Radiation** by Anonymous is licensed CC BY-NC-SA 3.0.

13.3: Radioactivity in Medicine and Other Applications

Learning Objectives

- List common applications of radioactive isotopes

Radioactive isotopes have the same chemical properties as stable isotopes of the same element, but they emit radiation, which can be detected. If we replace one (or more) atom(s) with radioisotope(s) in a compound, we can track them by monitoring their radioactive emissions. This type of compound is called a radioactive tracer (or radioactive label). Radioisotopes are used to follow the paths of biochemical reactions or to determine how a substance is distributed within an organism. Radioactive tracers are also used in many medical applications, including both diagnosis and treatment. They are used to measure engine wear, analyze the geological formation around oil wells, and much more.

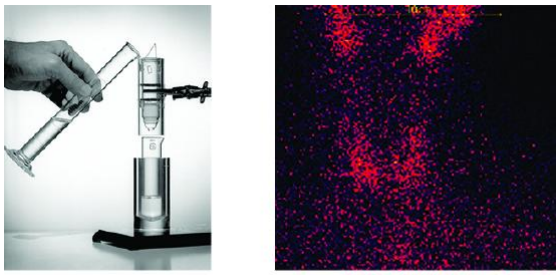
Radioisotopes have revolutionized medical practice, where they are used extensively. Over 10 million nuclear medicine procedures and more than 100 million nuclear medicine tests are performed annually in the United States. Four typical examples of radioactive tracers used in medicine are technetium-99 ($^{99}_{43}\mathrm{Tc}$), thallium-201 ($^{201}_{81}\mathrm{Tl}$), iodine-131 ($^{131}_{53}\mathrm{I}$), and sodium-24 ($^{24}_{11}\mathrm{Na}$). Damaged tissues in the heart, liver, and lungs absorb certain compounds of technetium-99 preferentially. After it is injected, the location of the technetium compound, and hence the damaged tissue, can be determined by detecting the γ rays emitted by the Tc-99 isotope. Thallium-201 (Figure **13.3.1**) becomes concentrated in healthy heart tissue, so the two isotopes, Tc-99 and Tl-201, are used together to study heart tissue. Iodine-131 concentrates in the thyroid gland, the liver, and some parts of the brain. It can therefore be used to monitor goiter and treat thyroid conditions, such as Grave's disease, as well as liver and brain tumors. Salt solutions containing compounds of sodium-24 are injected into the bloodstream to help locate obstructions to the flow of blood.



Figure **13.3.1**: Administering thallium-201 to a patient and subsequently performing a stress test offer medical professionals an opportunity to visually analyze heart function and blood flow. (credit: modification of work by "Blue0ctane"/Wikimedia Commons)

A medical professional is assisting a topless elderly man on a treadmill with sensors and electrical wires connected to his torso.

Radioisotopes used in medicine typically have short half-lives—for example, the ubiquitous Tc-99m has a half-life of 6.01 hours. This makes Tc-99m essentially impossible to store and prohibitively expensive to transport, so it is made on-site instead. Hospitals and other medical facilities use Mo-99 (which is primarily extracted from U-235 fission products) to generate Tc-99. Mo-99 undergoes β decay with a half-life of 66 hours, and the Tc-99 is then chemically extracted (Figure **13.3.2**). The parent nuclide Mo-99 is part of a molybdate ion, $\mathrm{MoO_4^{2-}}$; when it decays, it forms the pertechnetate ion, $\mathrm{TcO_4^-}$. These two water-soluble ions are separated by column chromatography, with the higher charge molybdate ion adsorbing onto the alumina in the column, and the lower charge pertechnetate ion passing through the column in the solution. A few micrograms of Mo-99 can produce enough Tc-99 to perform as many as 10,000 tests.



(a) (b)

Figure **13.3.2**: (a) The first Tc-99m generator (circa 1958) is used to separate Tc-99 from Mo-99. The MoO_4^{2-} *is retained by the matrix in the column, whereas the* TcO_4^- *passes through and is collected. (b) Tc-99 was used in this scan of the neck of a patient with Grave's disease. The scan shows the location of high concentrations of Tc-99. (credit a: modification of work by the Department of Energy; credit b: modification of work by "MBq"/Wikimedia Commons)*

The first image shows a hand pouring a liquid from a measuring cylinder into a column held up by a clamp. Below the column is a glass tube. The second picture shows red dots on a dark background dispersed everywhere with four spots of heavily concentrated regions.

Radioisotopes can also be used, typically in higher doses than as a tracer, as treatment. Radiation therapy is the use of high-energy radiation to damage the DNA of cancer cells, which kills them or keeps them from dividing (Figure **13.3.3**). A cancer patient may receive external beam radiation therapy delivered by a machine outside the body, or internal radiation therapy (brachytherapy) from a radioactive substance that has been introduced into the body. Note that chemotherapy is similar to internal radiation therapy in that the cancer treatment is injected into the body, but differs in that chemotherapy uses chemical rather than radioactive substances to kill the cancer cells.

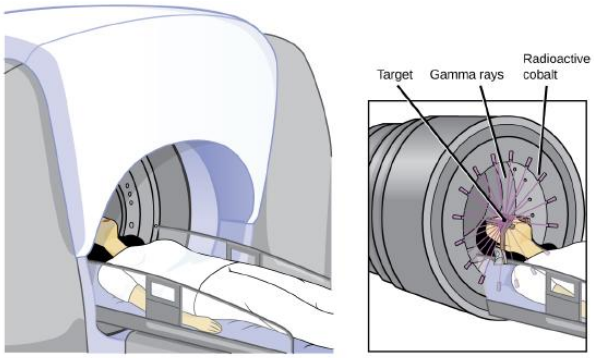


Figure **13.3.3**: The cartoon in (a) shows a cobalt-60 machine used in the treatment of cancer. The diagram in (b) shows how the gantry of the Co-60 machine swings through an arc, focusing radiation on the targeted region (tumor) and minimizing the amount of radiation that passes through nearby regions.

A. A woman lies down as she goes into a dome shaped medical machine. B. A closer view of the women's head shows gamma rays from radioactive cobalt attacks the target on the woman's head.

Cobalt-60 is a synthetic radioisotope produced by the neutron activation of Co-59, which then undergoes β decay to form Ni-60, along with the emission of γ radiation. The overall process is:

$$^{59}_{27}\text{Co} + {}^{1}_{0}\text{n} \longrightarrow {}^{60}_{27}\text{Co} \longrightarrow {}^{60}_{28}\text{Ni} + {}^{0}_{-1}\beta + 2{}^{0}_{0}\gamma$$

The overall decay scheme for this is shown graphically in Figure **13.3.4**.

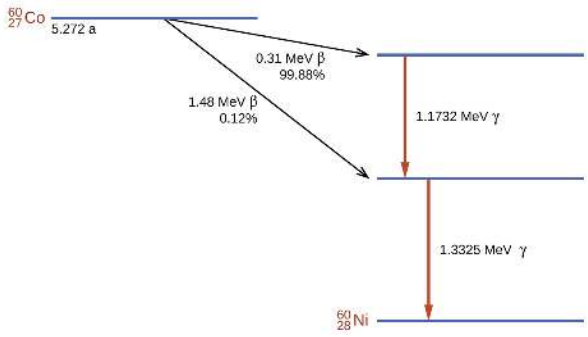


Figure 13.3.4: Co-60 undergoes a series of radioactive decays. The γ emissions are used for radiation therapy.

Radioisotopes are used in diverse ways to study the mechanisms of chemical reactions in plants and animals. These include labeling fertilizers in studies of nutrient uptake by plants and crop growth, investigations of digestive and milk-producing processes in cows, and studies on the growth and metabolism of animals and plants.

For example, the radioisotope C-14 was used to elucidate the details of how photosynthesis occurs. The overall reaction is:

$$6\,CO_2(g) + 6\,H_2O(l) \longrightarrow C_6H_{12}O_6(s) + 6\,O_2(g),$$

but the process is much more complex, proceeding through a series of steps in which various organic compounds are produced. In studies of the pathway of this reaction, plants were exposed to CO_2 containing a high concentration of $^{14}_{6}C$. At regular intervals, the plants were analyzed to determine which organic compounds contained carbon-14 and how much of each compound was present. From the time sequence in which the compounds appeared and the amount of each present at given time intervals, scientists learned more about the pathway of the reaction.

Commercial applications of radioactive materials are equally diverse (Figure 13.3.5). They include determining the thickness of films and thin metal sheets by exploiting the penetration power of various types of radiation. Flaws in metals used for structural purposes can be detected using high-energy gamma rays from cobalt-60 in a fashion similar to the way X-rays are used to examine the human body. In one form of pest control, flies are controlled by sterilizing male flies with γ radiation so that females breeding with them do not produce offspring. Many foods are preserved by radiation that kills microorganisms that cause the foods to spoil.

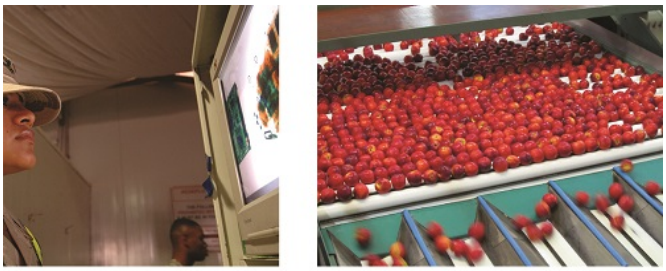


Figure 13.3.5: Common commercial uses of radiation include (a) X-ray examination of luggage at an airport and (b) preservation of food. (credit a: modification of work by the Department of the Navy; credit b: modification of work by the US Department of Agriculture)

A. A man is observing a monitor which shows the X-ray of luggages. B. Many apples on processing belts.

Americium-241, an α emitter with a half-life of 458 years, is used in tiny amounts in ionization-type smoke detectors (Figure 13.3.6). The α emissions from Am-241 ionize the air between two electrode plates in the ionizing chamber. A battery supplies a potential that causes movement of the ions, thus creating a small electric current. When smoke enters the chamber, the movement of the ions is impeded, reducing the conductivity of the air. This causes a marked drop in the current, triggering an alarm.

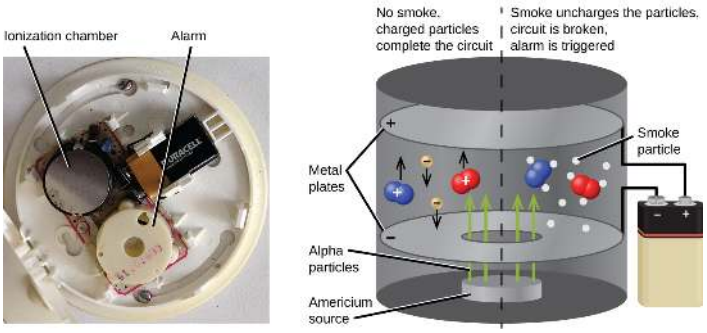


Figure 13.3.6: Inside a smoke detector, Am-241 emits α particles that ionize the air, creating a small electric current. During a fire, smoke particles impede the flow of ions, reducing the current and triggering an alarm. (credit a: modification of work by "Muffet"/Wikimedia Commons)

The inside of a smoke detector is shown with the alarm and ionization chamber labeled. In the picture beside it, a schematic shows the mechanisms of a smoke detector. The two oppositely charged metals plates in the detector are shown along with the Americium source on the bottom part emitting alpha particles. The schematic is divided into two parts, one to show the presence and the other for the absence of smoke.

Summary

Compounds known as radioactive tracers can be used to follow reactions, track the distribution of a substance, diagnose and treat medical conditions, and much more. Other radioactive substances are helpful for controlling pests, visualizing structures, providing fire warnings, and for many other applications. Hundreds of millions of nuclear medicine tests and procedures, using a wide variety of radioisotopes with relatively short half-lives, are performed every year in the US. Most of these radioisotopes have relatively short half-lives; some are short enough that the radioisotope must be made on-site at medical facilities. Radiation therapy uses high-energy radiation to kill cancer cells by damaging their DNA. The radiation used for this treatment may be delivered externally or internally.

Glossary

chemotherapy

similar to internal radiation therapy, but chemical rather than radioactive substances are introduced into the body to kill cancer cells

external beam radiation therapy

radiation delivered by a machine outside the body

internal radiation therapy

(also, brachytherapy) radiation from a radioactive substance introduced into the body to kill cancer cells

radiation therapy

use of high-energy radiation to damage the DNA of cancer cells, which kills them or keeps them from dividing

radioactive tracer

(also, radioactive label) radioisotope used to track or follow a substance by monitoring its radioactive emissions

13.3: Radioactivity in Medicine and Other Applications is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

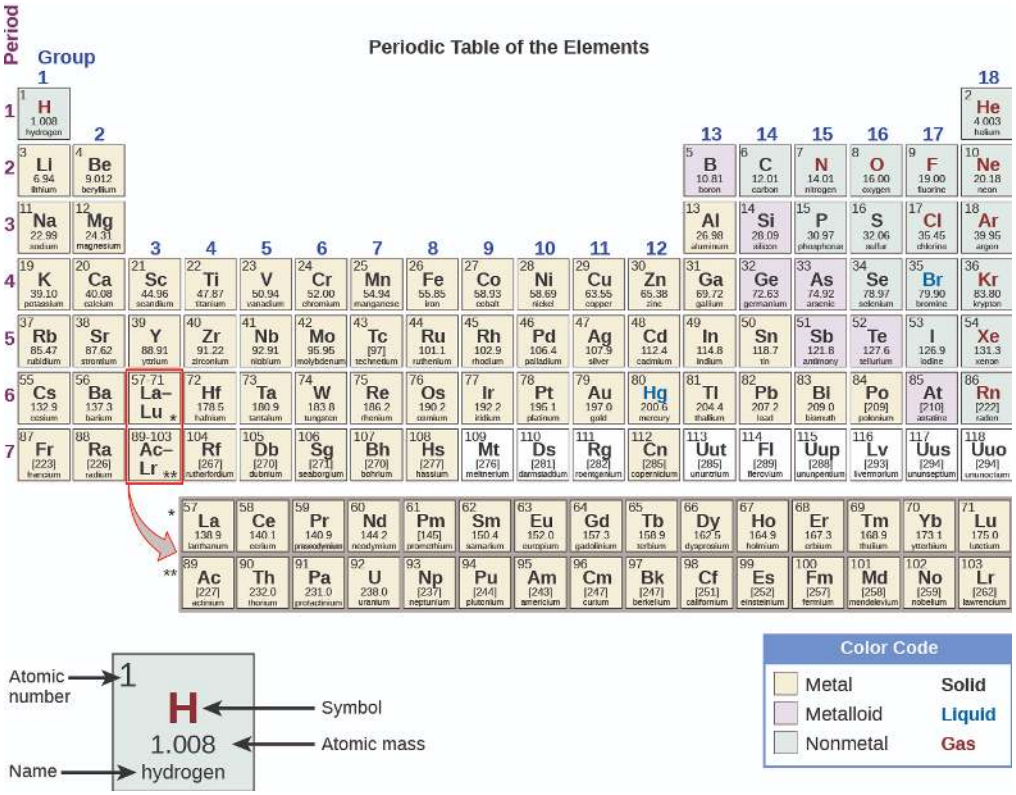
- **21.5: Uses of Radioisotopes** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

14: Appendices

This page is a placeholder created because the page was deleted, but has sub-pages.

This page titled 14: Appendices is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

14.1: The Periodic Table



This page titled 14.1: The Periodic Table is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

14.2: Essential Mathematics

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:

$$1000 = 1 \times 10^3 \tag{14.2.1}$$
$$100 = 1 \times 10^2 \tag{14.2.2}$$
$$10 = 1 \times 10^1 \tag{14.2.3}$$
$$1 = 1 \times 10^0 \tag{14.2.4}$$
$$0.1 = 1 \times 10^{-1} \tag{14.2.5}$$
$$0.001 = 1 \times 10^{-3} \tag{14.2.6}$$
$$2386 = 2.386 \times 1000 = 2.386 \times 10^3 \tag{14.2.7}$$
$$0.123 = 1.23 \times 0.1 = 1.23 \times 10^{-1} \tag{14.2.8}$$

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 $0.00000000036 \times 10^{-10}$.

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.

Adding Exponentials Add 5.00×10^{-5} and 3.00×10^{-3}.

Solution

$$3.00 \times 10^{-3} = 300 \times 10^{-5} \tag{14.2.9}$$
$$(5.00 \times 10^{-5}) + (300 \times 10^{-5}) = 305 \times 10^{-5} = 3.05 \times 10^{-3} \tag{14.2.10}$$

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.

Subtracting Exponentials Subtract 4.0×10^{-7} from 5.0×10^{-6}.

Solution

$$4.0 \times 10^{-7} = 0.40 \times 10^{-6} \tag{14.2.11}$$
$$(5.0 \times 10^{-6}) - (0.40 \times 10^{-6}) = 4.6 \times 10^{-6}$$

Multiplication of Exponentials

Multiply the digit terms in the usual way and add the exponents of the exponential terms.

Multiplying Exponentials Multiply 4.2×10^{-8} by 2.0×10^3.

Solution

$$(4.2 \times 10^{-8}) \times (2.0 \times 10^3) = (4.2 \times 2.0) \times 10^{(-8)+(+3)} = 8.4 \times 10^{-5} \tag{14.2.12}$$

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.

Dividing Exponentials Divide 3.6×10^5 by 6.0×10^{-4}.

Solution

$$\frac{3.6 \times 10^{-5}}{6.0 \times 10^{-4}} = \left(\frac{3.6}{6.0}\right) \times 10^{(-5)-(-4)} = 0.60 \times 10^{-1} = 6.0 \times 10^{-2} \tag{14.2.13}$$

Squaring of Exponentials

Square the digit term in the usual way and multiply the exponent of the exponential term by 2.

Squaring Exponentials Square the number 4.0×10^{-6}.

Solution

$$(4.0 \times 10^{-6})^2 = 4 \times 4 \times 10^{2\times(-6)} = 16 \times 10^{-12} = 1.6 \times 10^{-11} \tag{14.2.14}$$

Cubing of Exponentials

Cube the digit term in the usual way and multiply the exponent of the exponential term by 3.

Cubing Exponentials Cube the number 2×10^4.

Solution

$$(2 \times 10^4)^3 = 2 \times 2 \times 2 \times 10^{3\times4} = 8 \times 10^{12} \tag{14.2.15}$$

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.

Finding the Square Root of Exponentials Find the square root of 1.6×10^{-7}.

Solution

$$1.6 \times 10^{-7} = 16 \times 10^{-8} \tag{14.2.16}$$

$$\sqrt{16 \times 10^{-8}} = \sqrt{16} \times \sqrt{10^{-8}} = \sqrt{16} \times 10^{-\frac{8}{2}} = 4.0 \times 10^{-4} \tag{14.2.17}$$

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).

Addition and Subtraction with Significant Figures Add 4.383 g and 0.0023 g.

Solution

$$\underline{4.383}\ \text{g} \tag{14.2.18}$$

$$\underline{0.0023}\ \text{g} \tag{14.2.19}$$

$$\underline{4.385}\ \text{g} \tag{14.2.20}$$

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.

Multiplication and Division with Significant Figures Multiply 0.6238 by 6.6.

Solution

$$0.6238 \times 6.6 = 4.1 \tag{14.2.21}$$

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).

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,

$$60 = 10^{1.7782} \tag{14.2.22}$$

The common logarithm of a number less than 1 has a negative value. The logarithm of 0.03918 is −1.4069, or

$$0.03918 = 10^{-1.4069} = \frac{1}{10^{1.4069}} \tag{14.2.23}$$

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,

$$10 = e^{2.303} = 2.7182818^{2.303} \tag{14.2.24}$$

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.

$$\log xy = \log x + \log y, \text{ and } \ln xy = \ln x + \ln y \tag{14.2.25}$$

2. The logarithm of the number resulting from the division of two numbers is the difference between the logarithms of the two numbers.

$$\log \frac{x}{y} = \log x - \log y, \text{ and } \ln \frac{x}{y} = \ln x - \ln y \tag{14.2.26}$$

3. The logarithm of a number raised to an exponent is the product of the exponent and the logarithm of the number.

$$\log x^n = n \log x \text{ and } \ln x^n = n \ln x \tag{14.2.27}$$

The Solution of Quadratic Equations

Mathematical functions of this form are known as second-order polynomials or, more commonly, quadratic functions.

$$ax^2 + bx + c = 0 \tag{14.2.28}$$

The solution or roots for any quadratic equation can be calculated using the following formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \tag{14.2.29}$$

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

$$x = \frac{-13 \pm \sqrt{(13)^2 - 4 \times 3 \times (-10)}}{2 \times 3} \tag{14.2.30}$$

$$x = \frac{-13 \pm \sqrt{169 + 120}}{6} = \frac{-13 \pm \sqrt{289}}{6} = \frac{-13 \pm 17}{6} \tag{14.2.31}$$

The two roots are therefore

$$x = \frac{-13 + 17}{6} = \frac{2}{3} \text{ and } x = \frac{-13 - 17}{6} = -5 \tag{14.2.32}$$

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.

Two-Dimensional (*x*-*y*) Graphing

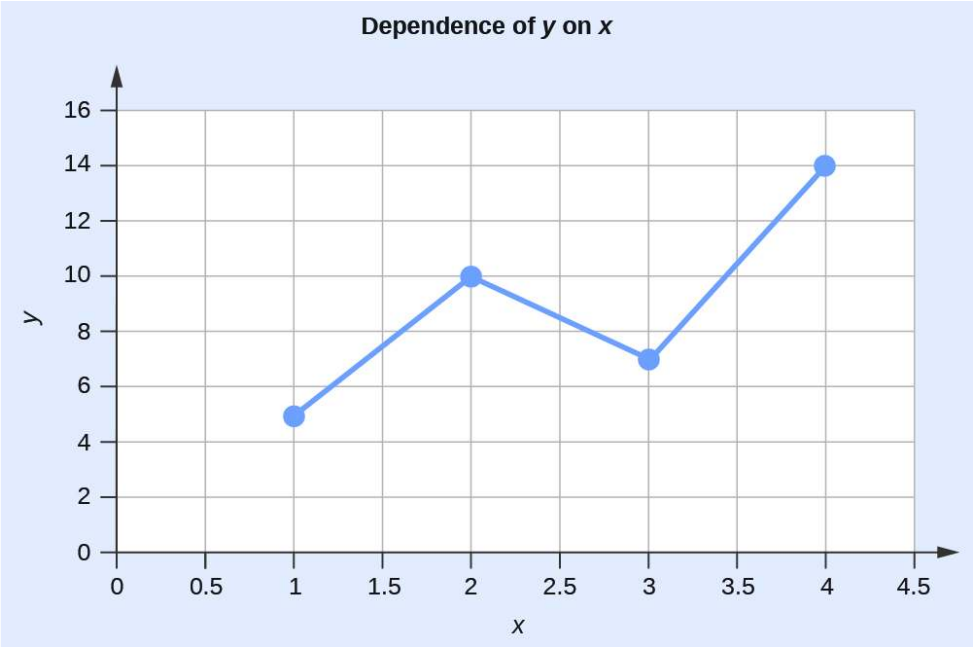
The relationship between any two properties of a system can be represented graphically by a two-dimensional data plot. Such a graph has two axes: a horizontal one corresponding to the independent variable, or the variable whose value is being controlled (*x*), and a vertical axis corresponding to the 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.

Graphing the Dependence of *y* on *x*

x	*y*
1	5
2	10
3	7
4	14

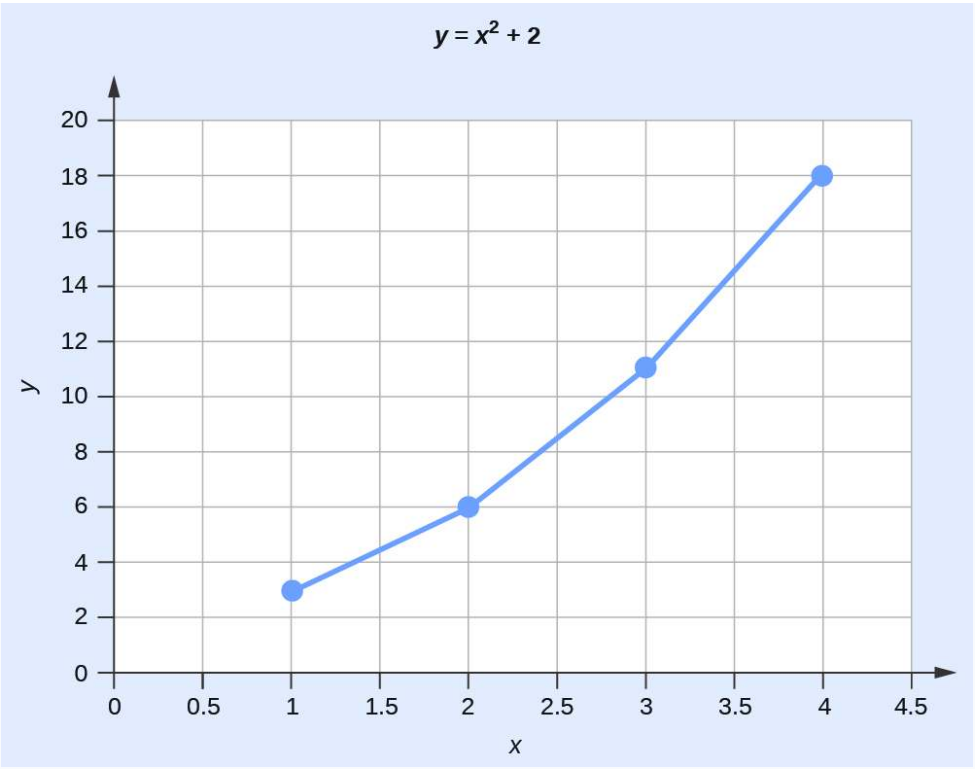
This table contains the following points: (1,5), (2,10), (3,7), and (4,14). Each of these points can be plotted on a graph and connected to produce a graphical representation of the dependence of *y* on *x*.



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.

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.

x	$y = x^2 + 2$
1	3
2	6
3	11
4	18



This page titled 14.2: Essential Mathematics is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

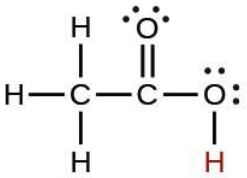
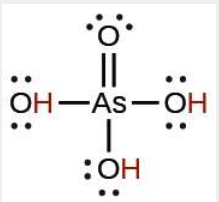
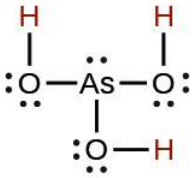
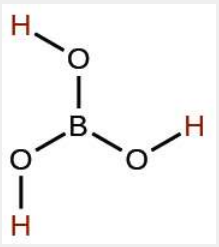
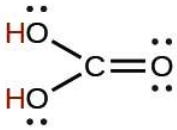
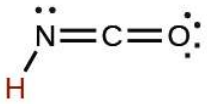
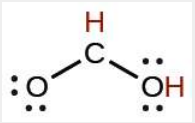
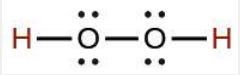
14.3: Fundamental Physical Constants

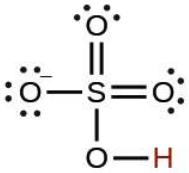
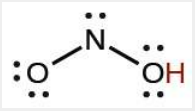
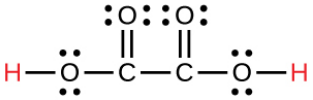
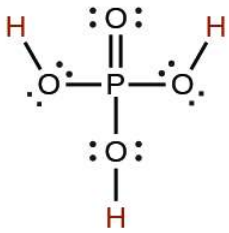
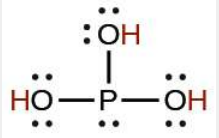
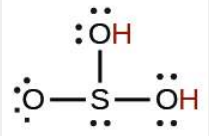
Fundamental Physical Constants	
Name and Symbol	Value
atomic mass unit (amu)	$1.6605402 \times 10^{-27}$ kg
Avogadro's number	6.0221367×10^{23} mol^{-1}
Boltzmann's constant (k)	1.380658×10^{-23} J K^{-1}
charge-to-mass ratio for electron (e/m_e)	$1.75881962 \times 10^{11}$ C kg^{-1}
electron charge (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 14.3: Fundamental Physical Constants is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

14.4: Ionization Constants of Weak Acids

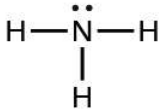
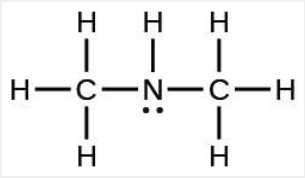
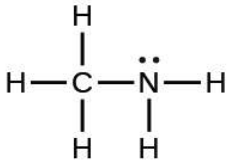
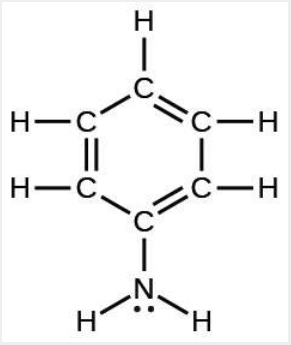
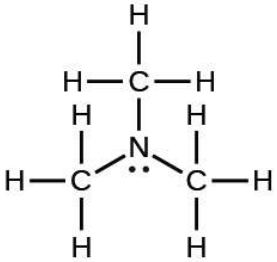
https://chem.libretexts.org/@go/page/216803

Ionization Constants of Weak Acids			
Acid	Formula	K_a at 25 °C	Lewis Structure
acetic	$CH_3CO_2\mathbf{H}$	1.8×10^{-5}	
arsenic	$\mathbf{H_3}AsO_4$	5.5×10^{-3}	
	$H_2AsO_4^-$	1.7×10^{-7}	
	$HAsO_4^{2-}$	5.1×10^{-12}	
arsenous	$\mathbf{H_3}AsO_3$	5.1×10^{-10}	
boric	$\mathbf{H_3}BO_3$	5.4×10^{-10}	
carbonic	$\mathbf{H_2}CO_3$	4.3×10^{-7}	
	HCO_3^-	5.6×10^{-11}	
cyanic	**H**CNO	2×10^{-4}	
formic	$HCO_2\mathbf{H}$	1.8×10^{-4}	
hydrazoic	$\mathbf{H}N_3$	2.5×10^{-5}	
hydrocyanic	**H**CN	4.9×10^{-10}	
hydrofluoric	**H**F	3.5×10^{-4}	
hydrogen peroxide	$\mathbf{H_2}O_2$	2.4×10^{-12}	

Ionization Constants of Weak Acids			
Acid	Formula	K_a at 25 °C	Lewis Structure
hydrogen selenide	H_2Se	1.29×10^{-4}	
	HSe^-	1×10^{-12}	
hydrogen sulfate ion	HSO_4^-	1.2×10^{-2}	
hydrogen sulfide	H_2S	8.9×10^{-8}	
	HS^-	1.0×10^{-19}	
hydrogen telluride	H_2Te	2.3×10^{-3}	
	HTe^-	1.6×10^{-11}	
hypobromous	HBrO	2.8×10^{-9}	
hypochlorous	HClO	2.9×10^{-8}	
nitrous	HNO_2	4.6×10^{-4}	
oxalic	$H_2C_2O_4$	6.0×10^{-2}	
	$HC_2O_4^-$	6.1×10^{-5}	
phosphoric	H_3PO_4	7.5×10^{-3}	
	$H_2PO_4^-$	6.2×10^{-8}	
	HPO_4^{2-}	4.2×10^{-13}	
phosphorous	H_3PO_3	5×10^{-2}	
	$H_2PO_3^-$	2.0×10^{-7}	
sulfurous	H_2SO_3	1.6×10^{-2}	
	HSO_3^-	6.4×10^{-8}	

This page titled 14.4: Ionization Constants of Weak Acids is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

14.5: Ionization Constants of Weak Bases

Ionization Constants of Weak Bases		
Base	Lewis Structure	K_b at 25 °C
ammonia		1.8×10^{-5}
dimethylamine		5.9×10^{-4}
methylamine		4.4×10^{-4}
phenylamine (aniline)		4.3×10^{-10}
trimethylamine		6.3×10^{-5}

This page titled 14.5: Ionization Constants of Weak Bases is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

14.6: Units and Conversion Factors

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)
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)

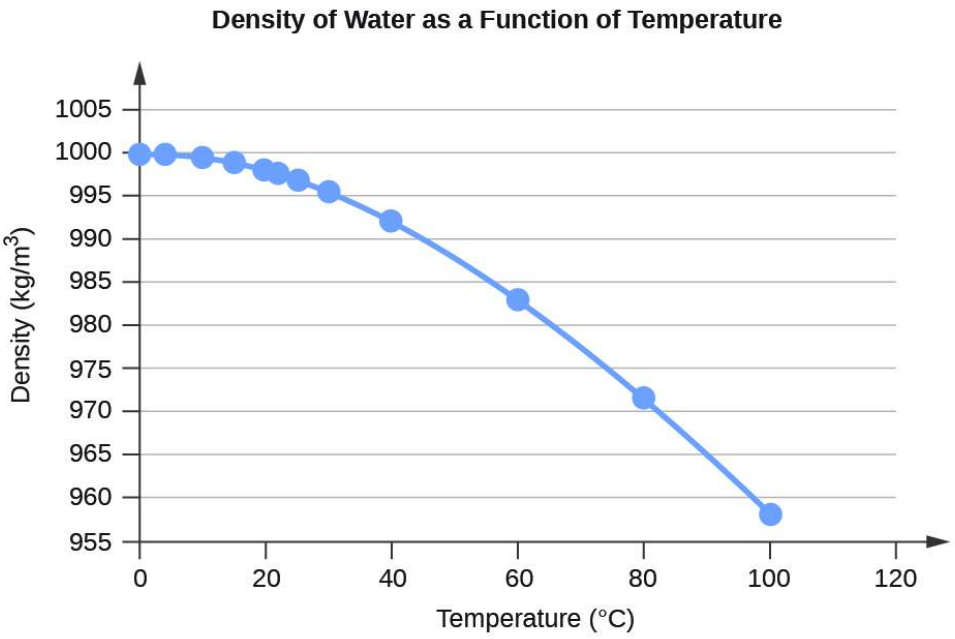
Footnotes

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 14.6: Units and Conversion Factors is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

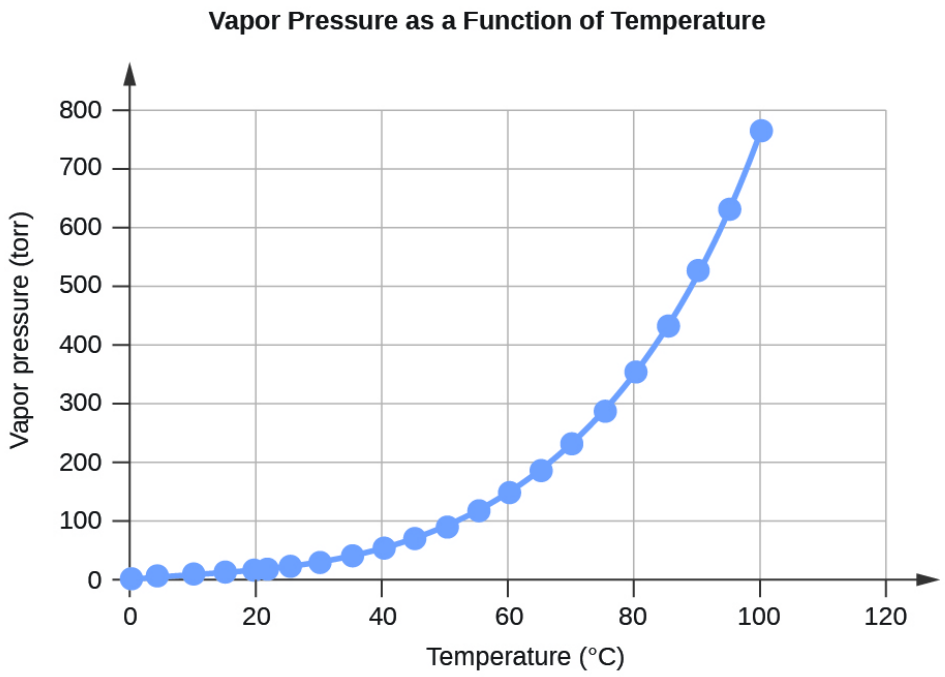
14.7: Water Properties

Water Density (kg/m^3) 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

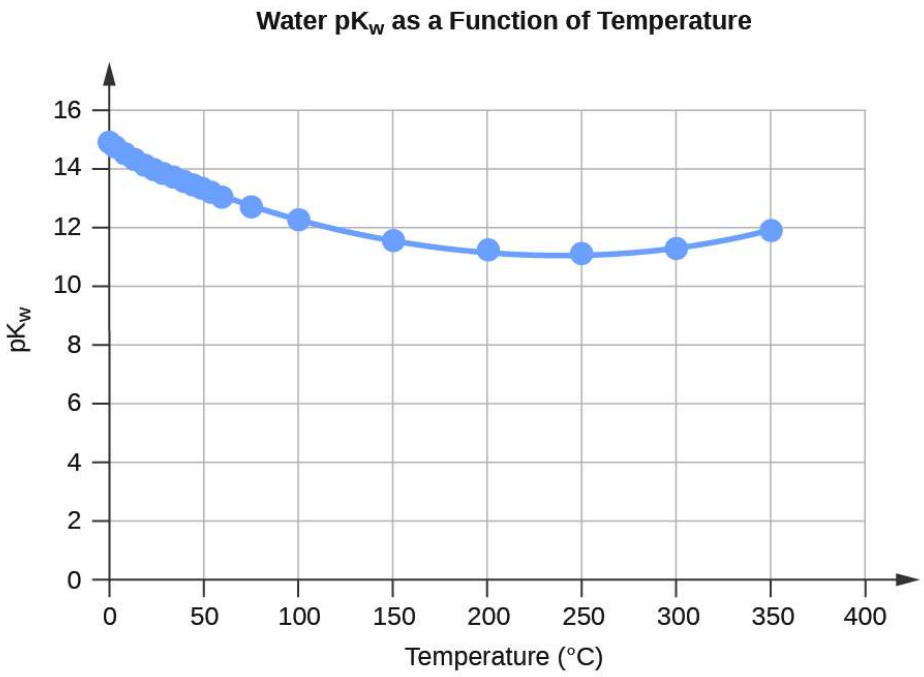


https://chem.libretexts.org/@go/page/216806

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
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 K_w and pK_w at Different Temperatures (°C)		
Temperature	K_w 10^{-14}	pK_w[2]
0	0.112	14.95
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

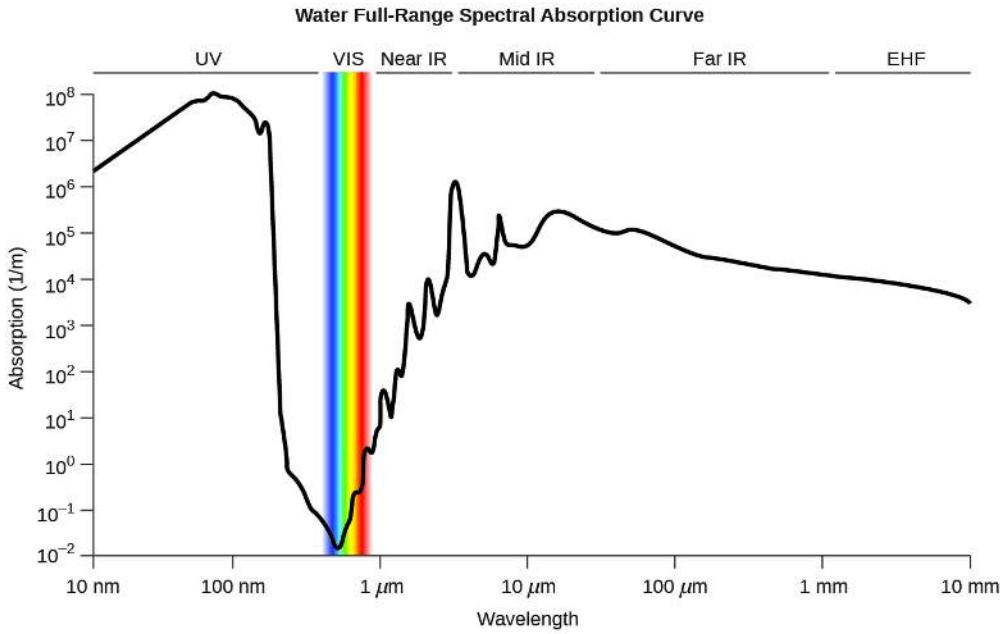


Specific Heat Capacity for Water
$C°(H_2O(l)) = 4184\ J{\cdot}K^{-1}{\cdot}kg^{-1} = 4.184\ J{\cdot}g^{-1}{\cdot}°C^{-1}$
$C°(H_2O(s)) = 1864\ J{\cdot}K^{-1}{\cdot}kg^{-1}$
$C°(H_2O(g)) = 2093\ J{\cdot}K^{-1}{\cdot}kg^{-1}$

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
$K_f = 1.86°C{\cdot}kg{\cdot}mol^{-1}$ (cryoscopic constant)
$K_b = 0.51°C{\cdot}kg{\cdot}mol^{-1}$ (ebullioscopic constant)

<figure class="ui-has-child-figcaption" id="CNX_Chem_00_EE_LiqWatAbso">



<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).</figcaption> </figure>

Footnotes

1. 1 Data for t < 0 °C are for supercooled water
2. 2 $pK_w = -\log_{10}(K_w)$

This page titled 14.7: Water Properties is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

Index

B

Balancing a Chemical Equation

5.3: How to Write Balanced Chemical Equations

C

Coefficients and Subscripts

5.3: How to Write Balanced Chemical Equations

combustion reaction

5.8: Oxidation–Reduction Reactions

complete ionic equation

5.6: Writing Chemical Equations for Reactions in Solution- Molecular, Complete Ionic, and Net Ionic Equations

N

net ionic equation

5.6: Writing Chemical Equations for Reactions in Solution- Molecular, Complete Ionic, and Net Ionic Equations

O

oxidation number

5.8: Oxidation–Reduction Reactions

P

precipitation reaction

5.5: Precipitation Reactions

R

redox reaction

5.8: Oxidation–Reduction Reactions

S

spectator ions

5.6: Writing Chemical Equations for Reactions in Solution- Molecular, Complete Ionic, and Net Ionic Equations

Glossary

Sample Word 1 | Sample Definition 1

Detailed Licensing

Overview

Title: Old Textbook for Chemistry 143 - 2019 to 2021

Webpages: 98

Applicable Restrictions: Noncommercial

All licenses found:

- CC BY 4.0: 76.5% (75 pages)
- Undeclared: 22.4% (22 pages)
- CC BY-NC 4.0: 1% (1 page)

By Page

- Old Textbook for Chemistry 143 - 2019 to 2021 - *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: Chemistry in Context - *CC BY 4.0*
    - 1.2: Measurements - *CC BY 4.0*
    - 1.3: Measurement Uncertainty, Accuracy, and Precision - *CC BY 4.0*
    - 1.4: Mathematical Treatment of Measurement Results - *CC BY 4.0*
    - 1.5: Phases and Classification of Matter - *CC BY 4.0*
    - 1.6: Physical and Chemical Properties - *CC BY 4.0*
    - 1.E: Essential Ideas of Chemistry (Exercises) - *CC BY 4.0*
  - 2: Atoms, Molecules, and Ions - *CC BY 4.0*
    - 2.1: Early Ideas in Atomic Theory - *CC BY 4.0*
    - 2.2: Evolution of Atomic Theory - *CC BY 4.0*
    - 2.3: Atomic Structure and Symbolism - *CC BY 4.0*
    - 2.4: Chemical Formulas - *CC BY 4.0*
    - 2.5: Formula Mass and the Mole Concept - *CC BY 4.0*
    - 2.6: Determining Empirical and Molecular Formulas - *CC BY 4.0*
    - 2.7: Chemical Nomenclature - *CC BY 4.0*
  - 3: Electronic Structure and Periodic Properties - *CC BY 4.0*
    - 3.1: Electromagnetic Energy - *CC BY 4.0*
    - 3.2: The Bohr Model - *CC BY 4.0*
    - 3.3: Electronic Structure of Atoms (Electron Configurations) - *CC BY 4.0*
    - 3.4: The Periodic Table - *CC BY 4.0*
    - 3.5: Periodic Variations in Element Properties - *CC BY 4.0*
    - 3.6: Molecular and Ionic Compounds - *CC BY 4.0*
    - 3.E: Electronic Structure and Periodic Properties (Exercises) - *CC BY 4.0*
  - 4: Chemical Bonding and Molecular Geometry - *CC BY 4.0*
    - 4.1: Ionic Bonding - *CC BY 4.0*
    - 4.2: Covalent Bonding - *CC BY 4.0*
    - 4.3: Lewis Symbols and Structures - *CC BY 4.0*
    - 4.4: Molecular Structure and Polarity - *CC BY 4.0*
  - 5: Chemical Reactions - *Undeclared*
    - 5.1: Evidence of a Chemical Reaction - *Undeclared*
    - 5.2: Chemical Equations - *Undeclared*
    - 5.3: How to Write Balanced Chemical Equations - *Undeclared*
    - 5.4: Aqueous Solutions and Solubility - Compounds Dissolved in Water - *Undeclared*
    - 5.5: Precipitation Reactions - *Undeclared*
    - 5.6: Writing Chemical Equations for Reactions in Solution- Molecular, Complete Ionic, and Net Ionic Equations - *Undeclared*
    - 5.7: Acid–Base and Gas Evolution Reactions - *Undeclared*
    - 5.8: Oxidation–Reduction Reactions - *CC BY-NC 4.0*
    - 5.9: Classifying Chemical Reactions - *Undeclared*
  - 6: Stoichiometry of Chemical Reactions - *CC BY 4.0*
    - 6.1: Reaction Stoichiometry - *CC BY 4.0*
    - 6.2: Reaction Yields - *CC BY 4.0*
    - 6.3: Quantitative Chemical Analysis - *CC BY 4.0*
    - 6.E: Stoichiometry of Chemical Reactions (Exercises) - *CC BY 4.0*
  - 7: Gases - *CC BY 4.0*
    - 7.1: Gas Pressure - *CC BY 4.0*

- 7.2: Relating Pressure, Volume, Amount, and Temperature- The Ideal Gas Law - *CC BY 4.0*
- 7.3: Stoichiometry of Gaseous Substances, Mixtures, and Reactions - *CC BY 4.0*
- 7.4: The Kinetic-Molecular Theory - *CC BY 4.0*
- 7.E: Gases (Exercises) - *CC BY 4.0*

8: Thermochemistry - *CC BY 4.0*
- 8.1: Energy Basics - *CC BY 4.0*
- 8.2: Enthalpy - *CC BY 4.0*

9: Liquids and Solids - *CC BY 4.0*
- 9.1: Intermolecular Forces - *CC BY 4.0*
- 9.2: Properties of Liquids - *CC BY 4.0*
- 9.3: Phase Transitions - *CC BY 4.0*

10: Solutions and Colloids - *CC BY 4.0*
- 10.1: The Dissolution Process - *CC BY 4.0*
- 10.2: Molarity - *CC BY 4.0*
- 10.3: Other Units for Solution Concentrations - *CC BY 4.0*
- 10.4: Solubility - *CC BY 4.0*
- 10.5: Colligative Properties - *CC BY 4.0*
- 10.6: Colloids - *CC BY 4.0*

11: Fundamental Equilibrium Concepts - *CC BY 4.0*
- 11.1: Chemical Equilibria - *CC BY 4.0*
- 11.2: Equilibrium Constants - *CC BY 4.0*
- 11.3: Shifting Equilibria- Le Châtelier's Principle - *CC BY 4.0*
- 11.4: Equilibrium Calculations - *CC BY 4.0*

12: Acid-Base Equilibria - *CC BY 4.0*
- 12.1: Brønsted-Lowry Acids and Bases - *CC BY 4.0*
- 12.2: pH and pOH - *CC BY 4.0*
- 12.3: Relative Strengths of Acids and Bases - *CC BY 4.0*
- 12.4: Polyprotic Acids - *CC BY 4.0*
- 12.5: Buffers - *CC BY 4.0*
- 12.6: Acid-Base Titrations - *CC BY 4.0*

13: Nuclear Chemistry and Other Topics - *Undeclared*
- 13.1: Nuclear Chemistry Introduction - *Undeclared*
- 13.2: The Effects of Radiation on Life - *Undeclared*
- 13.3: Radioactivity in Medicine and Other Applications - *Undeclared*

14: Appendices - *CC BY 4.0*
- 14.1: The Periodic Table - *CC BY 4.0*
- 14.2: Essential Mathematics - *CC BY 4.0*
- 14.3: Fundamental Physical Constants - *CC BY 4.0*
- 14.4: Ionization Constants of Weak Acids - *CC BY 4.0*
- 14.5: Ionization Constants of Weak Bases - *CC BY 4.0*
- 14.6: Units and Conversion Factors - *CC BY 4.0*
- 14.7: Water Properties - *CC BY 4.0*

Back Matter - *Undeclared*
- Index - *Undeclared*
- Glossary - *Undeclared*
- Detailed Licensing - *Undeclared*