

# General Chemistry





# GENERAL CHEMISTRY

for Science Majors

ALLISON SOULT; ANDREW EKLUND; CAROL MARTINEZ; DON FRANTZ; DONALD CARPENETTI; EDWARD J. NETH; EMAD EL-GIAR; GEORGE KAMINSKI; JASON POWELL; JENNIFER LOOK; KLAUS THEOPOLD; MARK BLASER; PAUL FLOWERS; PAUL HOOKER; RICHARD LANGLEY; SIMON BOTT; THOMAS SORENSEN; TROY MILLIKEN; VICKI MORAVEC; AND WILLIAM R. ROBINSON

CONRAD JONES; DAVID DUNAWAY; JOHN B. HOPKINS; SOMA MUKHERJEE; AND YU WANG

LOUIS: The Louisiana Library Network



*General Chemistry Copyright © 2022 by LOUIS: The Louisiana Library Network is licensed under a [Creative Commons Attribution 4.0 International License](https://creativecommons.org/licenses/by/4.0/), except where otherwise noted.*

# CONTENTS

Preface	xi
---------	----

## Chapter 1: Essential Ideas

Key Terms, Key Equations, Summaries, and Exercises (Chapter 1)	3
OpenStax	
Chemistry in Context (1.1)	28
OpenStax	
Phases and Classification of Matter (1.2)	35
OpenStax	
Physical and Chemical Properties (1.3)	50
OpenStax	
Measurements (1.4)	56
OpenStax	
Measurement Uncertainty, Accuracy, and Precision (1.5)	67
OpenStax	
Mathematical Treatment of Measurement Results (1.6)	79
OpenStax	

## Chapter 2: Atoms, Molecules, and Ions

Key Terms, Key Equations, Summaries, and Exercises (Chapter 2)	91
OpenStax	
Early Ideas in Atomic Theory (2.1)	110
OpenStax	

Evolution of Atomic Theory (2.2)	117
OpenStax	
Atomic Structure and Symbolism (2.3)	124
OpenStax	
Chemical Formulas (2.4)	139
OpenStax	

## Chapter 3: Electronic Structure and Periodic Properties of Elements

Electromagnetic Energy (3.1)	167
OpenStax	
The Bohr Model (3.2)	187
OpenStax	
Development of Quantum Theory (3.3)	195
OpenStax	
Electronic Structure of Atoms (Electron Configurations) (3.4)	214
OpenStax	
Periodic Variations in Element Properties (3.5)	230
OpenStax	
The Periodic Table (3.6)	241
OpenStax	
Molecular and Ionic Compounds (3.7)	247
OpenStax	

## Chapter 4: Chemical Bonding and Molecular Geometry

Ionic Bonding (4.1)	261
OpenStax	
Covalent Bonding (4.2)	267
OpenStax	

Chemical Nomenclature (4.3)	277
OpenStax	
Lewis Symbols and Structures (4.4)	289
OpenStax	
Formal Charges and Resonance (4.5)	309
OpenStax	
Molecular Structure and Polarity (4.6)	318
OpenStax	

## Chapter 5: Advanced Theories of Bonding

Valence Bond Theory (5.1)	347
OpenStax	
Hybrid Atomic Orbitals (5.2)	357
OpenStax	
Multiple Bonds (5.3)	375
OpenStax	
Molecular Orbital Theory (5.4)	381
OpenStax	

## Chapter 6: Composition of Substances and Solutions

Formula Mass (6.1)	407
OpenStax	
Determining Empirical and Molecular Formulas (6.2)	412
OpenStax	
Molarity (6.3)	424
OpenStax	
Other Units for Solution Concentrations (6.4)	437
OpenStax	

## Chapter 7: Stoichiometry of Chemical Reactions

Writing and Balancing Chemical Equations (7.1)	447
OpenStax	
Classifying Chemical Reactions (7.2)	458
OpenStax	
Reaction Stoichiometry (7.3)	481
OpenStax	
Reaction Yields (7.4)	490
OpenStax	
Quantitative Chemical Analysis (7.5)	498
OpenStax	

## Chapter 8: Gases

Gas Pressure (8.1)	513
OpenStax	
Relating Pressure, Volume, Amount, and Temperature: The Ideal Gas Law (8.2)	528
OpenStax	
Stoichiometry of Gaseous Substances, Mixtures, and Reactions (8.3)	549
OpenStax	
Effusion and Diffusion of Gases (8.4)	570
OpenStax	
The Kinetic-Molecular Theory (8.5)	578
OpenStax	
Non-Ideal Gas Behavior (8.6)	587
OpenStax	

## Chapter 9: Thermochemistry

Energy Basics (9.1)	595
OpenStax	
Calorimetry (9.2)	610
OpenStax	
Enthalpy (9.3)	627
OpenStax	
Strengths of Ionic and Covalent Bonds (9.4)	651
OpenStax	
 Appendix A – The Periodic Table	663
OpenStax	
Appendix B – Essential Mathematics	664
OpenStax	
Appendix C – Units And Conversion Factors	674
OpenStax	
Appendix D – Fundamental Physical Constants	678
OpenStax	
Appendix E – Water Properties	680
OpenStax	
Appendix F – Composition of Commercial Acids and Bases	689
OpenStax	
Appendix G – Standard Thermodynamic Properties for Selected Substances	690
OpenStax	
Appendix H – Ionization Constants of Weak Acids	728
OpenStax	
Appendix I – Ionization Constants of Weak Bases	733
OpenStax	
Appendix J – Solubility Products	736
OpenStax	
Appendix K – Formation Constants for Complex Ions	745
OpenStax	

Appendix L – Standard Electrode (Half-Cell) Potentials	747
OpenStax	
Appendix M – Half-Lives for Several Radioactive Isotopes	758
OpenStax	
Appendix N: Checklist for Accessibility	762
Acknowledgments	765
OpenStax	



# PREFACE

---

Welcome to *Chemistry: Atoms First 2e*, an OpenStax resource. This textbook was written to increase student access to high-quality learning materials, maintaining the highest standards of academic rigor at little or no cost.

## The Creation of this Book

This textbook was created as part of the Interactive OER for Dual Enrollment project, facilitated by [LOUIS: The Louisiana Library Network](#) and funded by a \$2 million [Open Textbooks Pilot Program grant from the Department of Education](#).

This project supports the extension of access to high-quality post-secondary opportunities to high school students across Louisiana and beyond by creating materials that can be adopted for dual enrollment environments. Dual enrollment is the opportunity for a student to be enrolled in high school and college at the same time.

The cohort-developed OER course materials are released under a license that permits their free use, reuse, modification and sharing with others. This includes a corresponding course available in [MoodleNet](#) and [Canvas Commons](#) that can be imported to other Learning Management System platforms. For access/questions, contact [Affordable Learning Louisiana](#).

If you are adopting this textbook, we would be glad to know of your use via this [brief survey](#).

## Adaptation Statement

This book is an adaption of the OpenStax textbook [Chemistry: Atoms First 2e](#), licensed under a [Creative Commons Attribution 4.0 International \(CC BY\) license](#).

### Senior Contributing Authors

Paul Flowers, University of North Carolina at Pembroke

Edward J. Neth, University of Connecticut

William R. Robinson, PhD

Klaus Theopold, University of Delaware

Richard Langley, Stephen F. Austin State University

## Contributing Authors

Jennifer Look, Mercer University  
Allison Soult, University of Kentucky  
Simon Bott, University of Houston  
Donald Carpenetti, Craven Community College  
Andrew Eklund, Alfred University  
Emad El-Giar, University of Louisiana at Monroe  
Don Frantz, Wilfrid Laurier University  
Paul Hooker, Westminster College  
Carol Martinez, Central New Mexico Community College  
Troy Milliken, Jackson State University  
Vicki Moravec, Trine University  
George Kaminski, Worcester Polytechnic Institute  
Mark Blaser, Shasta College  
Jason Powell, Ferrum College  
Thomas Sorensen, University of Wisconsin–Milwaukee

The following changes were made to this book as a whole:

H5P activities/multimedia were inserted into sections to reinforce concepts.

Chapter 5: H5P activities authored and contributed by John B. Hopkins

Chapter 8: H5P activities authored and contributed by John B. Hopkins

Chapter 9: H5P activities taken from Chemistry 109 Fall 2021 by John Moore; Jia Zhou; and Etienne Garand; contributed by Conrad Jones

## Editors

- Esperanza Zenon, River Parishes Community College
- Conrad Jones, Southern University and A&M College

## Review Statement

This textbook and its accompanying course materials went through at least two review processes:

- Peer reviewers, coordinated by Jared Eusea, River Parish Community College, used an online course development standard rubric for assessing the quality and content of each course to ensure that the courses developed through Interactive OER for Dual Enrollment support online learners in that

environment. The evaluation framework reflects a commitment to accessibility and usability for all learners.

- Reviewers
  - Melissa Parks
  - Waneene Dorsey
  - Jesse Walczak
- The Institute for the Study of Knowledge Management in Education (ISKME) collaborated with LOUIS to review course materials and ensure their appropriateness for dual enrollment audiences. Review criteria were drawn from factors that apply across dual enrollment courses and subject areas, such as determining appropriate reading levels, assessing the fit of topics and examples for high school DE students, applying high-level principles for quality curriculum design, including designing for accessibility, appropriate student knowledge checks, and effective scaffolding of student tasks and prior knowledge requirements, addressing adaptability and open educational practices, and principles related to inclusion and representational social justice.
  - Reviewers
    - Cody Lewis
    - Jessica Dolecheck

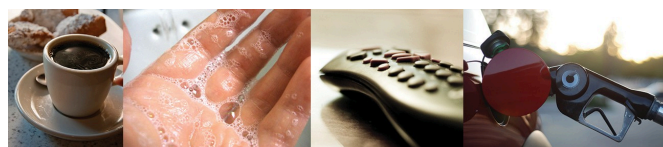


# CHAPTER 1: ESSENTIAL IDEAS

## Essential Ideas

## Chapter Outline

- Chemistry in Context
- Phases and Classification of Matter
- Physical and Chemical Properties
- Measurements
- Measurement Uncertainty, Accuracy, and Precision
- Mathematical Treatment of Measurement Results



**Figure 1.1** Chemical substances and processes are essential for our existence, providing sustenance, keeping us clean and healthy, fabricating electronic devices, enabling transportation, and much more. By: vxla and goeshees [Flickr CC BY NC SA](#)

## Introduction

Your alarm goes off and, after hitting “snooze” once or twice, you pry yourself out of bed. You make a cup of coffee to help you get going, and then you shower, get dressed, eat breakfast, and check your phone for messages. On your way to school, you stop to fill your car’s gas tank, almost making you late for the first day of chemistry class. As you find a seat in the classroom, you read the question projected on the screen: “Welcome to class! Why should we study chemistry?”

Do you have an answer? You may be studying chemistry because it fulfills an academic requirement, but if you consider your daily activities, you might find chemistry interesting for other reasons. 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.



# KEY TERMS, KEY EQUATIONS, SUMMARIES, AND EXERCISES (CHAPTER 1)

OpenStax

---

## Key Terms

### accuracy

how closely a measurement aligns with a correct value

### atom

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

### Celsius (°C)

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

### 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

### chemistry

study of the composition, properties, and interactions of matter

### compound

pure substance that can be decomposed into two or more elements

### cubic centimeter (cm<sup>3</sup> or cc)

volume of a cube with an edge length of exactly 1 cm

### cubic meter (m<sup>3</sup>)

SI unit of volume

### density

ratio of mass to volume for a substance or object

### 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

### element

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

### exact number

number derived by counting or by definition

### extensive property

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

### Fahrenheit

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

### 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

### hypothesis

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

### intensive property

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

### kelvin (K)

SI unit of temperature;  $273.15\text{ K} = 0\text{ °C}$

### kilogram (kg)

standard SI unit of mass;  $1\text{ kg} = \text{approximately } 2.2\text{ pounds}$

### law

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

### law of conservation of matter

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

### length

measure of one dimension of an object

### liquid

state of matter that has a definite volume but indefinite shape

### liter (L)

(also, cubic decimeter) unit of volume;  $1\text{ L} = 1,000\text{ cm}^3$

### macroscopic domain

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

### mass

fundamental property indicating amount of matter



**matter**

anything that occupies space and has mass

**meter (m)**

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

**microscopic domain**

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

**milliliter (mL)**

1/1,000 of a liter; equal to 1 cm<sup>3</sup>

**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

**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

**plasma**

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

**precision**

how closely a measurement matches the same measurement when repeated

**pure substance**

homogeneous substance that has a constant composition

**rounding**

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

**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

**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*)

**significant figures**

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

**solid**

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

### 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

### temperature

intensive property representing the hotness or coldness of matter

### theory

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

### uncertainty

estimate of amount by which measurement differs from true value

### unit

standard of comparison for measurements

### unit conversion factor

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

### volume

amount of space occupied by an object

### weight

force that gravity exerts on an object

## Key Equations

---

">density=mass/volume

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

---

---


$$^{\circ}\text{C} = 59 \times (^{\circ}\text{F} - 32)$$

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

$$^{\circ}\text{F} = (95 \times ^{\circ}\text{C}) + 32$$

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

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

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

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


---

## Summaries

### 1.1 Chemistry in Context

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.

### 1.2 Phases and Classification of Matter

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.

## 1.3 Physical and Chemical Properties

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 as 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.

## 1.4 Measurements

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 SI (International System) units such as meters, seconds, and kilograms, as well as derived units, such as liters (for volume) and  $\text{g}/\text{cm}^3$  (for density). In many cases, it is convenient to use prefixes that yield fractional and multiple units, such as microseconds ( $10^{-6}$  seconds) and megahertz ( $10^6$  hertz), respectively.

## 1.5 Measurement Uncertainty, Accuracy, and Precision

Quantities can be defined or measured. Measured quantities have an associated uncertainty that is represented by the number of significant figures in the quantity's number. The uncertainty of a calculated quantity depends on the uncertainties in the quantities used in the calculation and is reflected in how the value is rounded. Quantities are characterized with regard to accuracy (closeness to a true or accepted value) and precision (variation among replicate measurement results).

## 1.6 Mathematical Treatment of Measurement Results

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.

## Exercises

### 1.1 Chemistry in Context

1.

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

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.

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.

4.

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) The mass of a lead pipe is 14 lb.

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

5.

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

6.

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.

7.

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.

## 1.2 Phases and Classification of Matter

8.

Why is an object's mass, rather than its weight, used to indicate the amount of matter it contains?

9.

What properties distinguish solids from liquids? Liquids from gases? Solids from gases?

10.

How does a heterogeneous mixture differ from a homogeneous mixture? How are they similar?

11.

How does a homogeneous mixture differ from a pure substance? How are they similar?

12.

How does an element differ from a compound? How are they similar?

13.

How do molecules of elements and molecules of compounds differ? In what ways are they similar?

14.

How does an atom differ from a molecule? In what ways are they similar?

15.

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.

16.

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

17.

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

18.

A sulfur atom and a sulfur molecule are not identical. What is the difference?

19.

How are the molecules in oxygen gas, the molecules in hydrogen gas, and water molecules similar? How do they differ?

20.

Why are astronauts in space said to be “weightless,” but not “massless”?

21.

Prepare a list of the principal chemicals consumed and produced during the operation of an automobile.

22.

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.

23.

When elemental iron corrodes it combines with oxygen in the air to ultimately form red brown iron(III) oxide called 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?

24.

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.



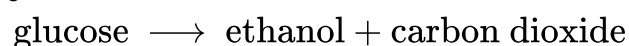
(b) When magnesium burns in air a white flaky ash of magnesium oxide is produced. Is the mass of magnesium oxide less than, greater than, or the same as the original piece of magnesium? Explain.

(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?

25.

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

“>glucose  $\rightarrow$  ethanol + carbon dioxide



(a) If 200.0 g of glucose is fully converted, what will be the total mass of ethanol and carbon dioxide produced?

(b) If the fermentation is carried out in an open container, would you expect the mass of the container and contents after fermentation to be less than, greater than, or the same as the mass of the container and contents before fermentation? Explain.

(c) If 97.7 g of carbon dioxide is produced, what mass of ethanol is produced?

## 1.3 Physical and Chemical Properties

26.

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  $-220^\circ\text{C}$  and boils at  $-188^\circ\text{C}$ . Finely divided metals burn in fluorine with a bright flame. Nineteen grams of fluorine will react with 1.0 gram of hydrogen.

27.

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

28.

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

29.

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?

30.

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?

31.

Explain the difference between extensive properties and intensive properties.

32.

Identify the following properties as either extensive or intensive.

- (a) volume
- (b) temperature
- (c) humidity
- (d) heat
- (e) boiling point

33.

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

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

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

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

## 1.4 Measurements

34.

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

35.

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

36.

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

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

37.

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

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

38.

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

- (a)  $10^3$
- (b)  $10^{-2}$
- (c) 0.1
- (d)  $10^{-3}$

(e) 1,000,000

(f) 0.000001

39.

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

(a) c

(b) d

(c) G

(d) k

(e) m

(f) n

(g) p

(h) T

40.

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

(a) Determine the density of this piece of jewelry.

(b) Assuming that the jewelry is made from only one substance, what substance is it likely to be? Explain.

41.

Visit this [PhET density simulation](#) and select the Same Volume Blocks.

(a) What are the mass, volume, and density of the yellow block?

(b) What are the mass, volume and density of the red block?

(c) List the block colors in order from smallest to largest mass.

(d) List the block colors in order from lowest to highest density.

(e) How are mass and density related for blocks of the same volume?

42.

Visit this [PhET density simulation](#) and select Custom Blocks and then My Block.

(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?

(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?

- (c) How would (a) and (b) be different if the liquid in the tank were ethanol instead of water?
- (d) How would (a) and (b) be different if the liquid in the tank were mercury instead of water?

43.

Visit this [PhET density simulation](#) and select Mystery Blocks.

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

## 1.5 Measurement Uncertainty, Accuracy, and Precision

44.

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

- (a) 711.0
- (b) 0.239
- (c) 90743
- (d) 134.2
- (e) 0.05499
- (f) 10000.0
- (g) 0.000000738592

45.

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

- (a) 704
- (b) 0.03344
- (c) 547.9
- (d) 22086
- (e) 1000.00
- (f) 0.0000000651
- (g) 0.007157

46.

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

- (a) the number of eggs in a basket

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

47.

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

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

48.

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

- (a) 38.7 g
- (b)  $2 \times 10^{18} \text{ m}$
- (c) 3,486,002 kg
- (d)  $9.74150 \times 10^{-4} \text{ J}$
- (e)  $0.0613 \text{ cm}^3$
- (f) 17.0 kg
- (g) 0.01400 g/mL

49.

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

- (a) 53 cm
- (b)  $2.05 \times 10^8 \text{ m}$
- (c) 86,002 J
- (d)  $9.740 \times 10^4 \text{ m/s}$

- (e)  $10.0613 \text{ m}^3$
- (f)  $0.17 \text{ g/mL}$
- (g)  $0.88400 \text{ s}$

50.

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

- (a) 0.0055 g active ingredients
- (b) 12 tablets
- (c) 3% hydrogen peroxide
- (d) 5.5 ounces
- (e) 473 mL
- (f) 1.75% bismuth
- (g) 0.001% phosphoric acid
- (h) 99.80% inert ingredients

51.

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

- (a) 0.436
- (b) 9.000
- (c) 27.2
- (d) 135
- (e)  $1.497 \times 10^{-3}$
- (f) 0.445

52.

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

- (a) 517
- (b) 86.3
- (c)  $6.382 \times 10^3$
- (d) 5.0008
- (e) 22.497
- (f) 0.885

53.

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

(a)  $628 \times 342$

$\times 342$

(b)  $(5.63 \times 10^2) \times (7.4 \times 10^3)$

$\times 10^2) \times (7.4 \times 10^3)$

$\times (7.4 \times 10^3)$

$\times 10^3)$

(c)  $28.013.483$

$\frac{28.0}{13.483}$

(d)  $8119 \times 0.000023$

$\times 0.000023$

(e)  $14.98 + 27,340 + 84.7593$

(f)  $42.7 + 0.259$

54.

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

(a)  $62.8 \times 34$

$\times 34$

(b)  $0.147 + 0.0066 + 0.012$

(c)  $38 \times 95 \times 1.792$

$\times 95 \times 1.792$

$\times 1.792$

(d)  $15 - 0.15 - 0.6155$

(e)  $8.78 \times (0.05000.478)$

$8.78 \times \left( \frac{0.0500}{0.478} \right)$

(f)  $140 + 7.68 + 0.014$

(g)  $28.7 - 0.0483$

(h)  $(88.5 - 87.57)45.13$

$\frac{(88.5 - 87.57)}{45.13}$

55.

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

(a) Which archer is most precise?



- (b) Which archer is most accurate?
- (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.

56.

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

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

## 1.6 Mathematical Treatment of Measurement Results

57.

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

58.

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

- (a) kilometers in 1 mile
- (b) liters in 1 cubic foot
- (c) grams in 1 ounce

59.

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?

60.

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?

61.

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?

62.

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?

63.

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

64.

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

65.

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

66.

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

67.

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

68.

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?

69.

Many medical laboratory tests are run using  $5.0\ \mu\text{L}$  blood serum. What is this volume in milliliters?

70.

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

71.

Use scientific (exponential) notation to express the following quantities in terms of the SI base units in [Table 1.3](#):

- (a) 0.13 g
- (b) 232 Gg
- (c) 5.23 pm
- (d) 86.3 mg
- (e) 37.6 cm
- (f)  $54\ \mu\text{m}$
- (g) 1 Ts
- (h) 27 ps
- (i) 0.15 mK

72.

Complete the following conversions between SI units.

- (a)  $612\ \text{g} = \underline{\hspace{2cm}}\ \text{mg}$
- (b)  $8.160\ \text{m} = \underline{\hspace{2cm}}\ \text{cm}$
- (c)  $3779\ \mu\text{g} = \underline{\hspace{2cm}}\ \text{g}$
- (d)  $781\ \text{mL} = \underline{\hspace{2cm}}\ \text{L}$
- (e)  $4.18\ \text{kg} = \underline{\hspace{2cm}}\ \text{g}$
- (f)  $27.8\ \text{m} = \underline{\hspace{2cm}}\ \text{km}$
- (g)  $0.13\ \text{mL} = \underline{\hspace{2cm}}\ \text{L}$
- (h)  $1738\ \text{km} = \underline{\hspace{2cm}}\ \text{m}$
- (i)  $1.9\ \text{Gg} = \underline{\hspace{2cm}}\ \text{g}$

73.

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

74.

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

75.

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

76.

Make the conversion indicated in each of the following:

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

77.

Make the conversion indicated in each of the following:

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

78.

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

79.

A chemist's 50-Trillion Angstrom Run (see [Exercise 1.78](#)) would be an archeologist's 10,900 cubit run. How long is one cubit in meters and in feet? ( $1 \text{ Å} = 1 \times 10^{-8} \text{ cm}$ )

80.

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.

81.

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?

82.

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?

83.

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

84.

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?

85.

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?

86.

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? “>(1 ppb Hg=1 ng Hg1 g water)

$$(1 \text{ ppb Hg} = \frac{1 \text{ ng Hg}}{1 \text{ g water}})$$

87.

Calculate the density of aluminum if 27.6 cm<sup>3</sup> has a mass of 74.6 g.

88.

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

89.

Calculate these masses.

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

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

90.

Calculate these masses.

(a) What is the mass of 4.00 cm<sup>3</sup> of sodium, density = 0.97 g/cm<sup>3</sup>?

(b) What is the mass of 125 mL gaseous chlorine, density = 3.16 g/L?

91.

Calculate these volumes.

(a) What is the volume of 25 g iodine, density = 4.93 g/cm<sup>3</sup>?

(b) What is the volume of 3.28 g gaseous hydrogen, density = 0.089 g/L?

92.

Calculate these volumes.

(a) What is the volume of 11.3 g graphite, density = 2.25 g/cm<sup>3</sup>?

(b) What is the volume of 39.657 g bromine, density = 2.928 g/cm<sup>3</sup>?

93.

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

94.

Convert the temperature of scalding water,  $54\text{ }^{\circ}\text{C}$ , into degrees Fahrenheit and kelvin.

[95.](#)

Convert the temperature of the coldest area in a freezer,  $-10\text{ }^{\circ}\text{F}$ , to degrees Celsius and kelvin.

96.

Convert the temperature of dry ice,  $-77\text{ }^{\circ}\text{C}$ , into degrees Fahrenheit and kelvin.

[97.](#)

Convert the boiling temperature of liquid ammonia,  $-28.1\text{ }^{\circ}\text{F}$ , into degrees Celsius and kelvin.

98.

The label on a pressurized can of spray disinfectant warns against heating the can above  $130\text{ }^{\circ}\text{F}$ . What are the corresponding temperatures on the Celsius and kelvin temperature scales?

[99.](#)

The weather in Europe was unusually warm during the summer of 1995. The TV news reported temperatures as high as  $45\text{ }^{\circ}\text{C}$ . What was the temperature on the Fahrenheit scale?

# CHEMISTRY IN CONTEXT (1.1)

OpenStax

---

## Chemistry in Context

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

- Outline the historical development of chemistry
- Provide examples of the importance of chemistry in everyday life
- Describe the scientific method
- 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 was 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 1.2**).



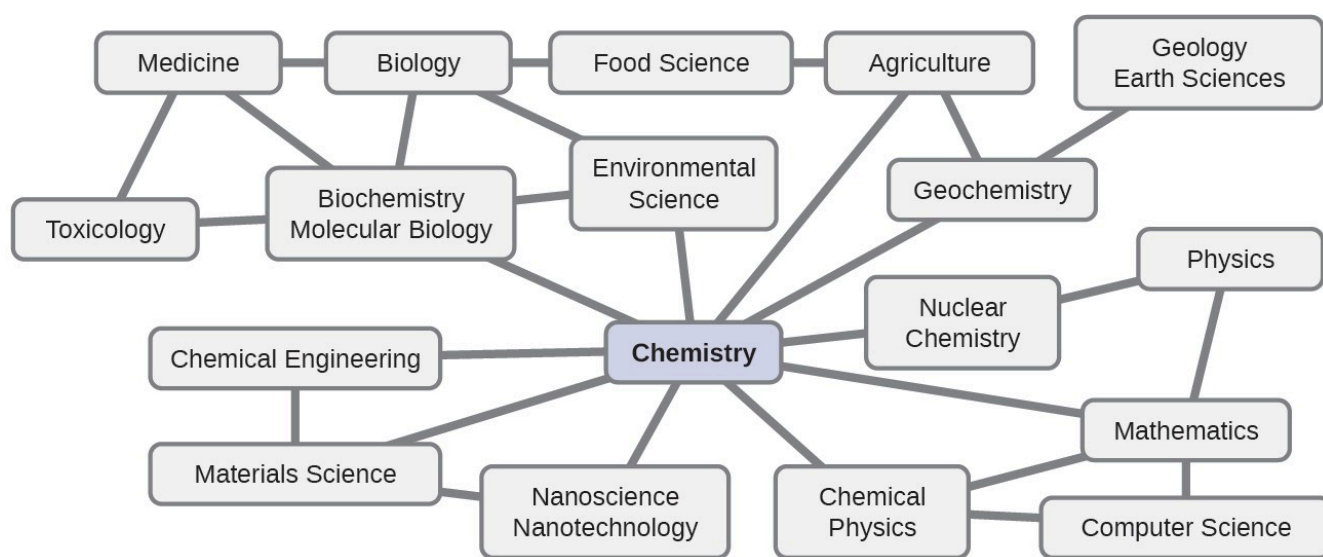
**Figure 1.2** Alchemist's Workshop. This portrayal shows an alchemist's workshop circa 1580. Although alchemy made some useful contributions to how to manipulate matter, it was not scientific by modern standards. By: Chemical Heritage Foundation [Openstax CC BY NC SA](#)

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.

## 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 1.3**). 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 1.3** 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. By: Rice University Openstax CC BY NC SA

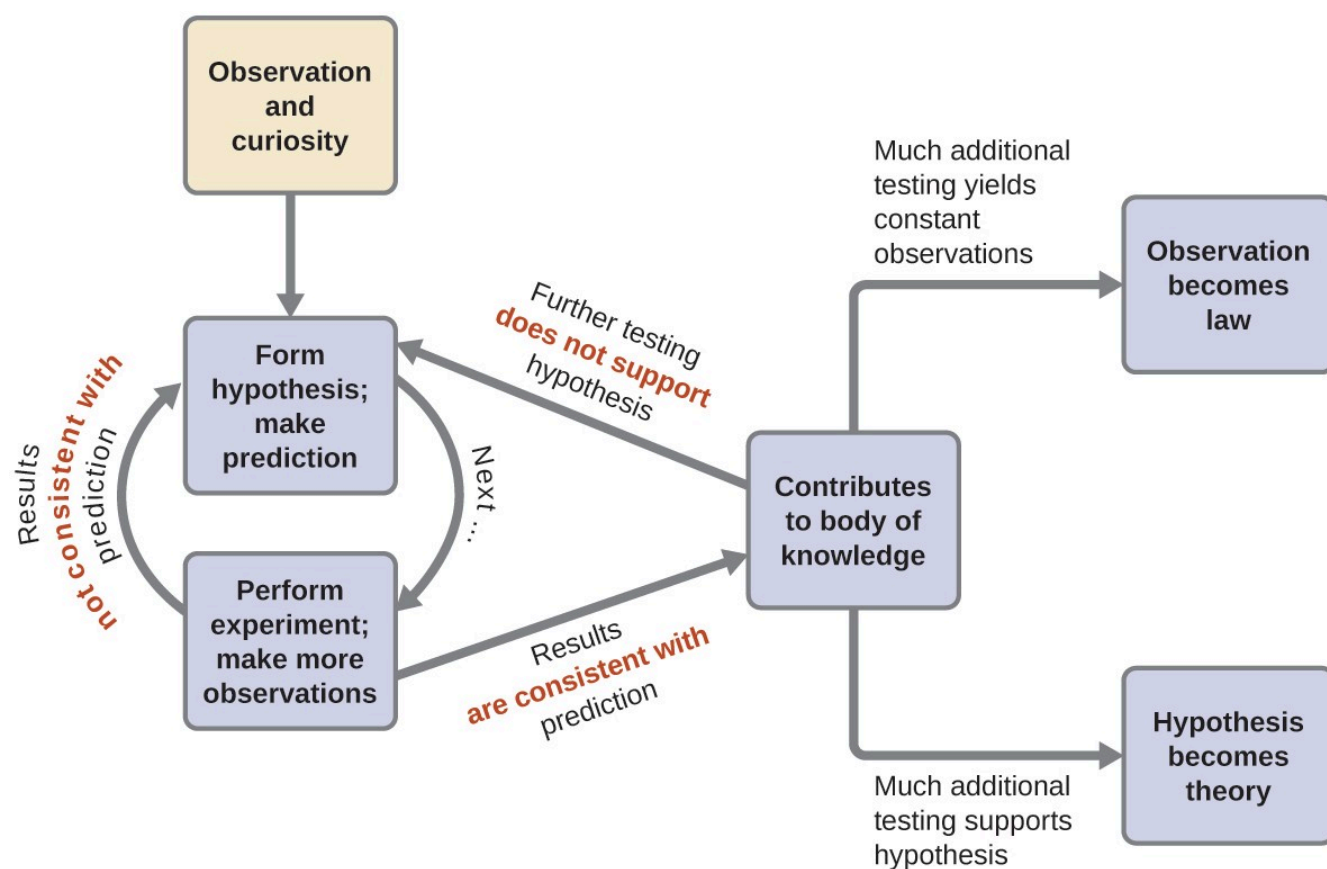
What are some changes in matter that are essential to daily life? Digesting and assimilating food, synthesizing polymers that are used to make clothing, containers, cookware, and credit cards, and refining crude oil into gasoline and other products are just a few examples. As you proceed through this 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. A hypothesis is tested by experimentation, calculation, and/or comparison with the experiments of others and then refined 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 1.4).





**Figure 1.4** 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. By: Rice University [Openstax](#) CC BY-NC-SA

## 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.

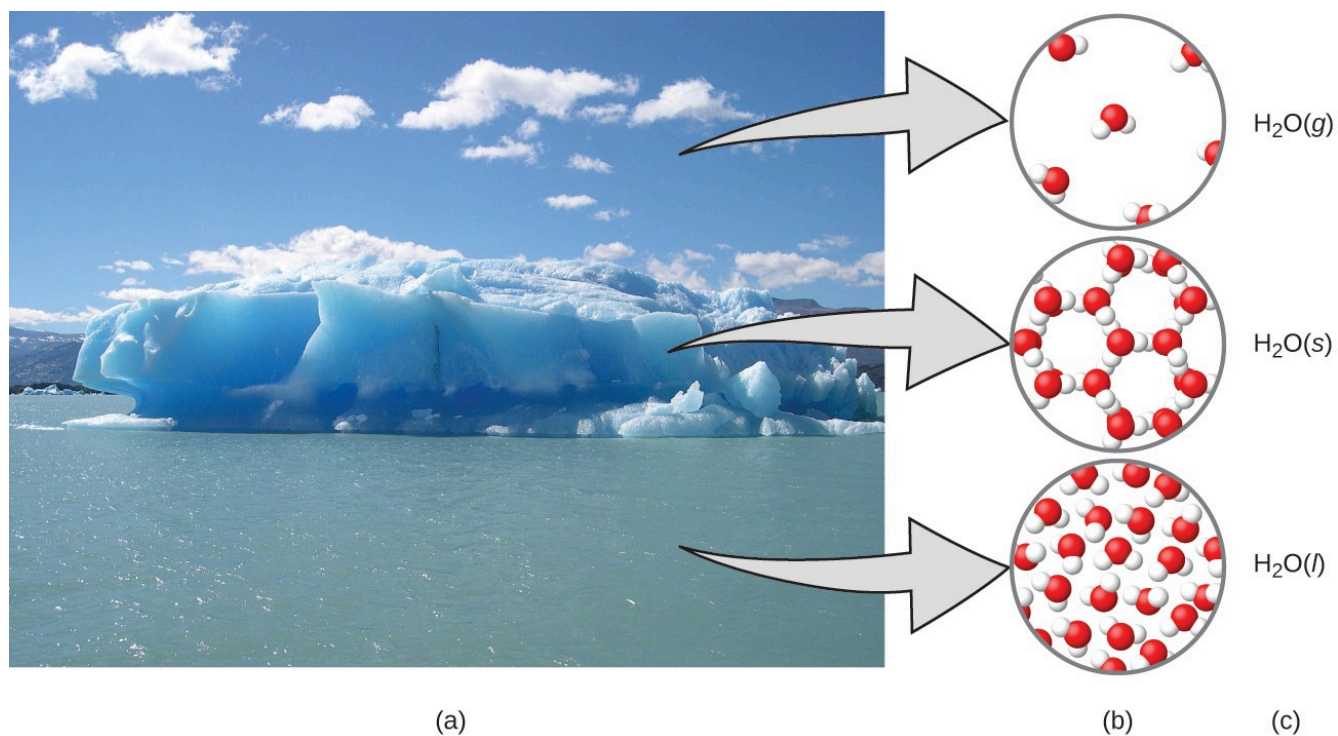
*Macro* is a Greek word that means “large.” The **macroscopic domain** is familiar to us: It is the realm of everyday things that are large enough to be sensed directly by human sight or touch. In daily life, this includes the food you eat and the breeze you feel on your face. The macroscopic domain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

*Micro* comes from Greek and means “small.” The **microscopic domain** of chemistry is often visited in the imagination. Some aspects of the microscopic domain are visible through standard optical microscopes, for example, many biological cells. More sophisticated instruments are capable of imaging even smaller entities such as molecules and atoms (see **Figure 1.5 (b)**).

However, most of the subjects in the microscopic domain of chemistry are too small to be seen even with the most advanced microscopes and may only 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.

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, drawings, and calculations. 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 1.5**) are macroscopic observations. But some properties of water fall into the microscopic domain—what cannot be observed with the naked eye. The description of water as comprising 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  $\text{H}_2\text{O}$ , 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 1.5** (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  $\text{H}_2\text{O}$  symbolizes water, and (g), (s), and (l) symbolize its phases. Note that clouds actually comprise 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. By: Rice University [Openstax CC BY NC SA](#)

# PHASES AND CLASSIFICATION OF MATTER (1.2)

OpenStax

---

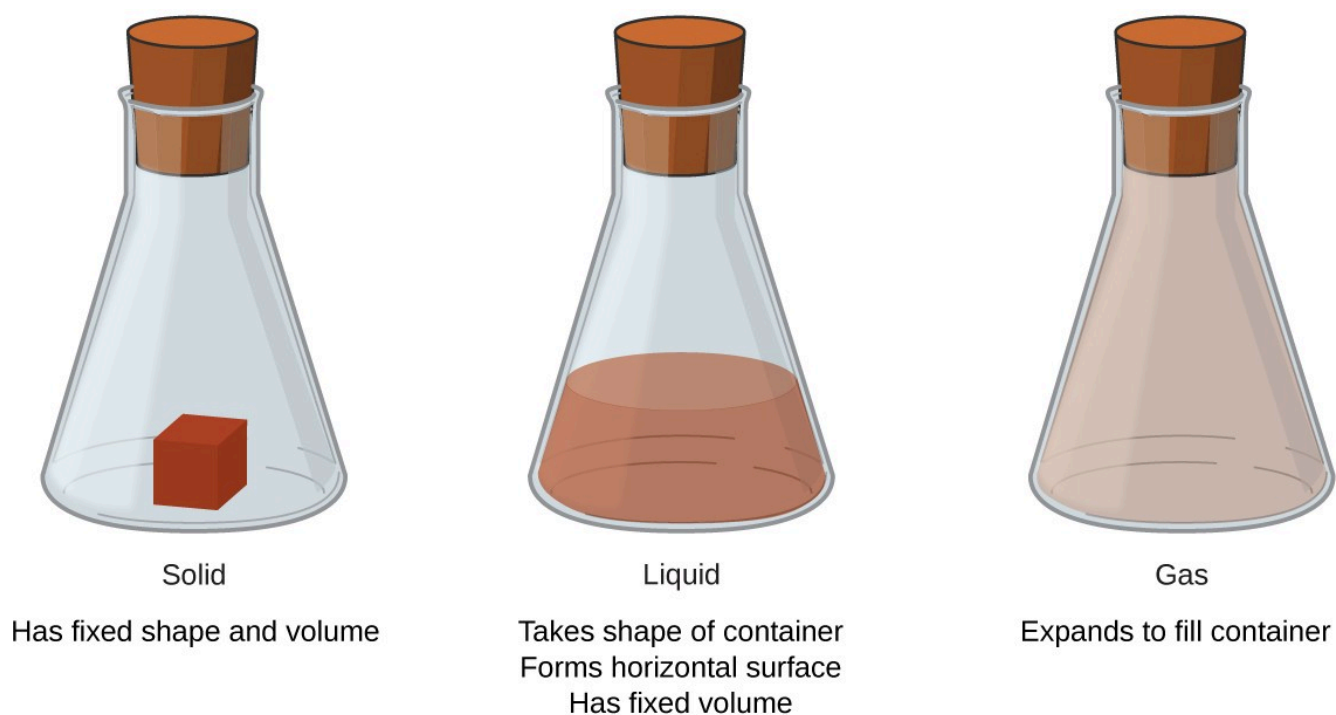
## Phases and Classification of Matter

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

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

**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 not inflate (increase its volume) when filled with gas.

Solids, liquids, and gases are the three states of matter commonly found on earth (**Figure 1.6**). A **solid** is rigid and possesses a definite shape. A **liquid** flows and takes the shape of its 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 1.6** The three most common states or phases of matter are solid, liquid, and gas. By: Rice University Openstax CC BY NC SA

A fourth state of matter, plasma, occurs naturally in the interiors of stars. A **plasma** is a gaseous state of matter that contains appreciable numbers of electrically charged particles (**Figure 1.7**). The presence of these charged particles imparts unique properties to plasmas that justify their classification as a state of matter distinct from gases. In addition to stars, plasmas are found in some other high-temperature environments (both natural and man-made), such as lightning strikes, certain television screens, and specialized analytical instruments used to detect trace amounts of metals.





**Figure 1.7** Torch Cutting Closeup. A plasma torch can be used to cut metal. Wikimedia Commons. By: Hypertherm [Wikimedia Commons CC BY NC SA](#)

### Link to Learning

In a tiny cell in a plasma television, the plasma emits ultraviolet light, which in turn causes the display at that location to appear a specific color. The composite of these tiny dots of color makes up the image that you see. Watch this video (<http://openstaxcollege.org/l/16plasma>) to learn more about plasma and the places you encounter it.

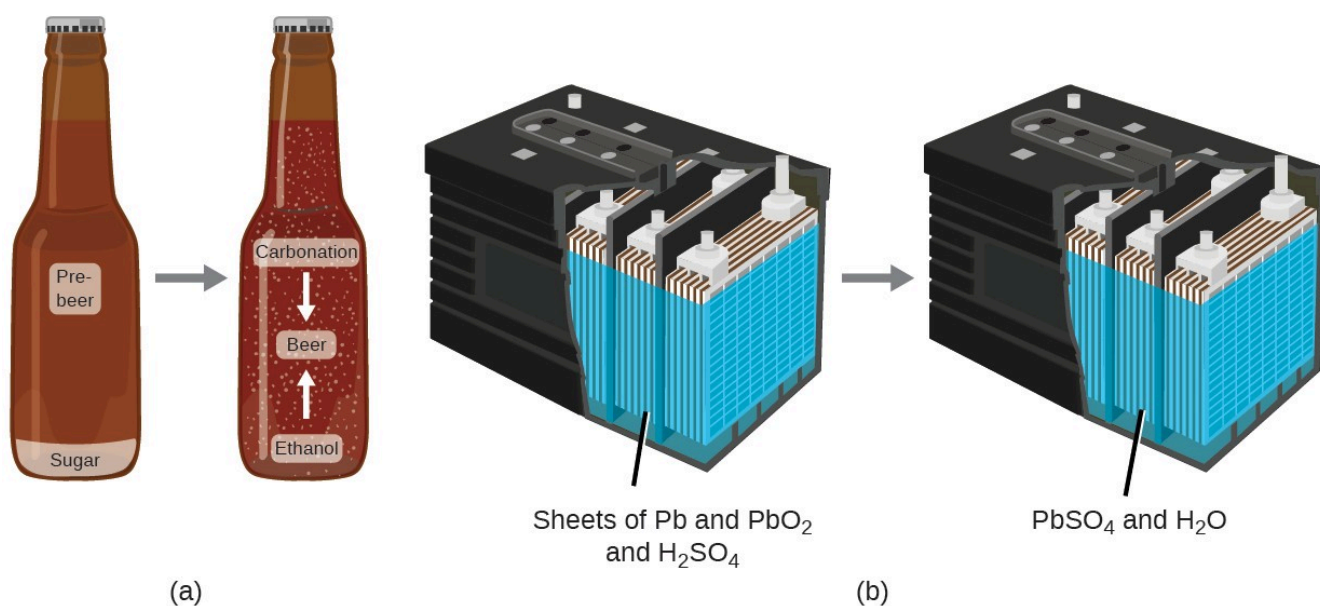
Some samples of matter appear to have properties of solids, liquids, and/or gases at the same time. This can occur when the sample is composed of many small pieces. For example, we can pour sand as if it were a liquid

because it is composed of many small grains of solid sand. Matter can also have properties of more than one state when it is a mixture, such as with clouds. Clouds appear to behave somewhat like gases, but they are actually mixtures of air (gas) and tiny particles of water (liquid or solid).

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

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

The **law of conservation of matter** summarizes many scientific observations about matter: It states that *there is no detectable change in the total quantity of matter present when matter converts from one type to another (a chemical change) or changes among solid, liquid, or gaseous states (a physical change)*. Brewing beer and the operation of batteries provide examples of the conservation of matter (**Figure 1.8**). 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 1.8** (a) The mass of beer precursor materials is the same as the mass of beer produced: Sugar has become alcohol and carbon dioxide. (b) The mass of the lead, lead oxide, and sulfuric acid consumed by the production of electricity is exactly equal to the mass of lead sulfate and water that is formed. By: Rice University [Openstax CC BY NC SA](#)

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.

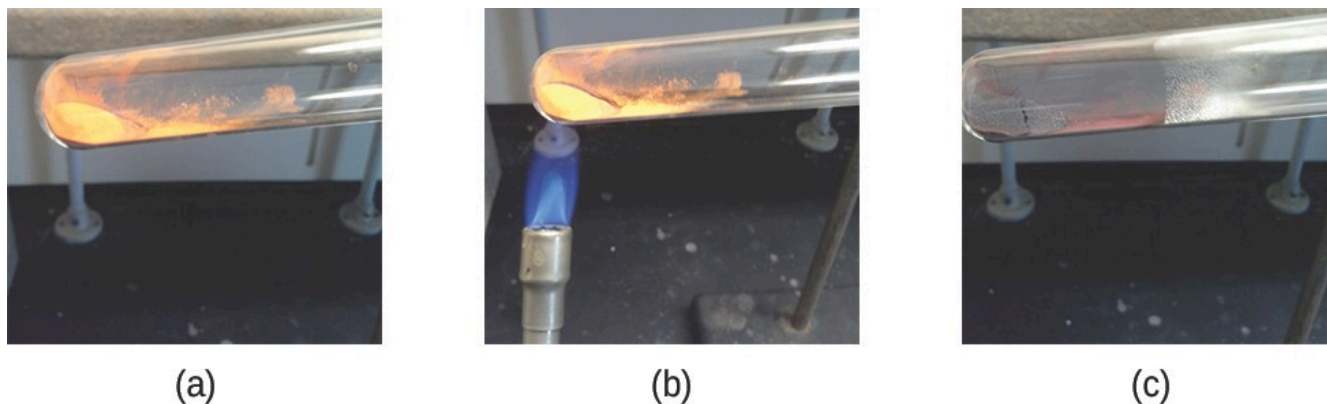
## Classifying Matter

Matter can be classified 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.

Pure substances may be divided 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 1.9**). 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 1.9** (a) The compound mercury(II) oxide, (b) when heated, (c) decomposes into silvery droplets of liquid mercury and invisible oxygen gas. By: Paul Flowers [Openstax CC BY NC SA](#)

### Link to Learning

Many compounds break down when heated. [This site](#) shows the breakdown of mercury oxide,  $\text{HgO}$ . You can also [view an example](#) of the photochemical decomposition of silver chloride ( $\text{AgCl}$ ), the basis of early photography.

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



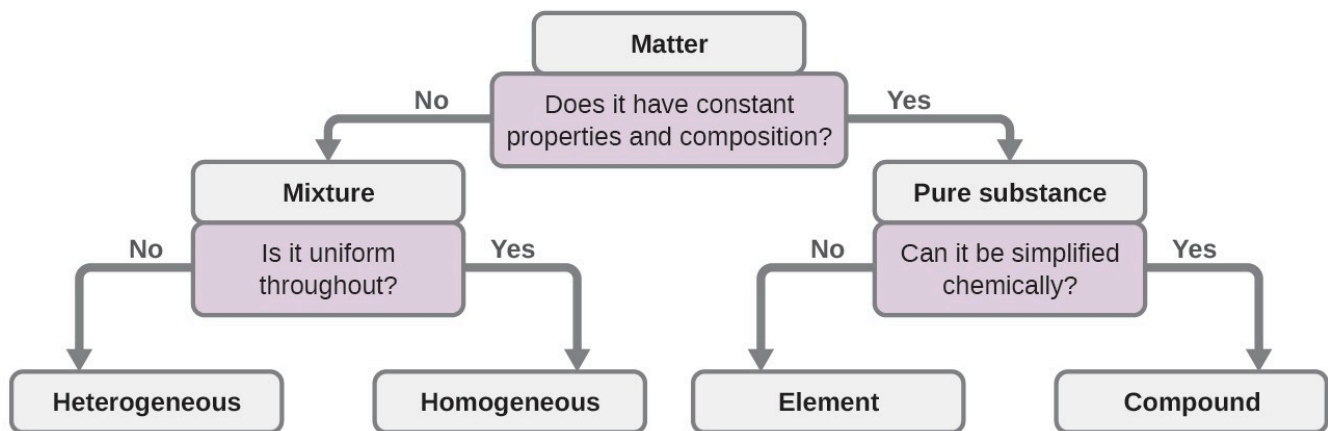
of a heterogeneous mixture (**Figure 1.10**). Its composition can vary because it may be prepared from varying amounts of oil, vinegar, and herbs. It is not the same from point to point throughout the mixture—one drop may be mostly vinegar, whereas a different drop may be mostly oil or herbs because 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 1.10**). 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 1.10** (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. By: John Mayer, Umberto Salvagnin, Jeff Bedford [Openstax CC BY NC SA](#)

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 that 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 1.11**.



**Figure 1.11** Depending on its properties, a given substance can be classified as a homogeneous mixture, a heterogeneous mixture, a compound, or an element. By: Rice University [Openstax CC BY-NC-SA](#)

Eleven elements make up about 99% of the earth's crust and atmosphere (**Table 1.1**). Oxygen constitutes nearly one-half and silicon about one-quarter of the total quantity of these elements. A majority of elements on earth are found in chemical combinations with other elements; about one-quarter of the elements are also found in the free state.

**Table 1.1** Elemental Composition of Earth By: Rice University [OpenStax CC BY-NC-SA 4.0](#)

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

**Table 1.2** By: Rice University [OpenStax CC BY-NC-SA 4.0](#)

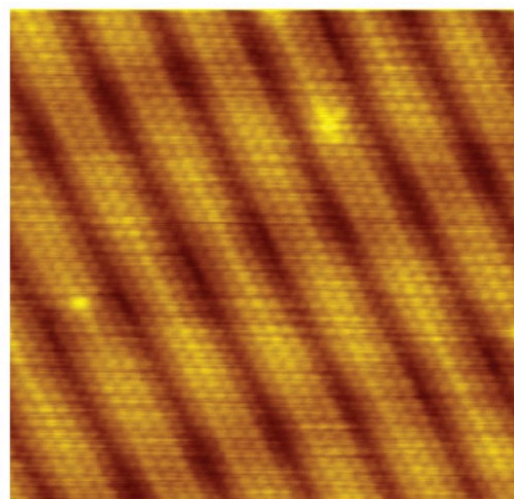
Element	Symbol	Percent Mass
iron	Fe	4.71
carbon	C	0.08
calcium	Ca	3.39
sulfur	S	0.06
sodium	Na	2.63
barium	Ba	0.04
potassium	K	2.40
nitrogen	N	0.03
magnesium	Mg	1.93
fluorine	F	0.03
hydrogen	H	0.87
strontium	Sr	0.02
titanium	Ti	0.58
all others	–	0.47

**Table 1.2** 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 1.12**). This atom would no longer be gold if it were divided any further.



(a)

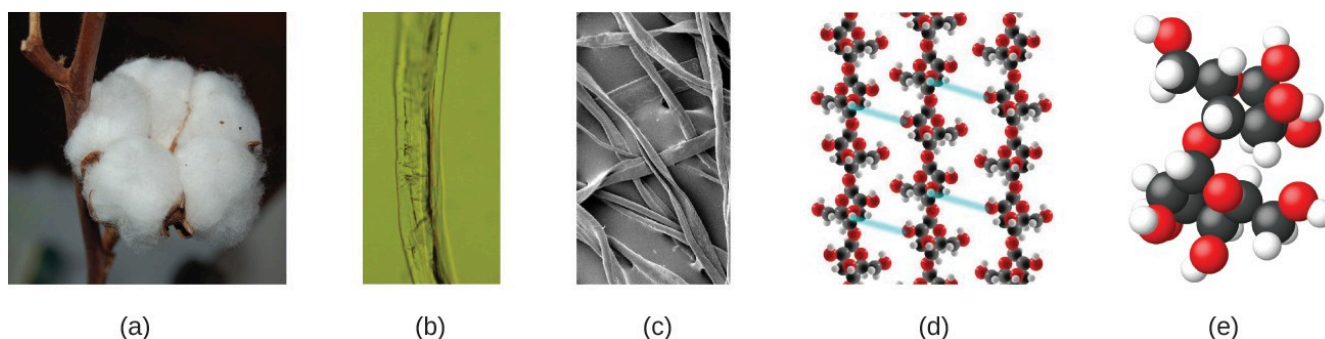


(b)

**Figure 1.12** (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. United States Geological Survey By: Erwinrossen [Wikimedia Commons CC BY NC SA](#)

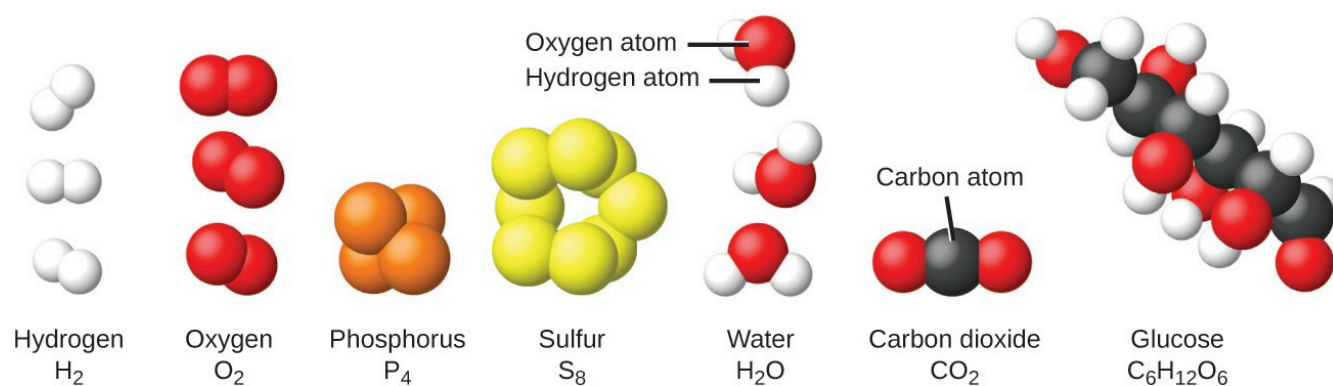
The first suggestion that matter is composed of atoms is attributed to the Greek philosophers Leucippus and Democritus, who developed their ideas in the fifth century BCE. However, it was not until the early nineteenth century that John Dalton (1766–1844), a British schoolteacher with a keen interest 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 1.13** shows increasingly close microscopic and atomic-level views of ordinary cotton.





**Figure 1.13** 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). By: Featheredtar [Openstax CC BY NC SA](https://openstax.org/licenses/by-nc-sa)

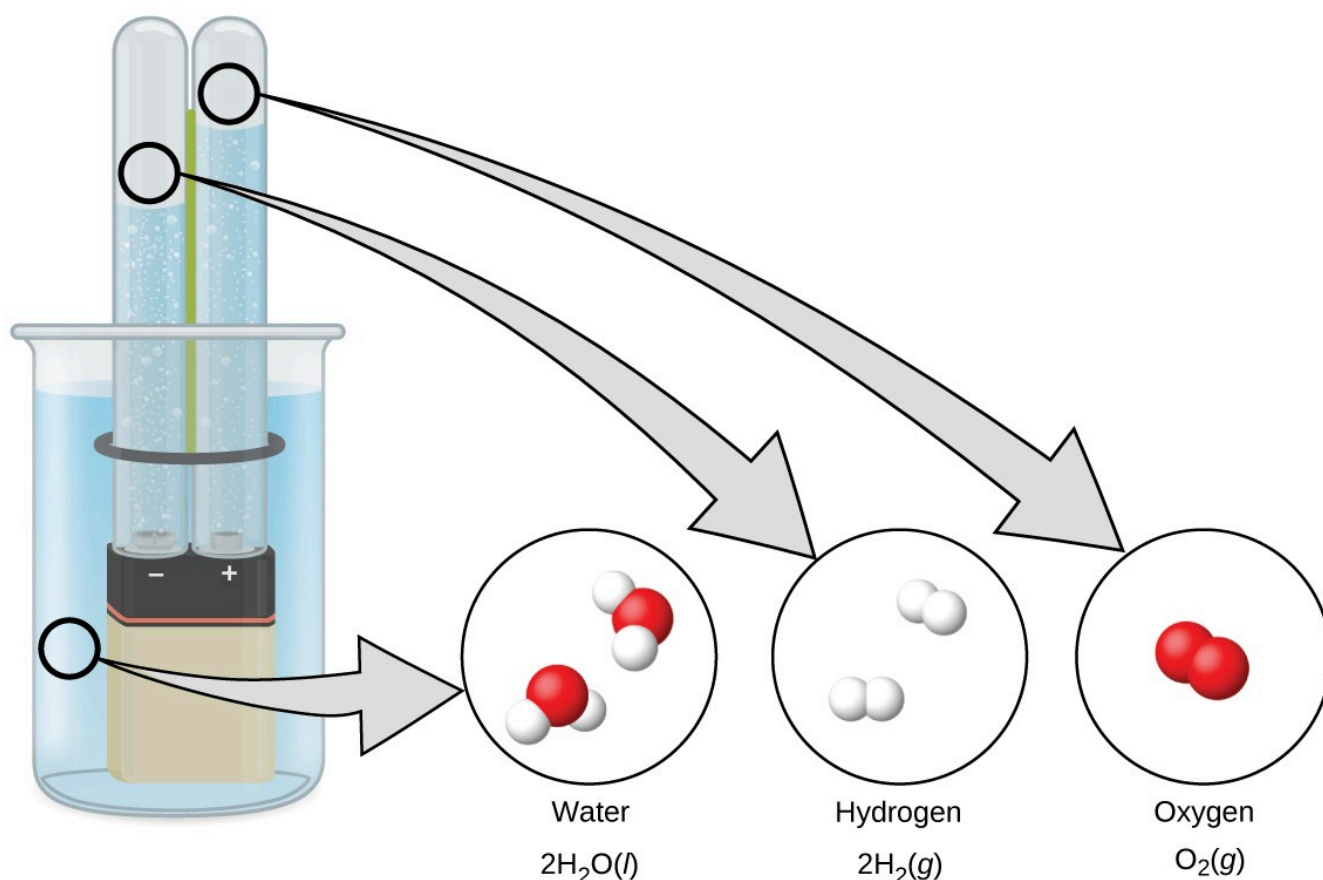
An atom is so light that its mass is also difficult to imagine. A billion lead atoms (1,000,000,000 atoms) weigh about  $3 \times 10^{-13}$  grams, a mass that is far too light to be weighed on even the world's most sensitive balances. It would require over 300,000,000,000,000 lead atoms (300 trillion, or  $3 \times 10^{14}$ ) 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 1.14**). 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 1.14** 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. By: Rice University [Openstax CC BY NC SA](#)

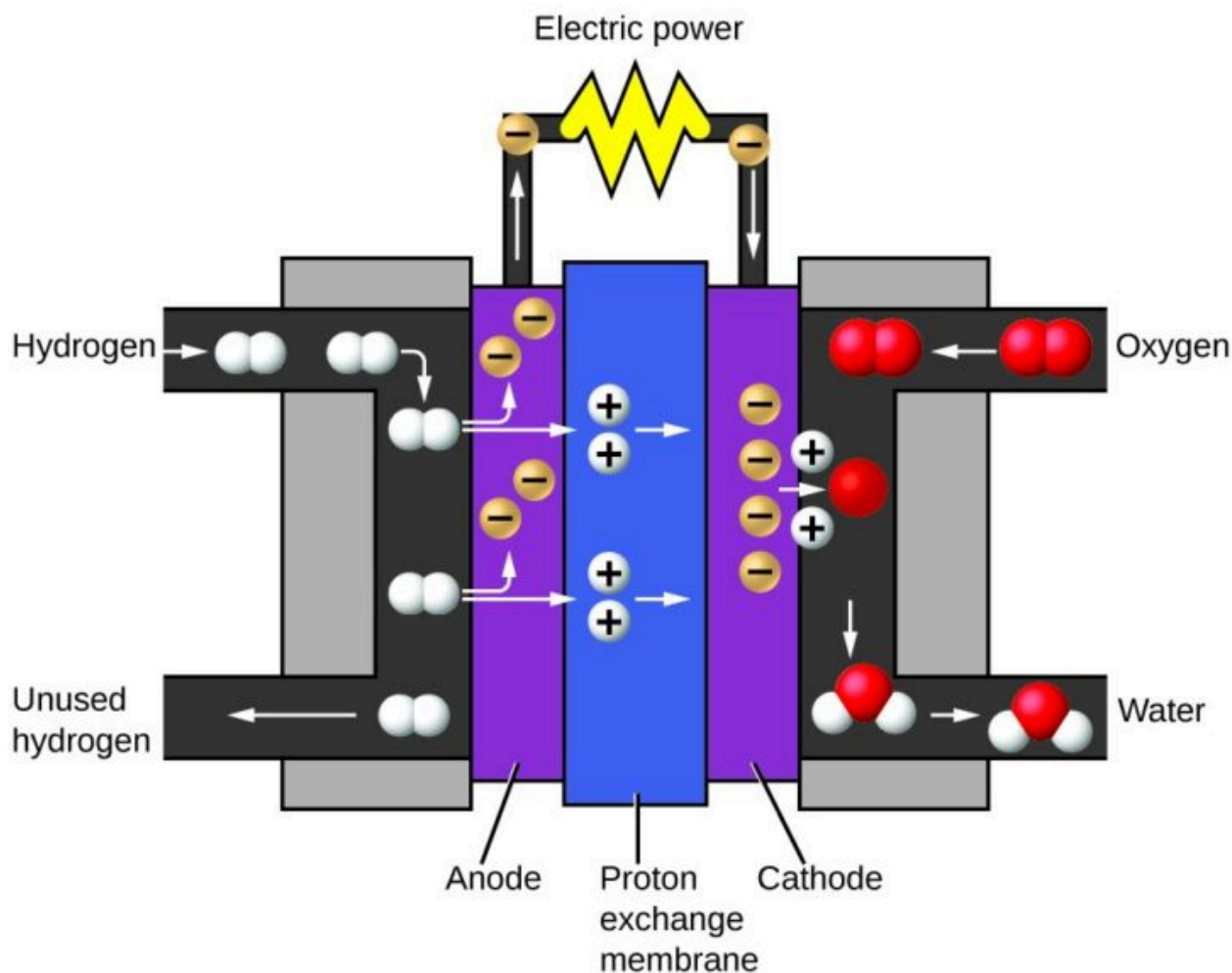
## Chemistry in Everyday Life: Decomposition of Water / Production of Hydrogen

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 1.15**.



**Figure 1.15** 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  $\text{H}_2\text{O}$  separates into  $\text{H}_2$  and  $\text{O}_2$  gases. By: Rice University [Openstax CC BY NC SA](#)

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 of what occurs,  $2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2(g) + \text{O}_2(g)$ , 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 the 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 1.16**). 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 1.16** A fuel cell generates electrical energy from hydrogen and oxygen via an electrochemical process and produces only water as the waste product. By: Rice University [Openstax CC BY NC SA](https://openstax.org/r/ocw-openstax)

## Chemistry in Everyday Life: Chemistry of Cell Phones

Imagine how different your life would be without cell phones (**Figure 1.17**) 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 composed 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 1.17** Almost one-third of naturally occurring elements are used to make a cell phone. By: John Taylor  
[Openstax CC BY NC SA](#)

# PHYSICAL AND CHEMICAL PROPERTIES

## (1.3)

OpenStax

---

### Physical and Chemical Properties

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

- Identify properties of and changes in matter as physical or chemical
- Identify properties of matter as extensive or intensive

The characteristics that 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. Some physical properties, such as density and color, may be observed without changing the physical state of the matter. 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 the chemical identities of the substances contained in the matter. Physical changes are observed when wax melts, when sugar dissolves in coffee, and when steam condenses into liquid water (**Figure 1.18**). 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.





(a)



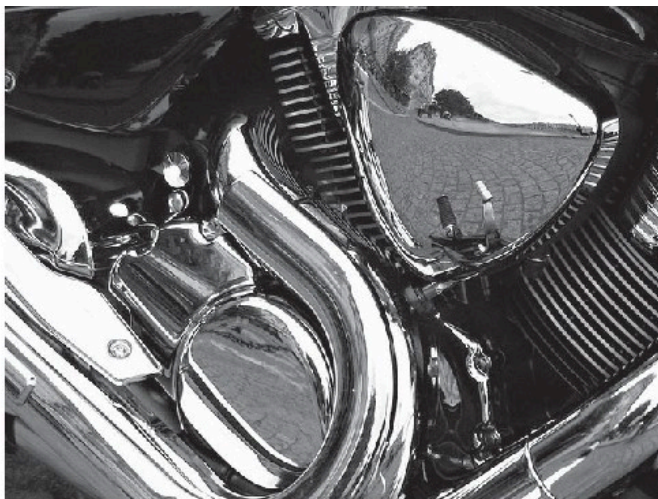
(b)

**Figure 1.18** (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. By: Rice University [Openstax CC BY NC SA](#)

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, and many other types of reactivity. Iron, for example, combines with oxygen in the presence of water to form rust; chromium does not oxidize (**Figure 1.19**). Nitroglycerin is very dangerous because it explodes easily; neon poses almost no hazard because it is very unreactive.



(a)



(b)

**Figure 1.19** (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. By: Rice University [Openstax CC BY NC SA](#)

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 1.20**).



(a)



(b)



(c)



(d)

**Figure 1.20** (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. By: Jeff Turner, Gloria Cabada-Leman, Roberto Verzo [Openstax CC BY NC SA](#)

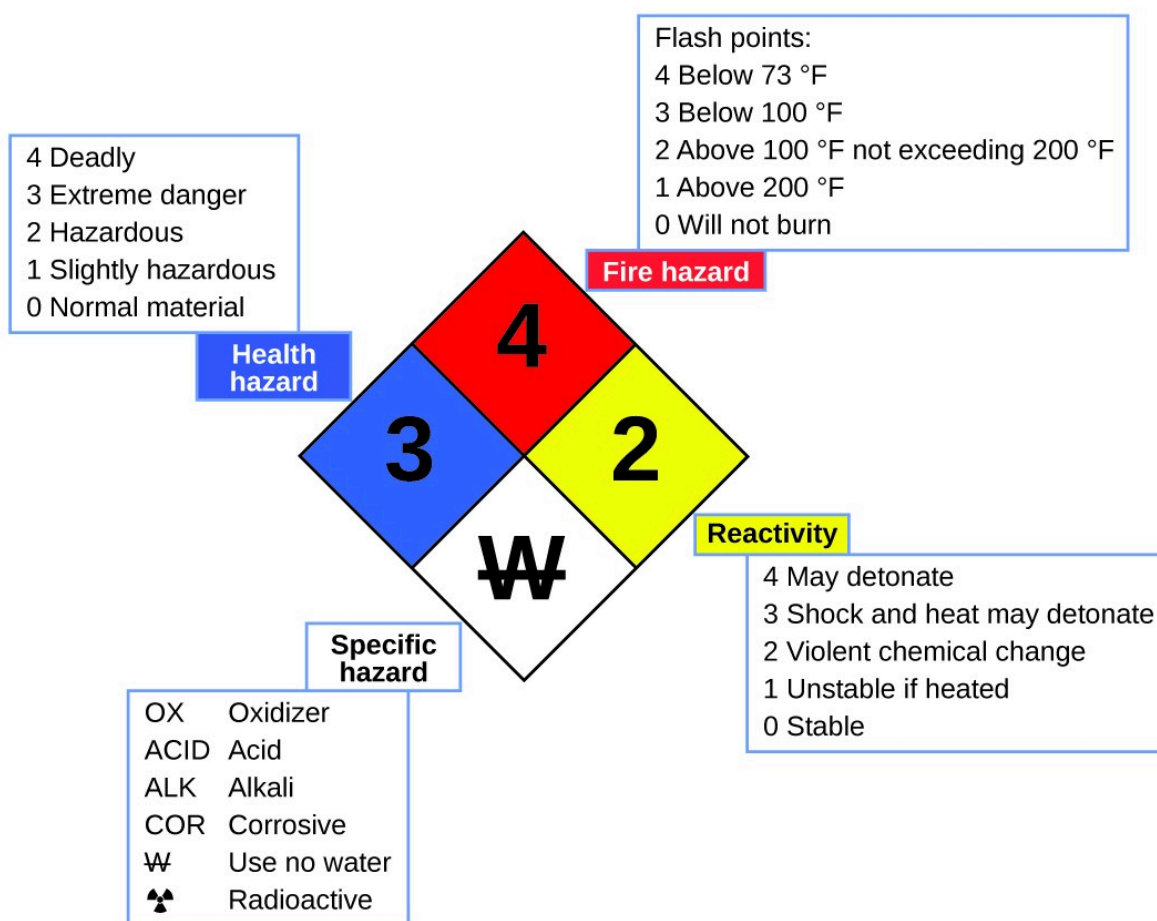
Properties of matter fall into one of two categories. If the property depends on the amount of matter present,



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 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 splattered 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 (an extensive property).

## Chemistry in Everyday Life: Hazard Diamond

You may have seen the symbol shown in **Figure 1.21** 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 1.21** The National Fire Protection Agency (NFPA) hazard diamond summarizes the major hazards of a chemical substance. By: Rice University [Openstax CC BY NC SA](#)

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. 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 intermediate conductivities).

The periodic table is a table of elements that places elements with similar properties close together (**Figure 1.22**). You will learn more about the periodic table as you continue your study of chemistry.

**Periodic Table of the Elements**

**Color Code**

<span style="background-color: #d3d3d3; border: 1px solid black; display: inline-block; width: 15px; height: 15px;"></span> Metal	<b>Solid</b>
<span style="background-color: #f0f0f0; border: 1px solid black; display: inline-block; width: 15px; height: 15px;"></span> Metalloid	<b>Liquid</b>
<span style="background-color: #e0e0e0; border: 1px solid black; display: inline-block; width: 15px; height: 15px;"></span> Nonmetal	<b>Gas</b>

**Hydrogen (H) Callout:**

Atomic number → 1  
 Symbol → H  
 Atomic mass → 1.008  
 Name → hydrogen

**Figure 1.22** 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. By: Rice University [Openstax CC BY NC SA](#)

# MEASUREMENTS (1.4)

OpenStax

---

## Measurements

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

- Explain the process of measurement
- Identify the three basic parts of a quantity
- Describe the properties and units of length, mass, volume, density, temperature, and time
- Perform basic unit calculations and conversions in the metric and other unit systems

Measurements provide much of the information that informs the hypotheses, theories, and laws describing 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.

(Scientific notation is also known as exponential notation; a review of this topic can be found in **Appendix B**.) For example, the maximum takeoff weight of a Boeing 777-200ER airliner is 298,000 kilograms, which can also be written as  $2.98 \times 10^5$  kg. The mass of the average mosquito is about 0.0000025 kilograms, which can be written as  $2.5 \times 10^{-6}$  kg.

**Units**, such as liters, pounds, and centimeters, are standards of comparison for measurements. A 2-liter bottle of a soft drink contains a volume of beverage that is twice that of the accepted volume of 1 liter. The meat used to prepare a 0.25-pound hamburger weighs one-fourth as much as the accepted weight of 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.

The measurement units for seven fundamental properties (“base units”) are listed in [Table 1.3](#). 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. Units for other properties may be derived from these seven base units.

**Table 1.3 Base Units of the SI System By: Rice University** [OpenStax CC BY-NC-SA 4.0](#)

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

Everyday measurement units are often defined as fractions or multiples of other units. Milk is commonly packaged in containers of 1 gallon (4 quarts), 1 quart (0.25 gallon), and 1 pint (0.5 quart). This same approach is used with SI units, 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 1.4](#).

**Table 1.4 Common Unit Prefixes By: Rice University [OpenStax CC BY-NC-SA 4.0](#)**

Prefix	Symbol	Factor	Example
femto	f	$10^{-15}$	1 femtosecond (fs) = $1 \times 10^{-15}$ s (0.000000000000001 s)
pico	p	$10^{-12}$	1 picometer (pm) = $1 \times 10^{-12}$ m (0.000000000001 m)
nano	n	$10^{-9}$	4 nanograms (ng) = $4 \times 10^{-9}$ g (0.000000004 g)
micro	$\mu$	$10^{-6}$	1 microliter ( $\mu$ L) = $1 \times 10^{-6}$ L (0.000001 L)

**Table 1.5 Common Unit Prefixes By: Rice University [OpenStax CC BY-NC-SA 4.0](#)**

Prefix	Symbol	Factor	Example
milli	m	$10^{-3}$	2 millimoles (mmol) = $2 \times 10^{-3}$ mol (0.002 mol)
centi	c	$10^{-2}$	7 centimeters (cm) = $7 \times 10^{-2}$ m (0.07 m)
deci	d	$10^{-1}$	1 deciliter (dL) = $1 \times 10^{-1}$ L (0.1 L)
kilo	k	$10^3$	1 kilometer (km) = $1 \times 10^3$ m (1000 m)
mega	M	$10^6$	3 megahertz (MHz) = $3 \times 10^6$ Hz (3,000,000 Hz)
giga	G	$10^9$	8 gigayears (Gyr) = $8 \times 10^9$ yr (8,000,000,000 yr)
tera	T	$10^{12}$	5 terawatts (TW) = $5 \times 10^{12}$ W (5,000,000,000,000 W)

## Link to Learning

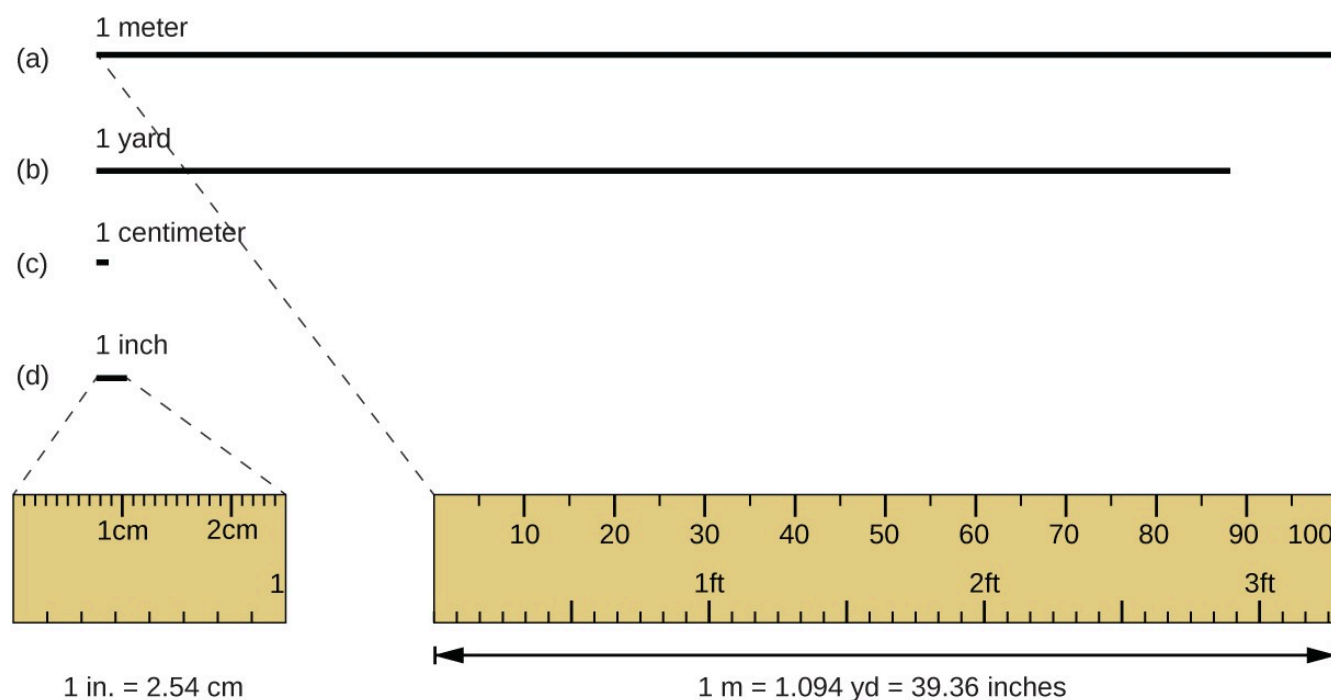
Need a refresher or more practice with scientific notation? Visit this site (<http://openstaxcollege.org/l/16notation>) to go over the basics of scientific notation.

## 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 1.23**); 1 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 1.23** 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. By: Rice University [Openstax CC BY NC SA](#)

## 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 1.24**). 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 1.24** This replica prototype kilogram is housed at the National Institute of Standards and Technology (NIST) in Maryland. (credit: National Institutes of Standards and Technology) By: Rice University [Openstax CC BY NC SA](#)

## 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 ( $^{\circ}$ ). The degree **Celsius ( $^{\circ}\text{C}$ )** 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 ( $0^{\circ}\text{C}$ ) and boils at 373.15 K ( $100^{\circ}\text{C}$ ) by definition, and normal human body temperature is approximately 310 K ( $37^{\circ}\text{C}$ ). 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 =  $0.000003\text{ s} = 3 \times 10^{-6}$  and 5 megaseconds =  $5,000,000\text{ s} = 5 \times 10^6\text{ s}$ . Alternatively, hours, days, and years can be used.

## Derived SI Units

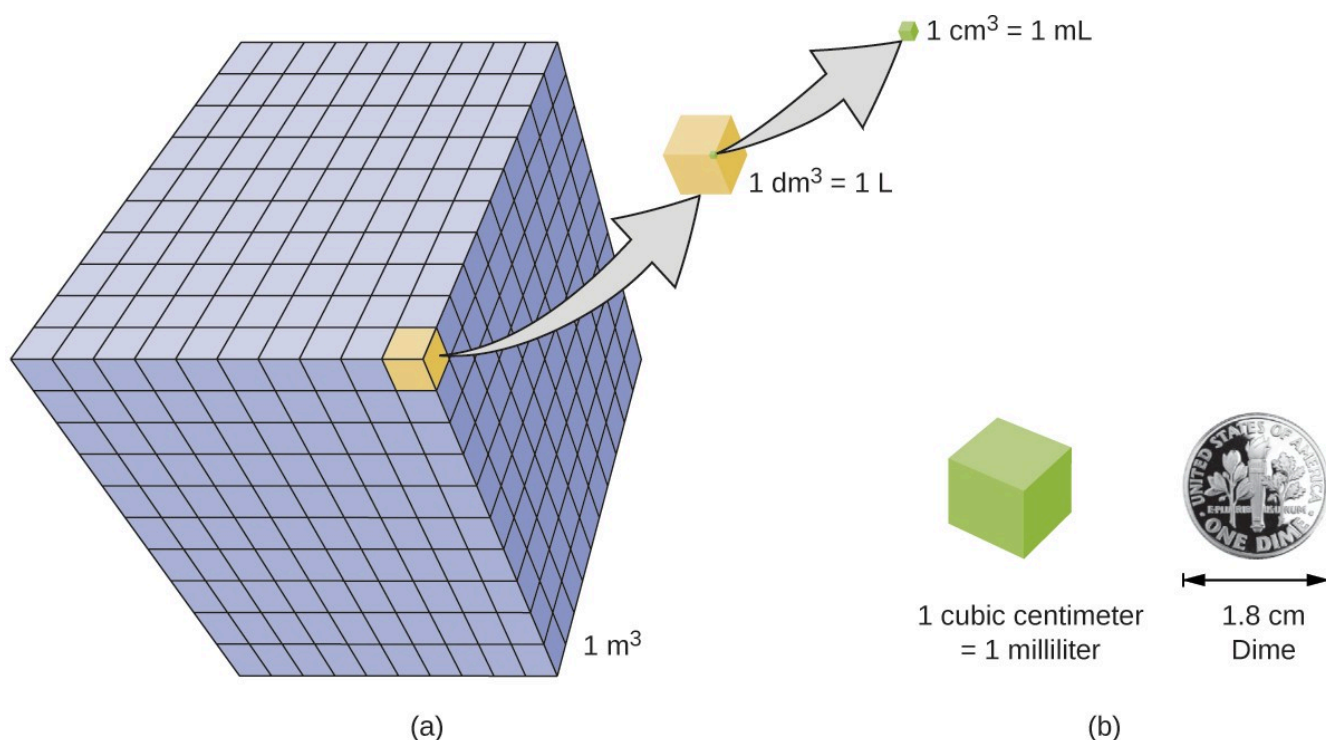
We can derive many units from the seven SI base units. For example, we can use the base unit of length to define a unit of volume and the base units of mass and length to define a unit of density.

### 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 1.25**). The standard volume is a **cubic meter (m<sup>3</sup>)**, 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.

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<sup>3</sup>). A **liter (L)** is the more common name for the cubic decimeter. One liter is about 1.06 quarts.

A **cubic centimeter (cm<sup>3</sup>)** is the volume of a cube with an edge length of exactly one centimeter. The abbreviation **cc** (for **cubic centimeter**) is often used by health professionals. A cubic centimeter is equivalent to a **milliliter (mL)** and is 1/1000 of a liter.



**Figure 1.25** (a) The relative volumes are shown for cubes of  $1 \text{ m}^3$ ,  $1 \text{ dm}^3$  ( $1 \text{ L}$ ), and  $1 \text{ cm}^3$  ( $1 \text{ mL}$ ) (not to scale). (b) The diameter of a dime is compared relative to the edge length of a  $1\text{-cm}^3$  ( $1\text{-mL}$ ) cube. By: Rice University [Openstax CC BY NC SA](#)

## 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 ( $\text{kg}/\text{m}^3$ ). For many situations, however, this is an inconvenient unit, and we often use grams per cubic centimeter ( $\text{g}/\text{cm}^3$ ) for the densities of solids and liquids and grams per liter ( $\text{g}/\text{L}$ ) for gases. Although there are exceptions, most liquids and solids have densities that range from about  $0.7 \text{ g}/\text{cm}^3$  (the density of gasoline) to  $19 \text{ g}/\text{cm}^3$  (the density of gold). The density of air is about  $1.2 \text{ g}/\text{L}$ . [Table 1.6](#) shows the densities of some common substances.

**Table 1.6 Densities of Common Substances By: Rice University [OpenStax CC BY-NC-SA 4.0](#)**

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

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

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

### Example 1.1

#### 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<sup>3</sup>. 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.

$$\begin{aligned}\text{volume of lead cube} &= 2.00\text{cm} \times 2.00\text{cm} \times 2.00\text{cm} = 9.00\text{cm}^3 \\ \text{density} &= \frac{\text{mass}}{\text{volume}} = \frac{90.7\text{g}}{8.00\text{cm}^3} = \frac{11.3\text{g}}{1.00\text{cm}^3} = 11.3 \text{ g/cm}^3\end{aligned}$$

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

## Check Your Learning

- (a) To three decimal places, what is the volume of a cube ( $\text{cm}^3$ ) 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)  $0.599 \text{ cm}^3$ ; (b)  $8.91 \text{ g/cm}^3$

## Link to Learning

To learn more about the relationship between mass, volume, and density, use [this interactive simulator](#) to explore the density of different materials, like wood, ice, brick, and aluminum.

## Example 1.2

### Using Displacement of Water to Determine Density

This PhET simulation (<http://openstaxcollege.org/l/16phetmasvolden>) 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 denser 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:

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

### Check Your Learning

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

# MEASUREMENT UNCERTAINTY, ACCURACY, AND PRECISION (1.5)

OpenStax

---

## Measurement Uncertainty, Accuracy, and Precision

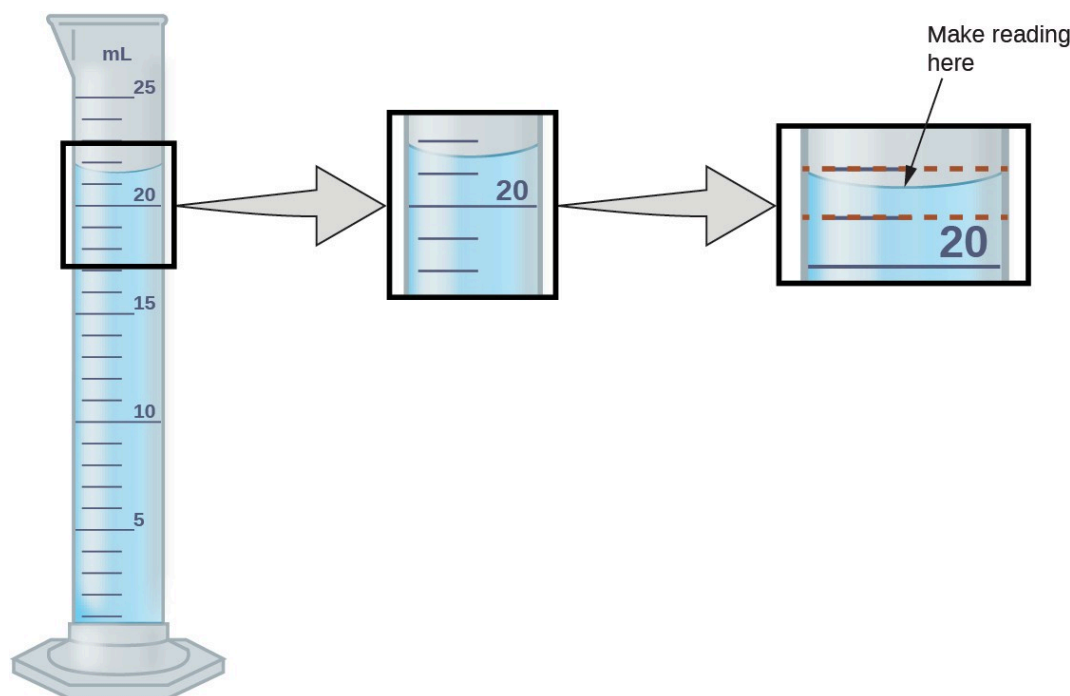
By the end of this section, you will be able to:

- 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**. By counting the eggs in a carton, one can determine *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 1.26** 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. By: Rice University [Openstax CC BY NC SA](#)

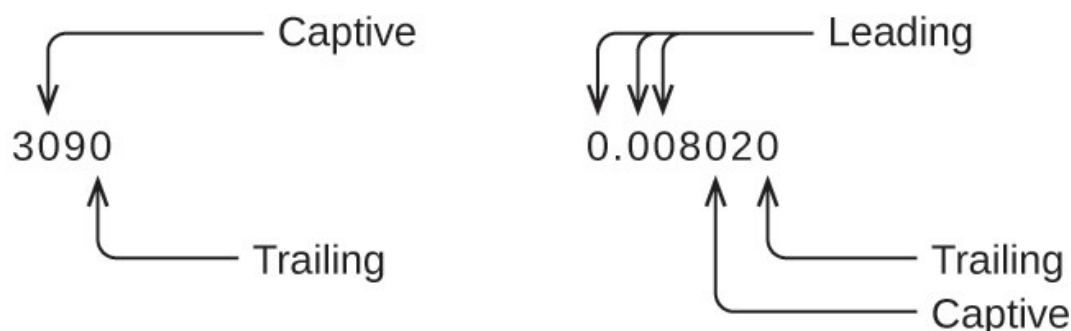
Refer to the illustration in **Figure 1.26**. The bottom of the meniscus in this case clearly lies between the 21 and 22 markings, meaning the liquid volume is *certainly* greater than 21 mL but less than 22 mL. The meniscus appears to be a bit closer to the 22-mL mark than to the 21-mL mark, and so a reasonable estimate of the liquid's volume would be 21.6 mL. In the number 21.6, then, the digits 2 and 1 are certain, but the 6 is an estimate. Some people might estimate the meniscus position to be equally distant from each of the markings and estimate the tenth-place digit as 5, while others may think it to be even closer to the 22-mL mark and estimate this digit to be 7. Note that it would be pointless to attempt to estimate a digit for the hundredths place, given that the tenths-place digit is uncertain. In general, numerical scales such as the one on this graduated cylinder will permit measurements to one-tenth of the smallest scale division. The scale in this case has 1-mL divisions, and so volumes may be measured to the nearest 0.1 mL.

This concept holds true for all measurements, even if you do not actively make an estimate. If you place a quarter on a standard electronic balance, you may obtain a reading of 6.72 g. The digits 6 and 7 are certain, and the 2 indicates that the mass of the quarter is likely between 6.71 and 6.73 grams. The quarter weighs *about* 6.72 grams, with a nominal uncertainty in the measurement of  $\pm 0.01$  gram. If the coin is weighed on a more sensitive balance, the mass might be 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.

A measurement result is properly reported when its significant digits accurately represent the certainty of

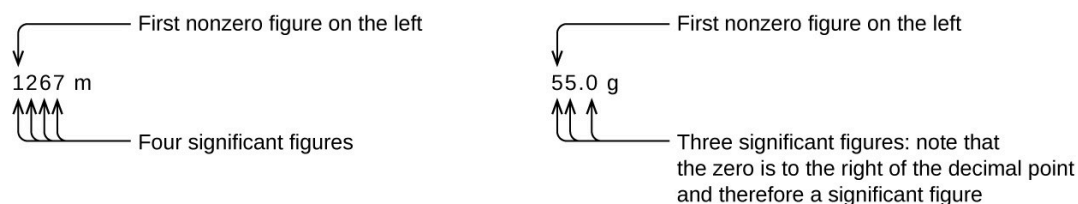


the measurement process. But what if you were analyzing a reported value and trying to determine what is significant and what is not? Well, for starters, all nonzero digits are significant, and it is only zeros that require some thought. We will use the terms “leading,” “trailing,” and “captive” for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



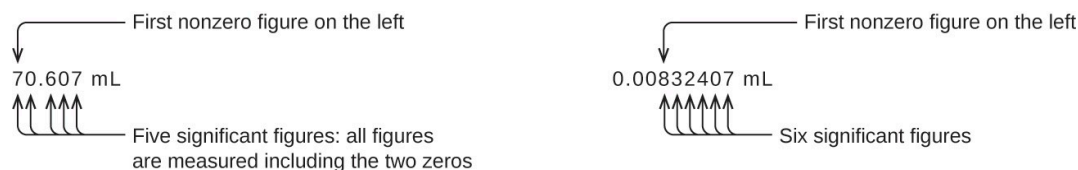
**Figure 1.27** By:  
Rice University  
[Openstax CC BY](#)  
[NC SA](#)

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.



**Figure 1.28** By:  
Rice University  
[Openstax CC BY](#)  
[NC SA](#)

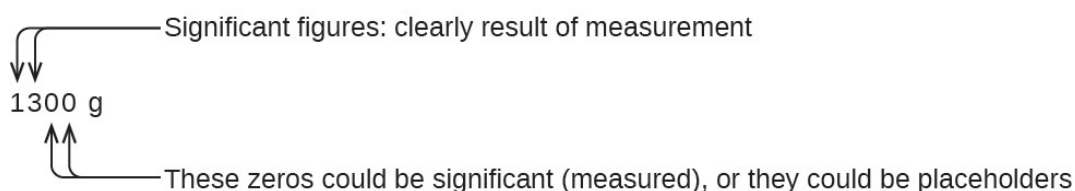
Captive zeros result from measurement and are therefore always significant. Leading zeros, however, are never significant—they merely tell us where the decimal point is located.



**Figure 1.29** By:  
Rice University  
[Openstax CC BY](#)  
[NC SA](#)

The leading zeros in this example are not significant. We could use exponential notation (as described in Appendix B) and express the number as  $8.32407 \times 10^{-3}$ ; 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:  $1.3 \times 10^3$  (two significant figures),  $1.30 \times 10^3$  (three significant figures, if the tens place was measured), or  $1.300 \times 10^3$  (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.



**Figure 1.30** By:  
Rice University  
[Openstax CC BY](#)  
[NC SA](#)

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 when evaluating 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  $3.17 \times 10^8$  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. Take the uncertainty in 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:

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

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

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

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

### Example 1.3

#### Rounding Numbers

Round the following to the indicated number of significant figures:

- 31.57 (to two significant figures)
- 8.1649 (to three significant figures)
- 0.051065 (to four significant figures)
- 0.90275 (to four significant figures)

#### Solution

- 31.57 rounds “up” to 32 (the dropped digit is 5, and the retained digit is even)
- 8.1649 rounds “down” to 8.16 (the dropped digit, 4, is less than 5)
- 0.051065 rounds “down” to 0.05106 (the dropped digit is 5, and the retained digit is even)
- 0.90275 rounds “up” to 0.9028 (the dropped digit is 5, and the retained digit is even)

#### Check Your Learning

Round the following to the indicated number of significant figures:

- 0.424 (to two significant figures)
- 0.0038661 (to three significant figures)
- 421.25 (to four significant figures)
- 28,683.5 (to five significant figures)

**Answer:** (a) 0.42; (b) 0.00387; (c) 421.2; (d) 28,684

## Example 1.4

### Addition and Subtraction with Significant Figures

Rule: When adding or subtracting numbers, round the result to the same number of decimal places as the number with the fewest decimal places (i.e., the least certain value in terms of addition and subtraction).

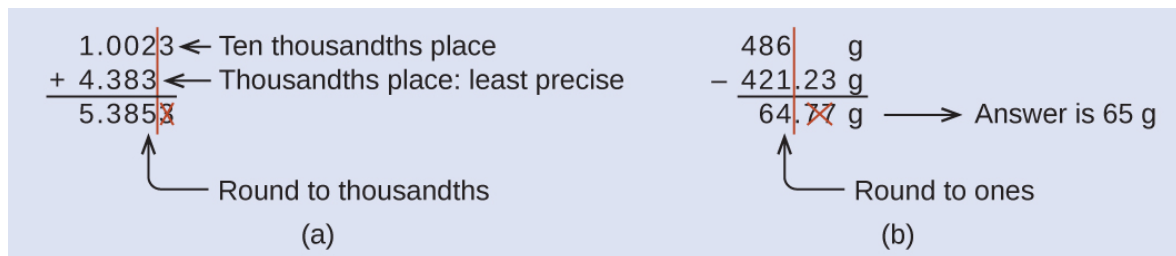
(a) Add 1.0023 g and 4.383 g.

(b) Subtract 421.23 g from 486 g.

### Solution

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

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



**Figure 1.31** By: Rice University [Openstax CC BY NC SA](https://openstax.org/r/chemistry-atoms-first)

### Check Your Learning

(a) Add 2.334 mL and 0.31 mL.

(b) Subtract 55.8752 m from 56.533 m.

**Answer:** (a) 2.64 mL; (b) 0.658 m

### Check Your Learning

(a) Multiply 2.334 cm and 0.320 cm.

(b) Divide 55.8752 m by 56.53 s.

**Answer:** (a)  $0.747 \text{ cm}^2$ ; (b)  $0.9884 \text{ m/s}$

## Example 1.5

### Multiplication and Division with Significant Figures

Rule: When multiplying or dividing numbers, round the result to the same number of digits as the number with the fewest significant figures (the least certain 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)  $0.6238 \text{ cm} \times 6.6 \text{ cm} = 4.11708 \text{ cm}^2$   $\diamond$  result is  $4.1 \text{ cm}^2$  (round to two significant figures)

four significant figures  $\times$  two significant figures  $\diamond$  two significant figures answer

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

(b)  $421.23 \text{ g} / 486 \text{ mL} = 0.866728... \text{ g/mL}$   $\diamond$  result is  $0.867 \text{ g/mL}$  (round to three significant figures) five significant figures three significant figures  $\diamond$  three significant figures answer  
 $421.23 \text{ g} / 486 \text{ mL} = 0.866728... \text{ g/mL}$   $\diamond$  result is  $0.867 \text{ g/mL}$  (round to three significant figures) five significant figures three significant figures  $\diamond$  three significant figures answer  
 $421.23 \text{ g} / 486 \text{ mL} = 0.866728... \text{ g/mL}$   $\diamond$  result is  $0.867 \text{ g/mL}$  (round to three significant figures) five significant figures three significant figures  $\diamond$  three significant figures answer

### Check Your Learning

(a) Multiply 2.334 cm and 0.320 cm.

(b) Divide 55.8752 m by 56.53 s.

**Answer:** (a)  $0.747 \text{ cm}^2$  (b)  $0.9884 \text{ m/s}$

## Example 1.6

### 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

$$V = l \times w \times d$$

$$= 13.44 \text{ dm} \times 5.920 \text{ dm} \times 2.54 \text{ dm}$$

$$= 202.09459... \text{ dm}^3 \text{ (value from calculator)}$$

$$= 202 \text{ dm}^3, \text{ or } 202 \text{ L (answer rounded to three significant figures)}$$

### Check Your Learning

What is the density of a liquid with a mass of 31.1415 g and a volume of 30.13 cm<sup>3</sup>?

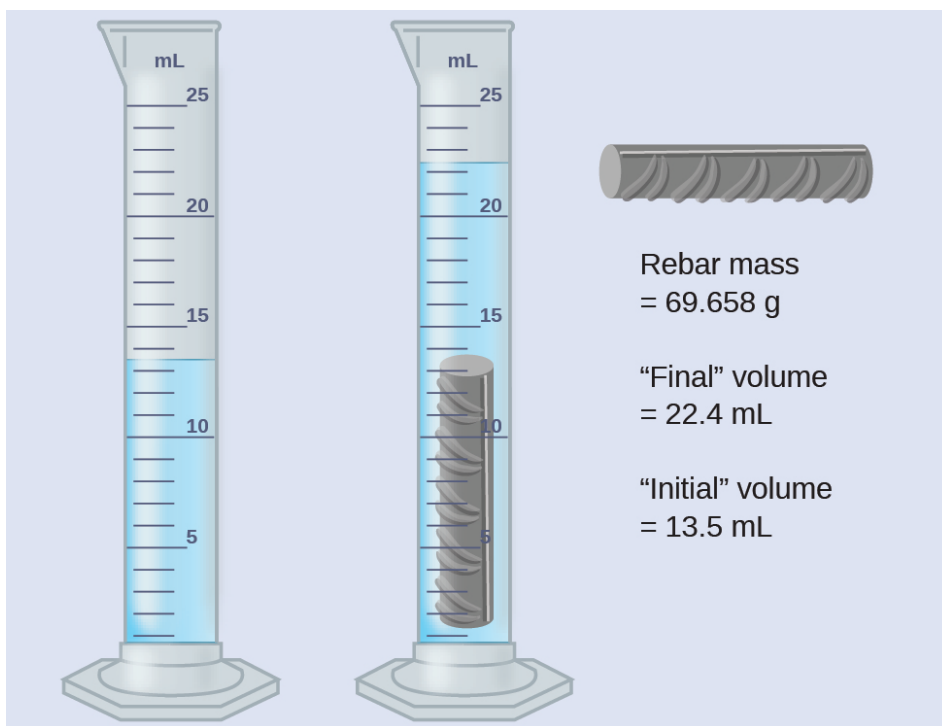
**Answer:** 1.034 g/mL

## Example 1.7

### Experimental Determination of Density Using Water Displacement

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

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



**Figure 1.32** By:  
Rice University  
[Openstax CC BY](#)  
[NC SA](#)

### 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)

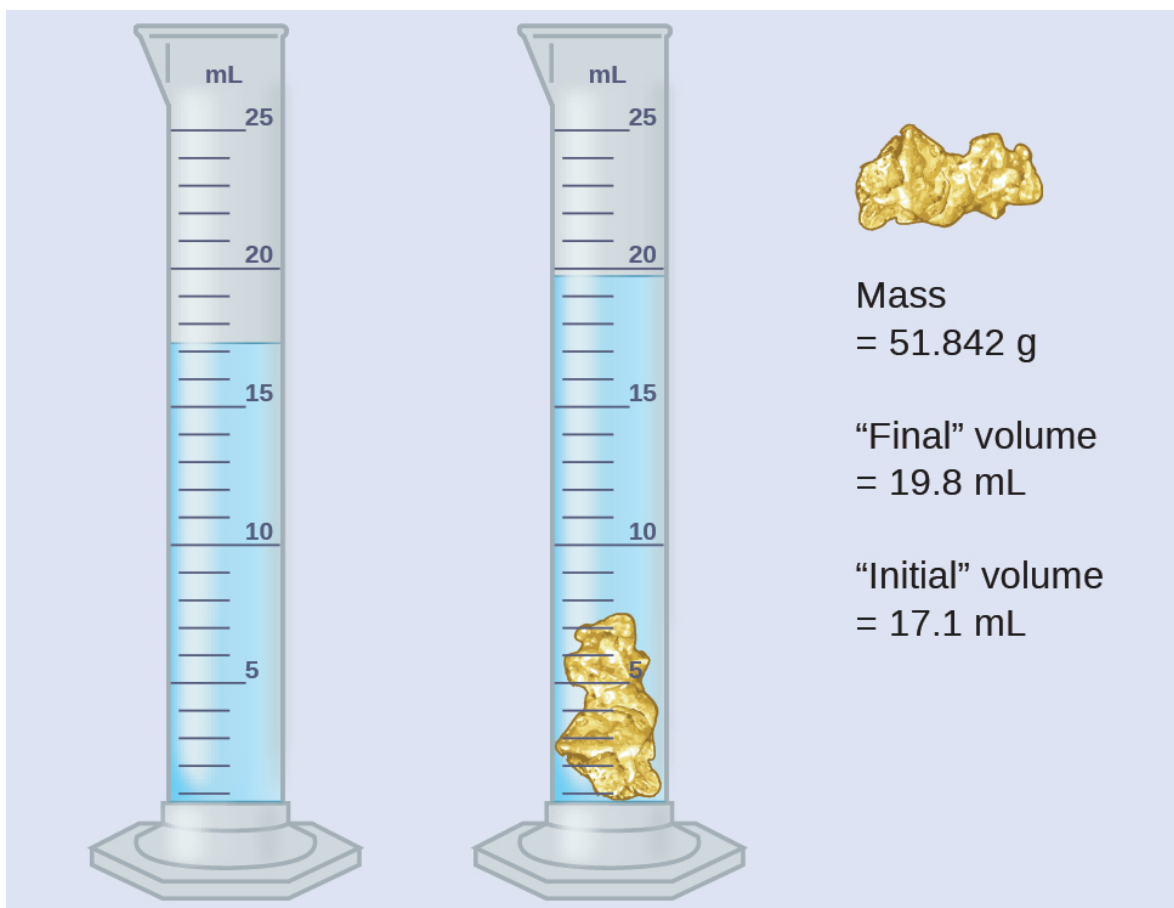
The density is the mass-to-volume ratio:

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

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

From Table 1.4, the density of iron is  $7.9 \text{ g/cm}^3$ , very close to that of rebar, which lends some support to the fact that rebar is mostly iron.

### Check Your Learning



**Figure 1.33** By: Rice University [Openstax CC BY NC SA](#)

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

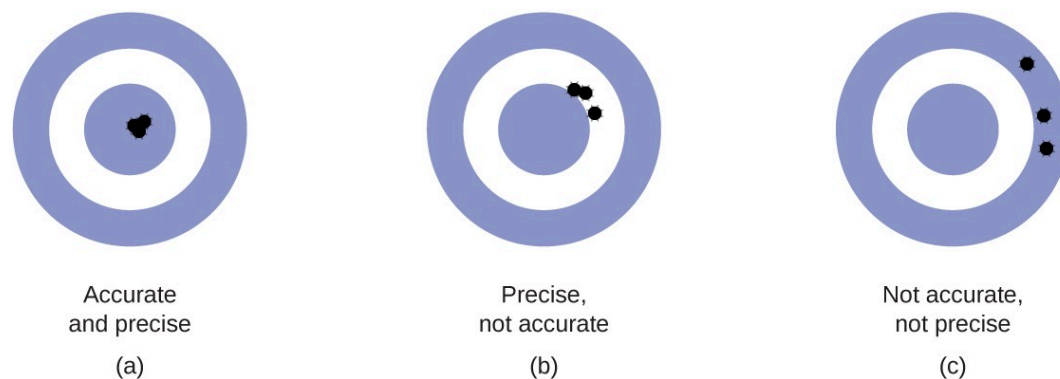
- (a) Use these values to determine the density of this material.
- (b) Do you have any reasonable guesses as to the identity of this material? Explain your reasoning.

**Answer:** (a)  $19 \text{ g/cm}^3$ ; (b) It is likely gold; 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 evaluate 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 1.34**).



**Figure 1.34** (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. By: Rice University  
[Openstax CC BY NC SA](#)

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 1.7](#).

**Table 1.7 Volume (mL) of Cough Medicine  
Delivered by 10-oz (296 mL) Dispensers By:  
Rice University [OpenStax CC BY-NC-SA 4.0](#)**

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	296.1
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).

# MATHEMATICAL TREATMENT OF MEASUREMENT RESULTS (1.6)

OpenStax

## Mathematical Treatment of Measurement Results

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

- Explain the dimensional analysis (factor label) approach to mathematical calculations involving quantities
- Use dimensional analysis to carry out unit conversions for a given property and computations involving two or more properties

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 ( $\text{m/s} = \text{m/s}$ ). 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 among 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 ( $\text{m}/\text{m/s} = \text{s}$ ) 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,  $\text{m}/\text{m}$ ), 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,

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

Several other commonly used conversion factors are given in [Table 1.8](#).

**Table 1.8 Common Conversion Factors By: Rice University [OpenStax](#)  
CC BY-NC-SA 4.0**

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 <sup>3</sup> = 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 a quantity (such as distance in inches) is multiplied by an appropriate unit conversion factor, the quantity is converted 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:

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

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  $\frac{in. \times cm}{in.}$ . Just as for numbers, a ratio of identical units is also numerically equal to one,

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

and the unit product thus simplifies to  $cm$ . (When identical units divide to yield a factor of 1, they are said to “cancel.”) Dimensional analysis may be used to confirm the proper application of unit conversion factors as demonstrated in the following example.

### Example 1.8

#### 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 1.8](#)).

#### Solution

Given the conversion factor, the mass in ounces may be derived using an equation similar to the one used for converting length from inches to centimeters.

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

The unit conversion factor may be represented as:

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

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

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

#### Check Your Learning

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 ensure that their *labels* (units) will appropriately cancel and/or combine to yield the desired unit in the result. As your study of chemistry continues, you will encounter many opportunities to apply this approach.

### Example 1.9

#### Computing Quantities from Measurement Results and Known Mathematical Relations

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

#### Solution

Since density =  $\frac{\text{mass}}{\text{volume}}$ , we need to divide the mass in grams by the volume in milliliters. In general: the number of units of B = the number of units of A  $\times$  unit conversion factor. The necessary conversion factors are given in [Table 1.8](#): 1 lb = 453.59 g; 1 L = 1.0567 qt; 1 L = 1,000 mL. Mass may be converted from pounds to grams as follows:

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

Volume may be converted from quarts to milliliters via two steps:

**Step 1.** Convert quarts to liters.

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

**Step 2.** Convert liters to milliliters.

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

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:

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

### Check Your Learning

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

**Answer:**

$$2.956 \times 10^{-2} \text{L}$$

### Example 1.10

#### Computing Quantities from Measurement Results and Known Mathematical Relations

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

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

#### Solution

- 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:

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

finally,

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

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

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

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

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

### Check Your Learning

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; (b) \$23

## 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, and the position of the trapped liquid along a printed scale may be used as a measure of temperature.

Temperature scales are defined relative to selected reference temperatures: 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:

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

The  $y$ -intercept of the equation,  $b$ , is then calculated using either of the equivalent temperature pairs, ( $100^{\circ}\text{C}$ ,  $212^{\circ}\text{F}$ ) or ( $0^{\circ}\text{C}$ ,  $32^{\circ}\text{F}$ ), as:

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

The equation relating the temperature ( $T$ ) scales is then:

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

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

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

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

$$T_{\circ C} = \frac{5}{9}(T_{\circ F} - 32)$$

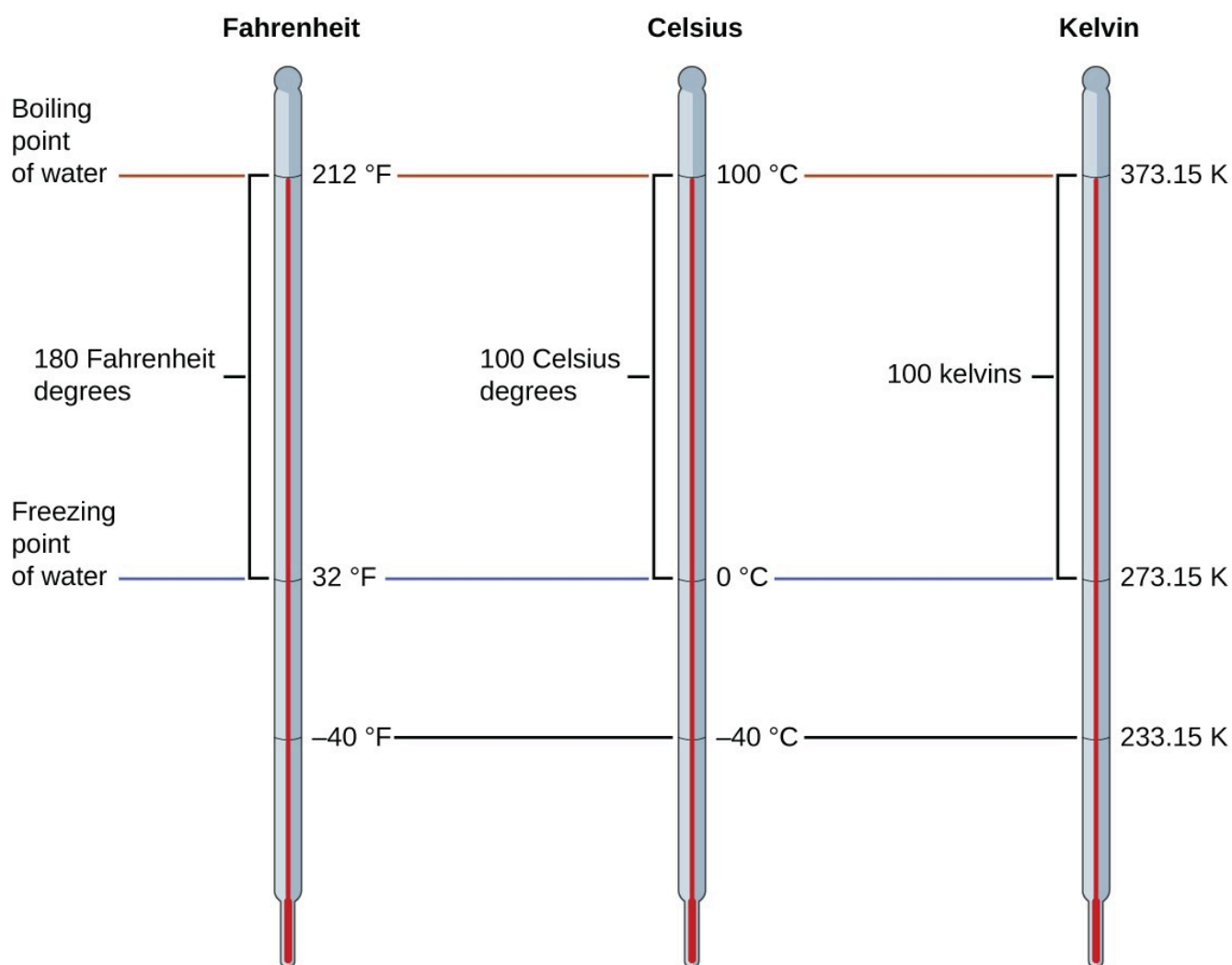
As mentioned earlier in this chapter, the SI unit of temperature is the kelvin (K). Unlike the Celsius and Fahrenheit scales, the kelvin scale is an absolute temperature scale in which 0 (zero) K corresponds to the lowest temperature that can theoretically be achieved. Since the kelvin temperature scale is absolute, a degree symbol is not included in the unit abbreviation, K. The early nineteenth-century discovery of the relationship between a gas's volume and temperature suggested that the volume of a gas would be zero at  $-273.15^{\circ}\text{C}$ . 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 is 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:

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

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

The 273.15 in these equations has been determined experimentally, so it is not exact. **Figure 1.28** shows the relationship among the three temperature scales.



**Figure 1.28** The Fahrenheit, Celsius, and kelvin temperature scales are compared. By: Rice University  
[Openstax CC BY NC SA](#)

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 1.11

#### 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

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

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

#### Check Your Learning

Convert 80.92 °C to K and °F.

**Answer:** 354.07 K, 177.7 °F

### Example 1.12

#### 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

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

(two significant figures)

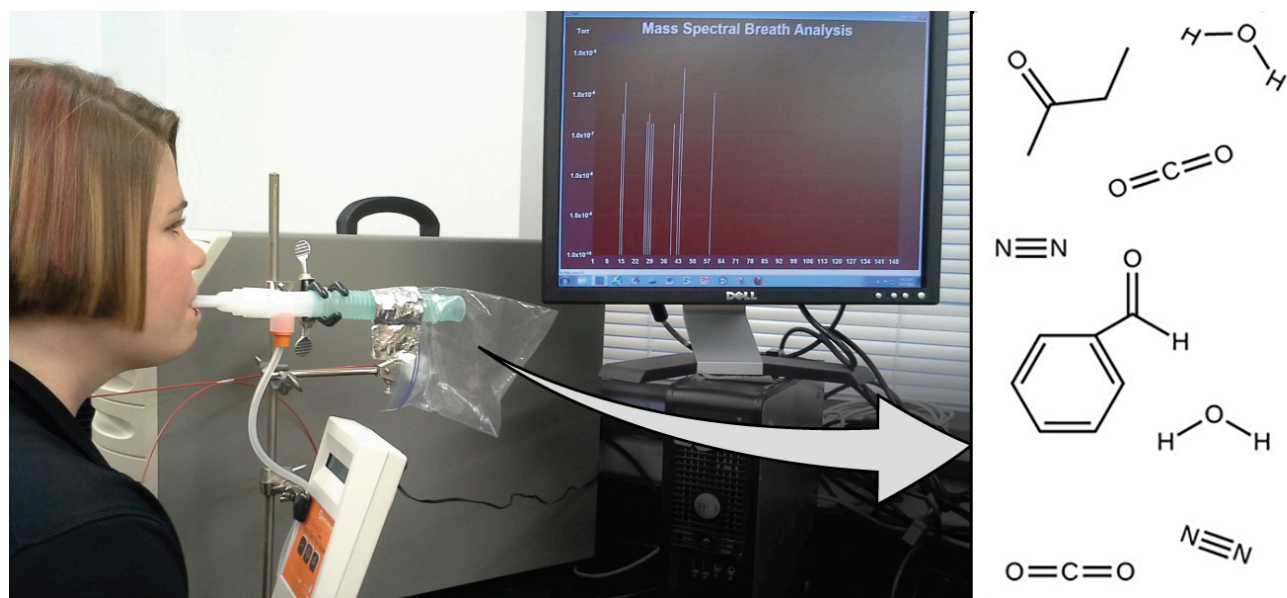
$$K = ^\circ C + 273.15 = 230 + 273 = 503 \text{ K} \longrightarrow 5.0 \times 10^2 \text{ K (Two significant figures)}$$

### Check Your Learning

Convert 50 °F to °C and K.

**Answer:** 10 °C, 280 K

# CHAPTER 2: ATOMS, MOLECULES, AND IONS



**Figure 2.1** Analysis of molecules in an exhaled breath can provide valuable information, leading to early diagnosis of diseases or detection of environmental exposure to harmful substances. By: Paul Flowers  
[Openstax](#) [CC BY NC SA](#)

## Chapter Outline

- Early Ideas in Atomic Theory
- Evolution of Atomic Theory
- Atomic Structure and Symbolism
- Chemical Formulas

## Introduction

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

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

This 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.

# KEY TERMS, KEY EQUATIONS, SUMMARIES, AND EXERCISES (CHAPTER 2)

OpenStax

---

## Key Terms

### alpha particle ( $\alpha$ particle)

positively charged particle consisting of two protons and two neutrons

### 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  $^{12}\text{C}$  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

### Dalton's atomic theory

set of postulates that established the fundamental properties of atoms

### electron

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

## empirical formula

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

## fundamental unit of charge

(also called the elementary charge) equals the magnitude of the charge of an electron ( $e$ ) with  $e =$

$1.602 \times 10^{-19} \text{ C}$

## ion

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

## isomers

compounds with the same chemical formula but different structures

## isotopes

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

## law of constant composition

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

## law of 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

## mass number ( $A$ )

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

## 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.

## neutron

uncharged, subatomic particle located in the nucleus

## nucleus

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

## proton

positively charged, subatomic particle located in the nucleus



### spatial isomers

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

### structural formula

shows the atoms in a molecule and how they are connected

### structural isomer

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

### unified atomic mass unit (u)

alternative unit equivalent to the atomic mass unit

## Key Equation

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

## Summaries

### 2.1 Early Ideas in Atomic Theory

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.

### 2.2 Evolution of Atomic Theory

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.

## 2.3 Atomic Structure and Symbolism

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  $\frac{1}{12}$  of the mass of a carbon-12 atom and is equal to  $1.6605 \times 10^{-24}$  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.

## 2.4 Chemical Formulas

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. 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  $6.022 \times 10^{23}$ , a quantity called Avogadro's number. The mass in grams of 1 mole of substance is its molar mass.

## Exercises

### 2.1 Early Ideas in Atomic Theory

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 of different elements touch, they are part of a single unit of a compound. The following chemical change represented by these spheres may violate one of the ideas of Dalton's atomic theory. Which one?

This equation contains the starting materials of a single, green sphere plus two smaller, purple spheres bonded together. When the starting materials are added together the products of the change are one purple sphere bonded with one green sphere plus one purple sphere bonded with one green sphere.

2.

Which postulate of Dalton's theory is consistent with the following observation concerning the weights of reactants and products? When 100 grams of solid calcium carbonate is heated, 44 grams of carbon dioxide and 56 grams of calcium oxide are produced.

3.

Identify the postulate of Dalton's theory that is violated by the following observations: 59.95% of one sample of titanium dioxide is titanium; 60.10% of a different sample of titanium dioxide is titanium.

4.

Samples of compound X, Y, and Z are analyzed, with results shown here.

Compound	Description	Mass of Carbon	Mass of Hydrogen
X	clear, colorless, liquid with strong odor	1.776 g	0.148 g
Y	clear, colorless, liquid with strong odor	1.974 g	0.329 g
Z	clear, colorless, liquid with strong odor	7.812 g	0.651 g

Do these data provide example(s) of the law of definite proportions, the law of multiple proportions, neither, or both? What do these data tell you about compounds X, Y, and Z?

## 2.2 Evolution of Atomic Theory

5.

The existence of isotopes violates one of the original ideas of Dalton's atomic theory. Which one?

6.

How are electrons and protons similar? How are they different?

7.

How are protons and neutrons similar? How are they different?

8.

Predict and test the behavior of  $\alpha$  particles fired at a "plum pudding" model atom.

(a) Predict the paths taken by  $\alpha$  particles that are fired at atoms with a Thomson's plum pudding model structure. Explain why you expect the  $\alpha$  particles to take these paths.

(b) If  $\alpha$  particles of higher energy than those in (a) are fired at plum pudding atoms, predict how their paths will differ from the lower-energy  $\alpha$  particle paths. Explain your reasoning.

(c) Now test your predictions from (a) and (b). Open the [Rutherford Scattering simulation](#) and select the "Plum Pudding Atom" tab. Set "Alpha Particles Energy" to "min," and select "show traces." Click on the gun to start firing  $\alpha$  particles. Does this match your prediction from (a)? If not, explain why the actual path would be that shown in the simulation. Hit the pause button, or "Reset All." Set "Alpha Particles Energy" to "max," and start firing  $\alpha$  particles. Does this match your prediction from (b)? If not, explain the effect of increased energy on the actual paths as shown in the simulation.

2.

Predict and test the behavior of  $\alpha$  particles fired at a Rutherford atom model.

(a) Predict the paths taken by  $\alpha$  particles that are fired at atoms with a Rutherford atom model structure. Explain why you expect the  $\alpha$  particles to take these paths.

(b) If  $\alpha$  particles of higher energy than those in (a) are fired at Rutherford atoms, predict how their paths will differ from the lower-energy  $\alpha$  particle paths. Explain your reasoning.

(c) Predict how the paths taken by the  $\alpha$  particles will differ if they are fired at Rutherford atoms of elements other than gold. What factor do you expect to cause this difference in paths, and why?

(d) Now test your predictions from (a), (b), and (c). Open the [Rutherford Scattering simulation](#) and select the “Rutherford Atom” tab. Due to the scale of the simulation, it is best to start with a small nucleus, so select “20” for both protons and neutrons, “min” for energy, show traces, and then start firing  $\alpha$  particles. Does this match your prediction from (a)? If not, explain why the actual path would be that shown in the simulation. Pause or reset, set energy to “max,” and start firing  $\alpha$  particles. Does this match your prediction from (b)? If not, explain the effect of increased energy on the actual path as shown in the simulation. Pause or reset, select “40” for both protons and neutrons, “min” for energy, show traces, and fire away. Does this match your prediction from (c)? If not, explain why the actual path would be that shown in the simulation. Repeat this with larger numbers of protons and neutrons. What generalization can you make regarding the type of atom and effect on the path of  $\alpha$  particles? Be clear and specific.

## 2.3 Atomic Structure and Symbolism

10.

In what way are isotopes of a given element always different? In what way(s) are they always the same?

11.

Write the symbol for each of the following ions:

- (a) the ion with a 1+ charge, atomic number 55, and mass number 133
- (b) the ion with 54 electrons, 53 protons, and 74 neutrons
- (c) the ion with atomic number 15, mass number 31, and a 3– charge
- (d) the ion with 24 electrons, 30 neutrons, and a 3+ charge

12.

Write the symbol for each of the following ions:

- (a) the ion with a 3+ charge, 28 electrons, and a mass number of 71
- (b) the ion with 36 electrons, 35 protons, and 45 neutrons
- (c) the ion with 86 electrons, 142 neutrons, and a 4+ charge

- (d) the ion with a 2+ charge, atomic number 38, and mass number 87

13.

Open the [Build an Atom simulation](#) and click on the Atom icon.

- (a) Pick any one of the first 10 elements that you would like to build and state its symbol.  
(b) Drag protons, neutrons, and electrons onto the atom template to make an atom of your element.

State the numbers of protons, neutrons, and electrons in your atom, as well as the net charge and mass number.

- (c) Click on “Net Charge” and “Mass Number,” check your answers to (b), and correct, if needed.  
(d) Predict whether your atom will be stable or unstable. State your reasoning.  
(e) Check the “Stable/Unstable” box. Was your answer to (d) correct? If not, first predict what you can do to make a stable atom of your element, and then do it and see if it works. Explain your reasoning.

14.

Open the [Build an Atom simulation](#)

- (a) Drag protons, neutrons, and electrons onto the atom template to make a neutral atom of Oxygen-16 and give the isotope symbol for this atom.  
(b) Now add two more electrons to make an ion and give the symbol for the ion you have created.

15.

Open the [Build an Atom simulation](#)

- (a) Drag protons, neutrons, and electrons onto the atom template to make a neutral atom of Lithium-6 and give the isotope symbol for this atom.  
(b) Now remove one electron to make an ion and give the symbol for the ion you have created.

16.

Determine the number of protons, neutrons, and electrons in the following isotopes that are used in medical diagnoses:

- (a) atomic number 9, mass number 18, charge of 1–  
(b) atomic number 43, mass number 99, charge of 7+  
(c) atomic number 53, atomic mass number 131, charge of 1–  
(d) atomic number 81, atomic mass number 201, charge of 1+  
(e) Name the elements in parts (a), (b), (c), and (d).

17.

The following are properties of isotopes of two elements that are essential in our diet. Determine the number of protons, neutrons and electrons in each and name them.

- (a) atomic number 26, mass number 58, charge of 2+  
(b) atomic number 53, mass number 127, charge of 1–

18.

Give the number of protons, electrons, and neutrons in neutral atoms of each of the following isotopes:

(a)  $^{10}_{5}\text{B}$

(b)  $^{199}_{80}\text{Hg}$

(c)  $^{63}_{29}\text{Cu}$

(d)  $^{13}_{6}\text{C}$

(e)  $^{77}_{34}\text{Se}$

19.

Give the number of protons, electrons, and neutrons in neutral atoms of each of the following isotopes:

(a)

initial; display: inline; font-style: normal; font-weight: normal; line-height: normal; font-size: 14px; text-indent: 0px; text-align: left; text-transform: none; letter-spacing: normal; word-spacing: normal; overflow-wrap: normal; white-space: nowrap; float: none; direction: ltr; max-width: none; max-height: none; min-width: 0px; min-height: 0px; border: 0px; padding: 0px; margin: 0px; position: relative;" tabindex="0" role="presentation" data-mathml=" ${}^7_3\text{Li}$ "> ${}^7_3\text{Li}$

(b) <span id="MathJax-Element-1422-Frame" class="MathJax" style="box-sizing: border-box; overflow: initial; display: inline; font-style: normal; font-weight: normal; line-height: normal; font-size: 14px; text-indent: 0px; text-align: left; text-transform: none; letter-spacing: normal; word-spacing: normal; overflow-wrap: normal; white-space: nowrap; float: none; direction: ltr; max-width: none; max-height: none; min-width: 0px; min-height: 0px; border: 0px; padding: 0px; margin: 0px; position: relative;" tabindex="0" role="presentation" data-mathml=" ${}^{125}_{52}\text{Te}$ "> ${}^{125}_{52}\text{Te}$

(c) <span id="MathJax-Element-1423-Frame" class="MathJax" style="box-sizing: border-box; overflow: initial; display: inline; font-style: normal; font-weight: normal; line-height: normal; font-size: 14px; text-indent: 0px; text-align: left; text-transform: none; letter-spacing: normal; word-spacing: normal; overflow-wrap: normal; white-space: nowrap; float: none; direction: ltr; max-width: none; max-height: none; min-width: 0px; min-height: 0px; border: 0px; padding: 0px; margin: 0px; position: relative;" tabindex="0" role="presentation" data-mathml=" ${}^{109}_{47}\text{Ag}$ "> ${}^{109}_{47}\text{Ag}$

(d) <span id="MathJax-Element-1424-Frame" class="MathJax" style="box-sizing: border-box; overflow: initial; display: inline; font-style: normal; font-weight: normal; line-height: normal; font-size: 14px; text-indent: 0px; text-align: left; text-transform: none; letter-spacing: normal; word-spacing: normal; overflow-wrap: normal; white-space: nowrap; float: none; direction: ltr; max-width: none; max-height: none; min-width: 0px; min-height: 0px; border: 0px; padding: 0px; margin: 0px; position: relative;" tabindex="0" role="presentation" data-mathml=" ${}^{15}_7\text{N}$ "> ${}^{15}_7\text{N}$

(e) <span id="MathJax-Element-1425-Frame" class="MathJax" style="box-sizing: border-box; overflow: initial; display: inline; font-style: normal; font-weight: normal; line-height: normal; font-size: 14px; text-indent: 0px; text-align: left; text-transform: none; letter-spacing: normal; word-spacing: normal; overflow-wrap: normal; white-space: nowrap; float: none; direction: ltr; max-width: none; max-height: none; min-width: 0px; min-height: 0px; border: 0px; padding: 0px; margin: 0px; position: relative;" tabindex="0" role="presentation" data-mathml=" ${}^{31}_{15}\text{P}$ "> ${}^{31}_{15}\text{P}$

20.

Click on the [site](#) and select the “Mix Isotopes” tab, hide the “Percent Composition” and “Average Atomic Mass” boxes, and then select the element boron.

(a) Write the symbols of the isotopes of boron that are shown as naturally occurring in significant amounts.

(b) Predict the relative amounts (percentages) of these boron isotopes found in nature. Explain the reasoning behind your choice.



(c) Add isotopes to the black box to make a mixture that matches your prediction in (b). You may drag isotopes from their bins or click on “More” and then move the sliders to the appropriate amounts.

(d) Reveal the “Percent Composition” and “Average Atomic Mass” boxes. How well does your mixture match with your prediction? If necessary, adjust the isotope amounts to match your prediction.

(e) Select “Nature’s” mix of isotopes and compare it to your prediction. How well does your prediction compare with the naturally occurring mixture? Explain. If necessary, adjust your amounts to make them match “Nature’s” amounts as closely as possible.

[21.](#)

Repeat [Exercise 2.20](#) using an element that has three naturally occurring isotopes.

[22.](#)

An element has the following natural abundances and isotopic masses: 90.92% abundance with 19.99 amu, 0.26% abundance with 20.99 amu, and 8.82% abundance with 21.99 amu. Calculate the average atomic mass of this element.

[23.](#)

Average atomic masses listed by IUPAC are based on a study of experimental results. Bromine has two isotopes,  $^{79}\text{Br}$  and  $^{81}\text{Br}$ , whose masses (78.9183 and 80.9163 amu, respectively) and abundances (50.69% and 49.31%, respectively) were determined in earlier experiments. Calculate the average atomic mass of bromine based on these experiments.

[24.](#)

Variations in average atomic mass may be observed for elements obtained from different sources. Lithium provides an example of this. The isotopic composition of lithium from naturally occurring minerals is 7.5%  $^6\text{Li}$  and 92.5%  $^7\text{Li}$ , which have masses of 6.01512 amu and 7.01600 amu, respectively. A commercial source of lithium, recycled from a military source, was 3.75%  $^6\text{Li}$  (and the rest  $^7\text{Li}$ ). Calculate the average atomic mass values for each of these two sources.

[25.](#)

The average atomic masses of some elements may vary, depending upon the sources of their ores. Naturally occurring boron consists of two isotopes with accurately known masses ( $^{10}\text{B}$ , 10.0129 amu and  $^{11}\text{B}$ , 11.00931 amu). The actual atomic mass of boron can vary from 10.807 to 10.819, depending on whether the mineral source is from Turkey or the United States. Calculate the percent abundances leading to the two values of the average atomic masses of boron from these two countries.

[26.](#)

The  $^{18}\text{O}$ : $^{16}\text{O}$  abundance ratio in some meteorites is greater than that used to calculate the average atomic mass

of oxygen on earth. Is the average mass of an oxygen atom in these meteorites greater than, less than, or equal to that of a terrestrial oxygen atom?

## 2.4 Chemical Formulas

27.

Explain why the symbol for an atom of the element oxygen and the formula for a molecule of oxygen differ.

28.

Explain why the symbol for the element sulfur and the formula for a molecule of sulfur differ.

29.

Write the molecular and empirical formulas of the following compounds:

(a)

Figure A shows a carbon atom that forms two, separate double bonds with two oxygen atoms.

(b)

Figure B shows a hydrogen atom which forms a single bond with a carbon atom. The carbon atom forms a triple bond with another carbon atom. The second carbon atom forms a single bond with a hydrogen atom.

(c)

Figure C shows a carbon atom forming a double bond with another carbon atom. Each carbon atom forms a single bond with two hydrogen atoms.

(d)

Figure D shows a sulfur atom forming single bonds with four oxygen atoms. Two of the oxygen atoms form a single bond with a hydrogen atom.

30.

Write the molecular and empirical formulas of the following compounds:

(a)

Figure A shows a structural diagram of four carbon atoms bonded together into a chain. The two carbon atoms on the left form a double bond with each other. All of the remaining carbon atoms form single bonds with each other. The leftmost carbon also forms single bonds with two hydrogen. The second carbon in the chain forms a single bond with a hydrogen atom. The third carbon in the chain forms a single bond with two hydrogen atoms each. The rightmost carbon forms a single bond with three hydrogen atoms each.

(b)

Figure B shows a structural diagram of a molecule that has a chain of four carbon atoms. The leftmost carbon atom forms a single bond with three hydrogen atoms each and single bond with the second carbon atom. The second carbon atom forms a triple bond with the third carbon atom. The third carbon atom forms a single bond to the fourth carbon atom. The fourth carbon atom forms a single bond to three hydrogen atoms each.

(c)

Figure C shows a structural diagram of two silicon atoms are bonded together with a single bond. Each of the silicon atoms form single bonds to two chlorine atoms each and one hydrogen atom.

(d)

Figure D shows a structural diagram of a phosphorus atom that forms a single bond to four oxygen atoms each. Three of the oxygen atoms each have a single bond to a hydrogen atom.

[31.](#)

Determine the empirical formulas for the following compounds:

- (a) caffeine,  $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$
- (b) sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$
- (c) hydrogen peroxide,  $\text{H}_2\text{O}_2$
- (d) glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$
- (e) ascorbic acid (vitamin C),  $\text{C}_6\text{H}_8\text{O}_6$

32.

Determine the empirical formulas for the following compounds:

- (a) acetic acid,  $\text{C}_2\text{H}_4\text{O}_2$
- (b) citric acid,  $\text{C}_6\text{H}_8\text{O}_7$
- (c) hydrazine,  $\text{N}_2\text{H}_4$
- (d) nicotine,  $\text{C}_{10}\text{H}_{14}\text{N}_2$
- (e) butane,  $\text{C}_4\text{H}_{10}$

[33.](#)

Write the empirical formulas for the following compounds:

- (a)

Figure A shows a structural diagram of two carbon atoms that form a single bond with each other. The left carbon atom forms single bonds with hydrogen atoms each. The right carbon forms a double bond to an oxygen atom. The right carbon also forms a single bond to another oxygen atom. This oxygen atom also forms a single bond to a hydrogen atom.

(b)

Figure B shows a structural diagram containing a leftmost carbon that forms single bonds to three hydrogen atoms each. This leftmost carbon also forms a single bond to a second carbon atom. The second carbon atom forms a double bond with an oxygen atom. The second carbon also forms a single bond to a second oxygen atom. This oxygen atom forms a single bond to a third carbon atom. This third carbon atom forms single bonds with two hydrogen atoms each as well as a single bond with another carbon atom. The rightmost carbon atom forms a single bond with three hydrogen atoms each.

34.

Open the [Build a Molecule simulation](#) and select the “Larger Molecules” tab. Select an appropriate atom’s “Kit” to build a molecule with two carbon and six hydrogen atoms. Drag atoms into the space above the “Kit” to make a molecule. A name will appear when you have made an actual molecule that exists (even if it is not the one you want). You can use the scissors tool to separate atoms if you would like to change the connections. Click on “3D” to see the molecule, and look at both the space-filling and ball-and-stick possibilities.

(a) Draw the structural formula of this molecule and state its name.

(b) Can you arrange these atoms in any way to make a different compound?

35.

Use the [Build a Molecule simulation](#) to repeat [Exercise 2.34](#), but build a molecule with two carbons, six hydrogens, and one oxygen.

(a) Draw the structural formula of this molecule and state its name.

(b) Can you arrange these atoms to make a different molecule? If so, draw its structural formula and state its name.

(c) How are the molecules drawn in (a) and (b) the same? How do they differ? What are they called (the type of relationship between these molecules, not their names)?

36.

Use the [Build a Molecule simulation](#) to repeat [Exercise 2.34](#), but build a molecule with three carbons, seven hydrogens, and one chlorine.

(a) Draw the structural formula of this molecule and state its name.

(b) Can you arrange these atoms to make a different molecule? If so, draw its structural formula and state its name.

(c) How are the molecules drawn in (a) and (b) the same? How do they differ? What are they called (the type of relationship between these molecules, not their names)?

37.

Write a sentence that describes how to determine the number of moles of a compound in a known mass of the compound if we know its molecular formula.

38.

Compare 1 mole of  $\text{H}_2$ , 1 mole of  $\text{O}_2$ , and 1 mole of  $\text{F}_2$ .

(a) Which has the largest number of molecules? Explain why.

(b) Which has the greatest mass? Explain why.

39.

Which contains the greatest mass of oxygen: 0.75 mol of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ), 0.60 mol of formic acid ( $\text{HCO}_2\text{H}$ ), or 1.0 mol of water ( $\text{H}_2\text{O}$ )? Explain why.

40.

Which contains the greatest number of moles of oxygen atoms: 1 mol of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ), 1 mol of formic acid ( $\text{HCO}_2\text{H}$ ), or 1 mol of water ( $\text{H}_2\text{O}$ )? Explain why.

41.

How are the molecular mass and the molar mass of a compound similar and how are they different?

42.

Calculate the molar mass of each of the following compounds:

(a) hydrogen fluoride,  $\text{HF}$

(b) ammonia,  $\text{NH}_3$

(c) nitric acid,  $\text{HNO}_3$

(d) silver sulfate,  $\text{Ag}_2\text{SO}_4$

(e) boric acid,  $\text{B}(\text{OH})_3$

43.

Calculate the molar mass of each of the following:

(a)  $\text{S}_8$

(b)  $\text{C}_5\text{H}_{12}$

(c)  $\text{Sc}_2(\text{SO}_4)_3$

(d)  $\text{CH}_3\text{COCH}_3$  (acetone)

(e)  $\text{C}_6\text{H}_{12}\text{O}_6$  (glucose)

44.

Calculate the empirical or molecular formula mass and the molar mass of each of the following minerals:

- (a) limestone,  $\text{CaCO}_3$
- (b) halite,  $\text{NaCl}$
- (c) beryl,  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$
- (d) malachite,  $\text{Cu}_2(\text{OH})_2\text{CO}_3$
- (e) turquoise,  $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8(\text{H}_2\text{O})_4$

45.

Calculate the molar mass of each of the following:

- (a) the anesthetic halothane,  $\text{C}_2\text{HBrClF}_3$
- (b) the herbicide paraquat,  $\text{C}_{12}\text{H}_{14}\text{N}_2\text{Cl}_2$
- (c) caffeine,  $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$
- (d) urea,  $\text{CO}(\text{NH}_2)_2$
- (e) a typical soap,  $\text{C}_{17}\text{H}_{35}\text{CO}_2\text{Na}$

46.

Determine the number of moles of compound and the number of moles of each type of atom in each of the following:

- (a) 25.0 g of propylene,  $\text{C}_3\text{H}_6$

(b)  $3.06 \times 10^{-3}$  g of the amino acid glycine,  $\text{C}_2\text{H}_5\text{NO}_2$

- (c) 25 lb of the herbicide Treflan,  $\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}_4\text{F}$  (1 lb = 454 g)

- (d) 0.125 kg of the insecticide Paris Green,  $\text{Cu}_4(\text{AsO}_3)_2(\text{CH}_3\text{CO}_2)_2$

- (e) 325 mg of aspirin,  $\text{C}_6\text{H}_4(\text{CO}_2\text{H})(\text{CO}_2\text{CH}_3)$

47.

Determine the mass of each of the following:

- (a) 0.0146 mol KOH

- (b) 10.2 mol ethane,  $\text{C}_2\text{H}_6$

(c) 1.6 mol of the compound  $\text{C}_6\text{H}_4(\text{CO}_2\text{H})(\text{CO}_2\text{CH}_3)$

min-height: 0px; border: 0px; padding: 0px; margin: 0px; position: relative;" tabindex="0" role="presentation" data-mathml="<math>\times 10^{-3}</math> mol Na<sub>2</sub> SO<sub>4</sub>

(d) 6.854 <math>\times 10^3</math> mol glucose, C<sub>6</sub> H<sub>12</sub> O<sub>6</sub>

(e) 2.86 mol Co(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub>

48.

Determine the number of moles of the compound and determine the number of moles of each type of atom in each of the following:

- (a) 2.12 g of potassium bromide, KBr
- (b) 0.1488 g of phosphoric acid, H<sub>3</sub>PO<sub>4</sub>
- (c) 23 kg of calcium carbonate, CaCO<sub>3</sub>
- (d) 78.452 g of aluminum sulfate, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>
- (e) 0.1250 mg of caffeine, C<sub>8</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub>

[49.](#)

Determine the mass of each of the following:

- (a) 2.345 mol LiCl
- (b) 0.0872 mol acetylene, C<sub>2</sub>H<sub>2</sub>
- (c) 3.3 <math>\times 10^{-2}</math> mol Na<sub>2</sub> CO<sub>3</sub>
- (d) 1.23 <math>\times 10^3</math> mol fructose, C<sub>6</sub> H<sub>12</sub> O<sub>6</sub>
- (e) 0.5758 mol FeSO<sub>4</sub>(H<sub>2</sub>O)<sub>7</sub>

50.

The approximate minimum daily dietary requirement of the amino acid leucine,  $\text{C}_6\text{H}_{13}\text{NO}_2$ , is 1.1 g. What is this requirement in moles?

51.

Determine the mass in grams of each of the following:

(a) 0.600 mol of oxygen atoms

(b) 0.600 mol of oxygen molecules,  $\text{O}_2$

(c) 0.600 mol of ozone molecules,  $\text{O}_3$

52.

A 55-kg woman has  $7.5 \times 10^{-3}$  mol of hemoglobin (molar mass = 64,456 g/mol) in her blood. How many hemoglobin molecules is this? What is this quantity in grams?

53.

Determine the number of atoms and the mass of zirconium, silicon, and oxygen found in 0.3384 mol of zircon,  $\text{ZrSiO}_4$ , a semiprecious stone.

54.

Determine which of the following contains the greatest mass of hydrogen: 1 mol of  $\text{CH}_4$ , 0.6 mol of  $\text{C}_6\text{H}_6$ , or 0.4 mol of  $\text{C}_3\text{H}_8$ .

55.

Determine which of the following contains the greatest mass of aluminum: 122 g of  $\text{AlPO}_4$ , 266 g of  $\text{Al}_2\text{Cl}_6$ , or 225 g of  $\text{Al}_2\text{S}_3$ .

56.

Diamond is one form of elemental carbon. An engagement ring contains a diamond weighing 1.25 carats (1 carat = 200 mg). How many atoms are present in the diamond?

57.

The Cullinan diamond was the largest natural diamond ever found (January 25, 1905). It weighed 3104 carats (1 carat = 200 mg). How many carbon atoms were present in the stone?

58.



One 55-gram serving of a particular cereal supplies 270 mg of sodium, 11% of the recommended daily allowance. How many moles and atoms of sodium are in the recommended daily allowance?

59.

A certain nut crunch cereal contains 11.0 grams of sugar (sucrose,  $C_{12}H_{22}O_{11}$ ) per serving size of 60.0 grams. How many servings of this cereal must be eaten to consume 0.0278 moles of sugar?

60.

A tube of toothpaste contains 0.76 g of sodium monofluorophosphate ( $Na_2PO_3F$ ) in 100 mL.

(a) What mass of fluorine atoms in mg was present?

(b) How many fluorine atoms were present?

61.

Which of the following represents the least number of molecules?

(a) 20.0 g of  $H_2O$  (18.02 g/mol)

(b) 77.0 g of  $CH_4$  (16.06 g/mol)

(c) 68.0 g of  $CaH_2$  (42.09 g/mol)

(d) 100.0 g of  $N_2O$  (44.02 g/mol)

(e) 84.0 g of  $HF$  (20.01 g/mol)

# EARLY IDEAS IN ATOMIC THEORY (2.1)

OpenStax

---

## Early Ideas in Atomic Theory

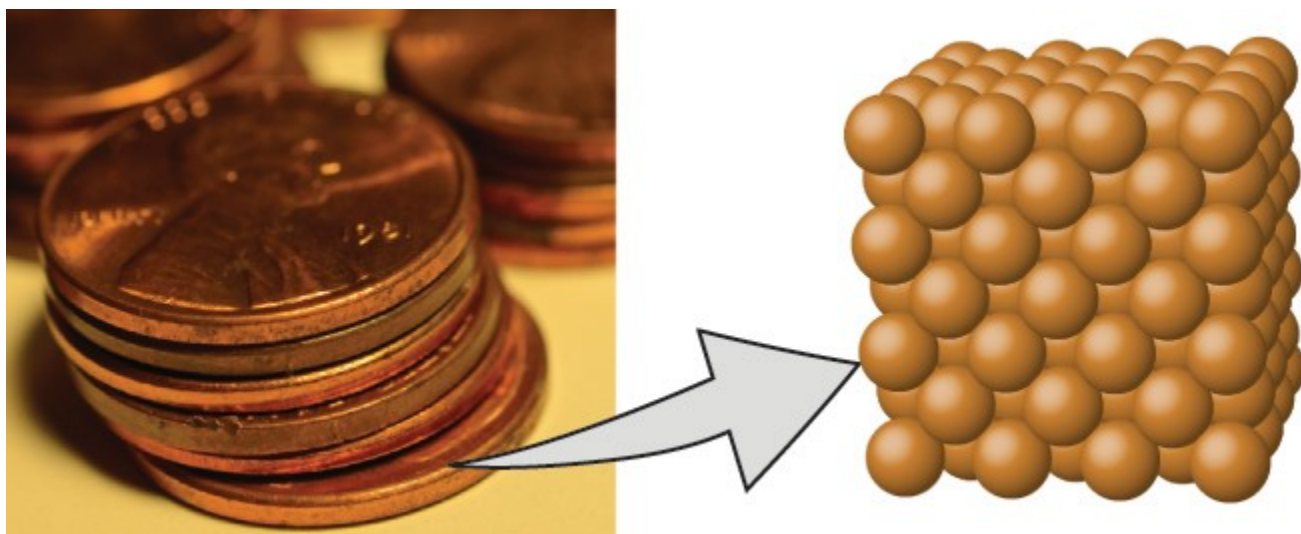
By the end of this section, you will be able to:

- 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 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.

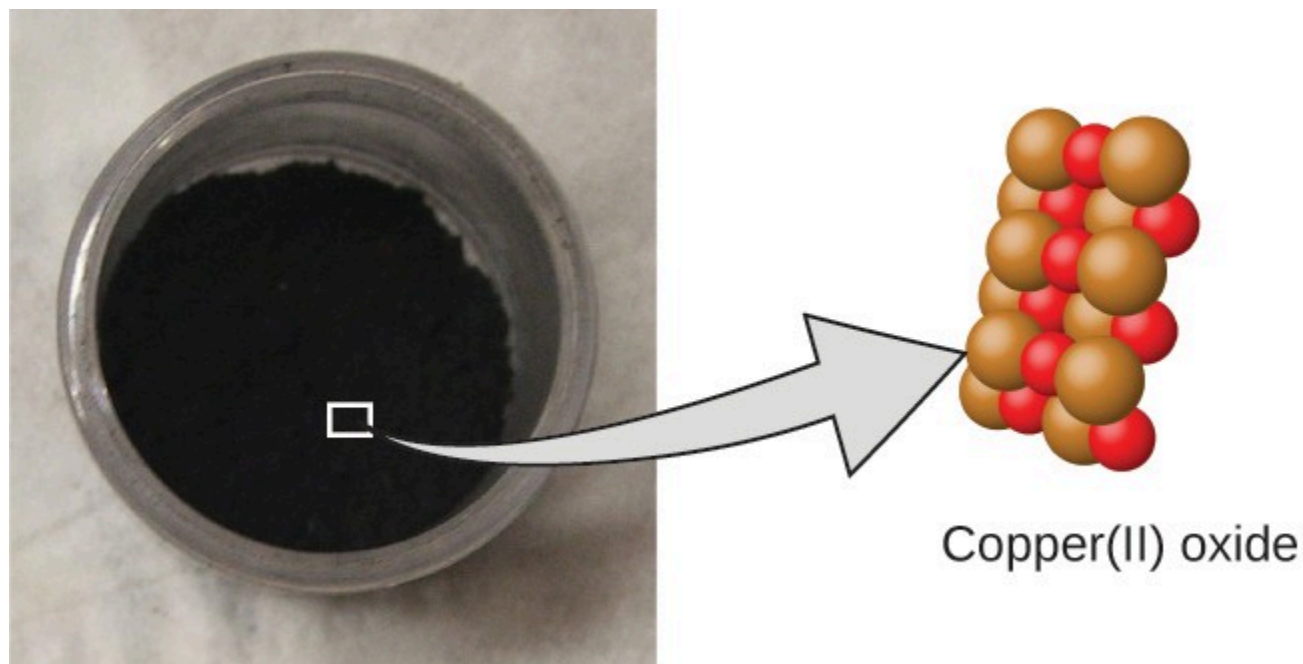
The Aristotelian view of the composition of matter held sway for over two thousand years until English schoolteacher John Dalton helped to revolutionize chemistry with his hypothesis that the behavior of matter could be explained using an atomic theory. First published in 1807, many of Dalton's hypotheses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

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



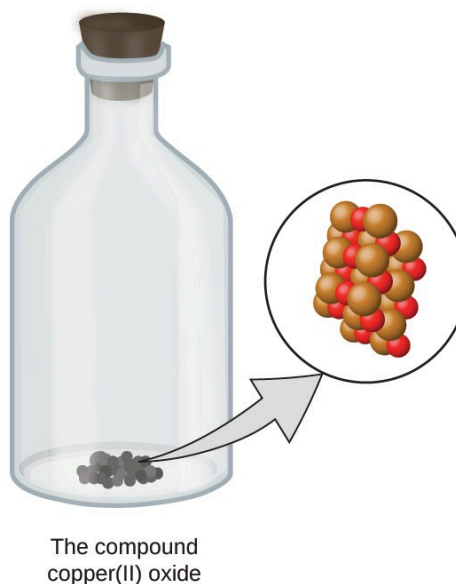
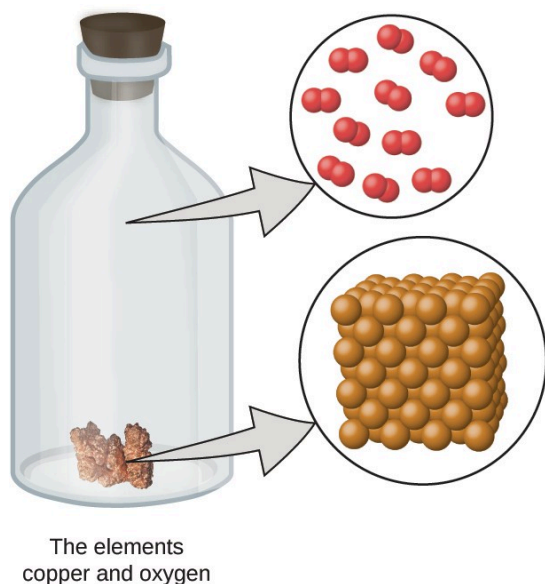
**Figure 2.2** A pre-1982 copper penny (left) contains approximately  $3 \times 10^{22}$  copper atoms (several dozen are represented as brown spheres at the right), each of which has the same chemical properties. By: slgckgc [Flickr CC BY NC SA](#)

- Atoms of one element differ in properties from atoms of all other elements.
- A compound consists of atoms of two or more elements combined in a small, whole-number ratio. In a given compound, the number of atoms of each of its elements is always present in the same ratio (**Figure 2.3**).



**Figure 2.3** Copper(II) oxide, a powdery, black compound, results from the combination of two types of atoms—copper (brown spheres) and oxygen (red spheres)—in a 1:1 ratio. By: Chemicalinterest [Openstax CC BY NC SA](#)

- 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 2.4**).



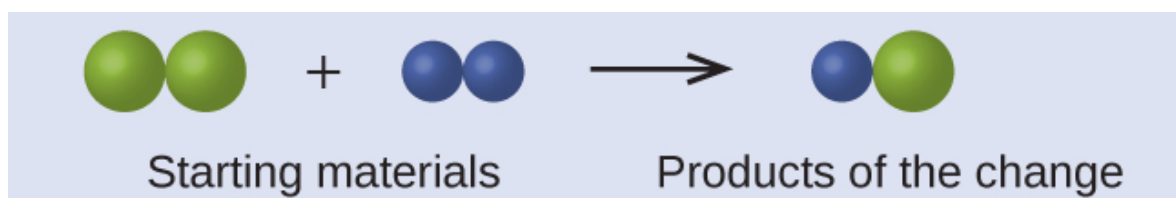
**Figure 2.4** When the elements copper (a shiny, red-brown solid, shown here as brown spheres) and oxygen (a clear and colorless gas, shown here as red spheres) react, their atoms rearrange to form a compound containing copper and oxygen (a powdery, black solid). By: Rice University [OpenStax](#) CC BY NC SA

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

#### 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?



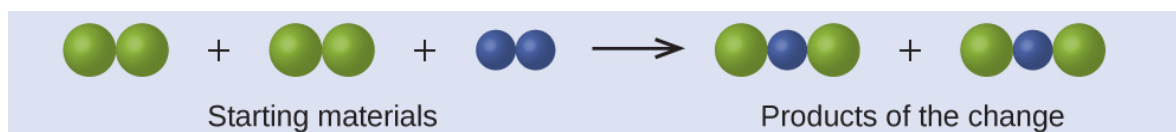
**Figure 2.5** By: Rice University [Openstax CC BY NC SA](#)

### 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.)

### Check Your Learning

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?



**Figure 2.6** By: Rice University [Openstax CC BY NC SA](#)

**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](#).

**Table 2.1 Constant Composition of Isooctane By: Rice University [OpenStax CC BY-NC-SA 4.0](#)**

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

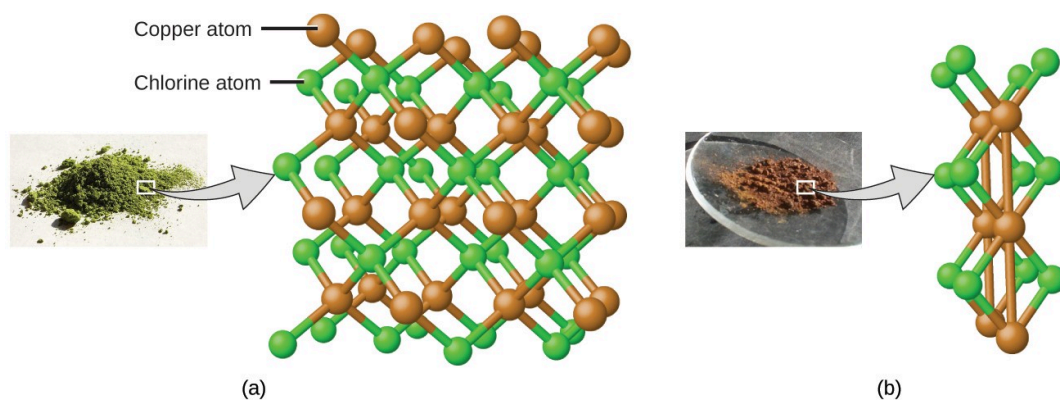
It is worth noting that although all samples of a particular compound have the same mass ratio, the converse is not true in general. That is, samples that have the same mass ratio are not necessarily the same substance. For example, there are many compounds other than isooctane that also have a carbon-to-hydrogen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

$$\frac{\frac{1.116\text{gCl}}{1\text{gCu}}}{\frac{0.558\text{gCl}}{1\text{gCu}}} = \frac{2}{1}$$

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

This can be explained by atomic theory if the copper-to-chlorine ratio in the brown compound is 1 copper atom to 2 chlorine atoms, and the ratio in the green compound is 1 copper atom to 1 chlorine atom. The ratio of chlorine atoms (and thus the ratio of their masses) is therefore 2 to 1 (**Figure 2.7**).

**Figure 2.7**

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. By: Benjah-bmm27, Walkerma [Wikimedia Commons CC BY NC SA](#)

## Example 2.2

### Laws of Definite and Multiple Proportions

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

### Solution

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

$$\frac{1.33gO}{1gC}$$

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

$$\frac{2.67gO}{1gC}$$



The ratio of these ratios is:

$$\frac{\frac{1.33\text{gO}}{1\text{gC}}}{\frac{2.67\text{gO}}{1\text{gC}}} = \frac{1}{2}$$

This supports the law of multiple proportions. This means that A and B are different compounds, with A having one-half as much carbon per amount of oxygen (or twice as much carbon per amount of oxygen) as B. A possible pair of compounds that would fit this relationship would be A = CO and B = CO<sub>2</sub>.

### Check Your Learning

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

**Answer:** In compound X, the mass ratio of carbon to hydrogen is  $\frac{14.13\text{gC}}{2.96\text{gH}}$ . In compound Y,

the mass ratio of carbon to hydrogen is  $\frac{19.91\text{gC}}{3.34\text{gH}}$ . The ratio of these ratios is

$$\frac{\frac{14.13\text{gC}}{2.96\text{gH}}}{\frac{19.91\text{gC}}{3.34\text{gH}}} = \frac{4.77\text{gC/gH}}{5.96\text{gC/gH}} = 0.800 = \frac{4}{5}$$

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



# EVOLUTION OF ATOMIC THEORY (2.2)

OpenStax

---

## Evolution of Atomic Theory

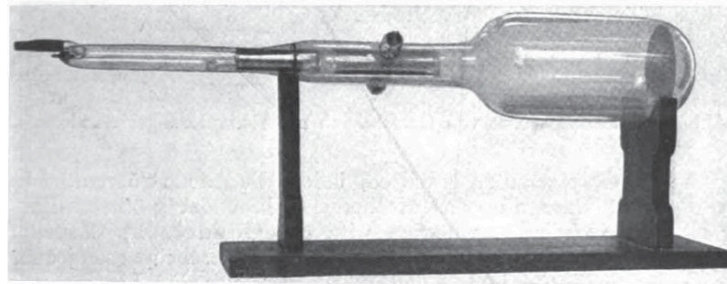
By the end of this section, you will be able to:

- 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

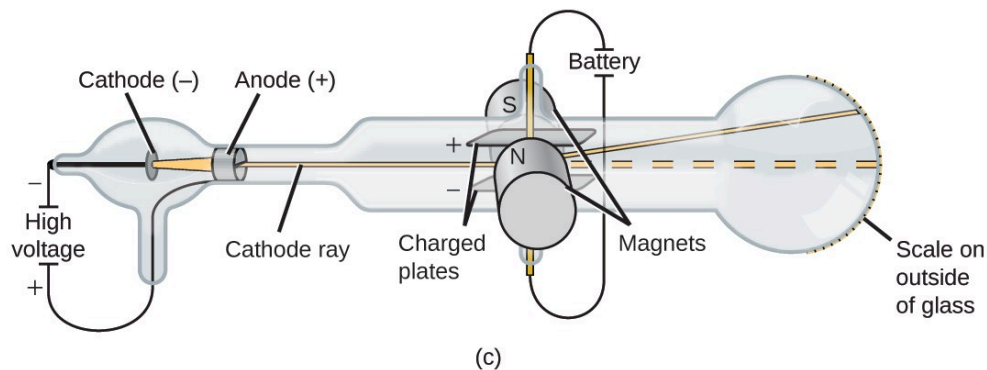
If matter is composed of atoms, what are atoms composed of? Are they the smallest particles, or is there something smaller? In the late 1800s, a number of scientists interested in questions like these investigated the electrical discharges that could be produced in low-pressure gases, with the most significant 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 2.8**).



(a)



(b)



(c)

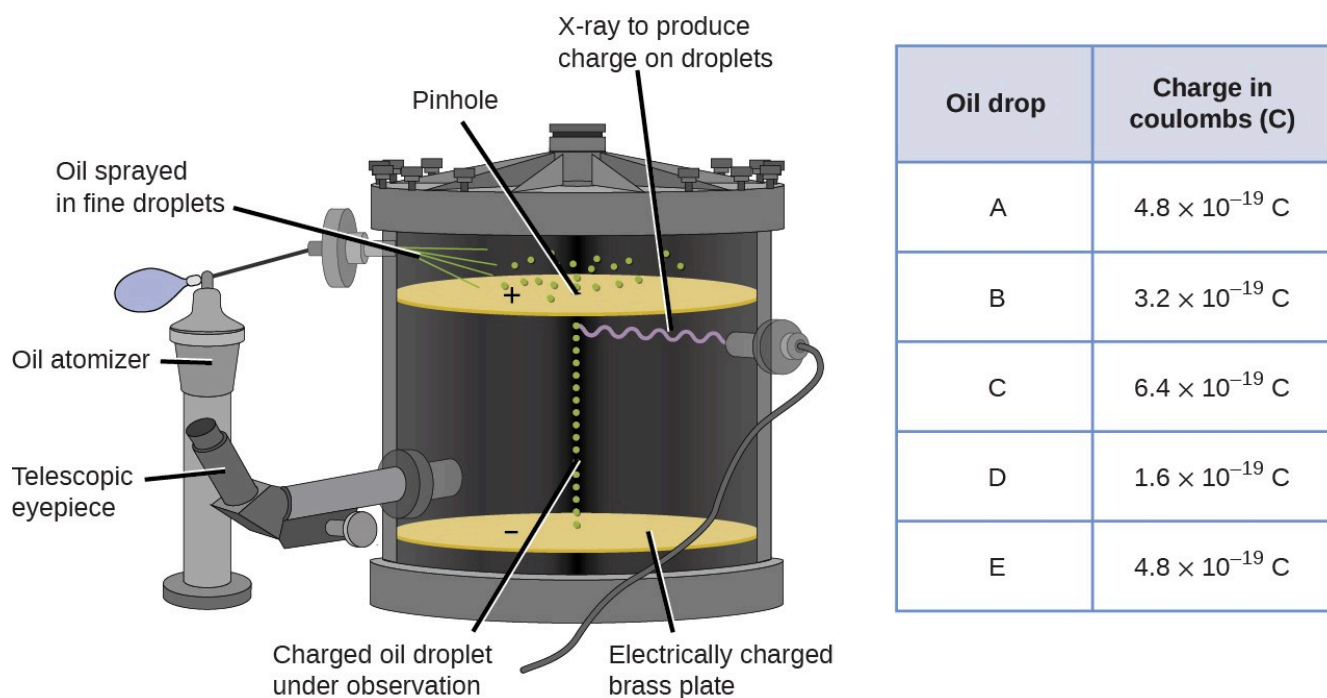
**Figure 2.8** (a) J. J. Thomson produced a visible beam in a cathode ray tube. (b) This is an early cathode ray tube, invented in 1897 by Ferdinand Braun. (c) In the cathode ray, the beam (shown in yellow) comes from the cathode and is accelerated past the anode toward a fluorescent scale at the end 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. By: Nobel Foundation, Eugen Nesper, Kurzon. [Wikimedia Commons CC BY NC SA](#)

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 than that of an atom. The term “electron” was coined in 1891 by Irish physicist George Stoney, from “*electric ion*.”

## Link to Learning

[Click here](http://openstax.org/l/16JThomson) (<http://openstax.org/l/16JThomson>) to hear Thomson describe his discovery in his own voice.

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 2.9**).



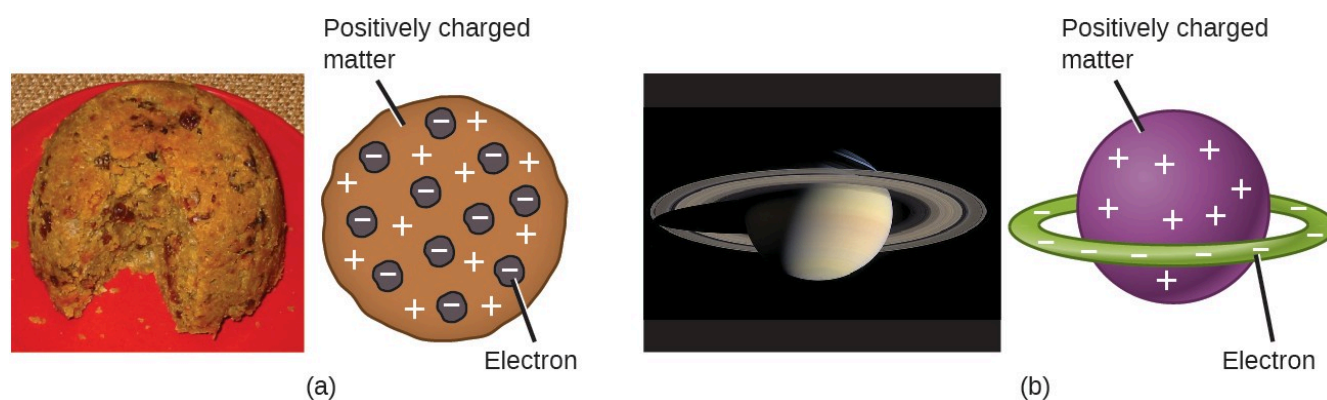
**Figure 2.9** Millikan’s experiment measured the charge of individual oil drops. The tabulated data are examples of a few possible values. By: Rice University [Openstax CC BY NC SA](#)

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,  $1.6 \times 10^{-19} \text{ C}$ . 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  $1.6 \times 10^{-19} \text{ C}$ ), two electrons (2 times  $1.6 \times 10^{-19} \text{ C}$ ), three electrons (3 times  $1.6 \times 10^{-19} \text{ C}$ ),

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 ( $1.759 \times 10^{11} \text{ C/kg}$ ), it only required a simple calculation to determine the mass of the electron as well.

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

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 2.10**).

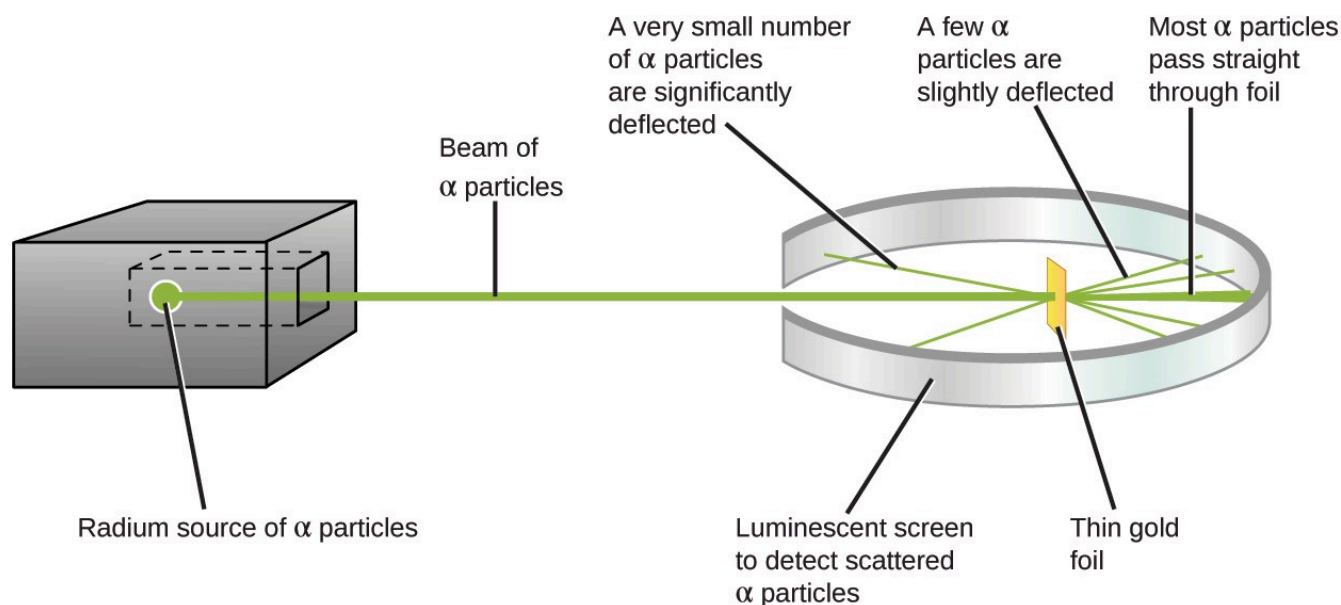


**Figure 2.10** (a) Thomson suggested that atoms resembled plum pudding, an English dessert consisting of moist cake with embedded raisins (“plums”). (b) Nagaoka proposed that atoms resembled the planet Saturn, with a ring of electrons surrounding a positive “planet.” By: Man vyi, NASA Wikimedia Commons [CC BY-NC-SA](#)

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** ( **$\alpha$  particles**) that were produced by the radioactive decay of radium;  $\alpha$  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  $\alpha$  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  $\alpha$  particles using a luminescent screen that glowed briefly where hit by an  $\alpha$  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 2.11**). 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.”<sup>1</sup>



**Figure 2.11** Geiger and Rutherford fired  $\alpha$  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. By: Rice University [Openstax CC BY NC SA](#)

Here is what Rutherford deduced: Because most of the fast-moving  $\alpha$  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  $\alpha$  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:

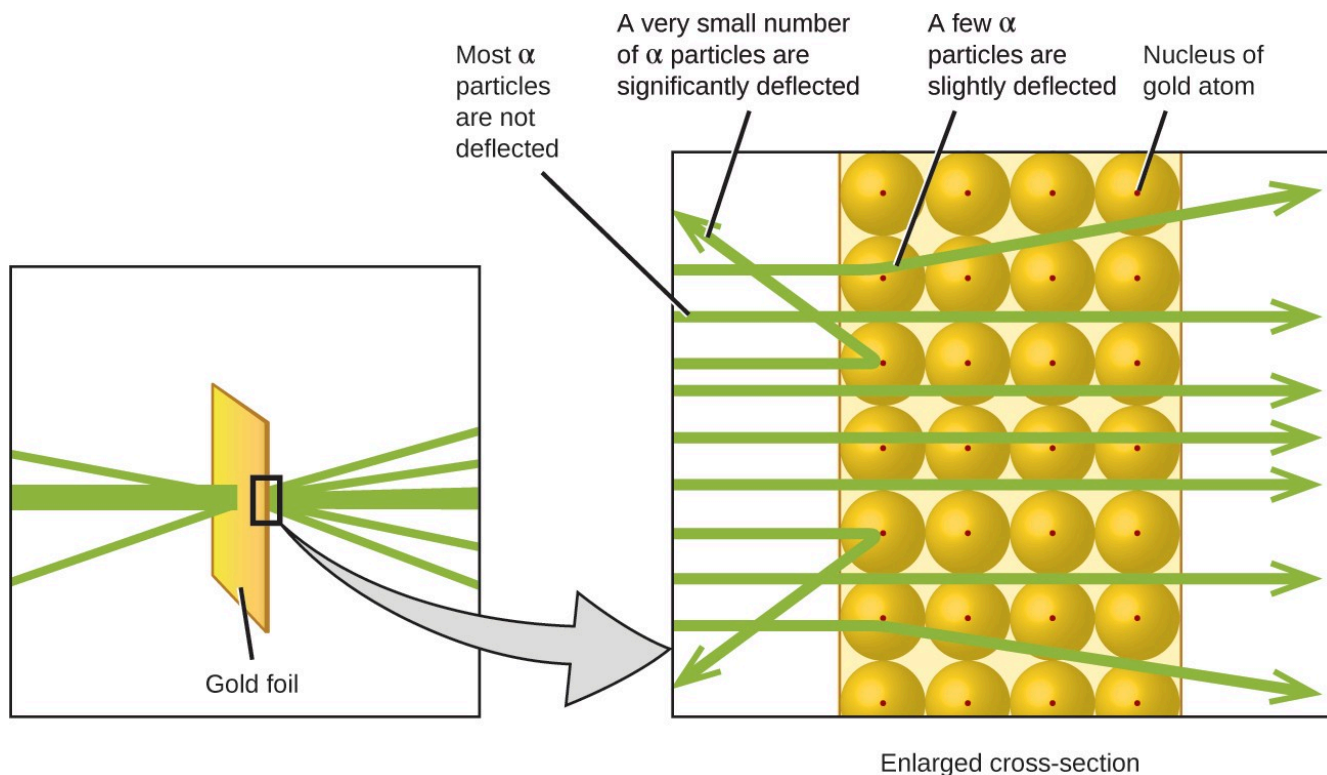
- The volume occupied by an atom must consist of a large amount of empty space.
- A small, relatively heavy, positively charged body, the **nucleus**, must be at the center of each atom.

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/items/backgroundtomode032734mbp/backgroundtomode032734mbp.pdf>.

## Link to Learning

[View this simulation](#) of the Rutherford gold foil experiment. Adjust the slit width to produce a narrower or broader beam of  $\alpha$  particles to see how that affects the scattering pattern.

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 2.12**). 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.



**Figure 2.12** The  $\alpha$  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  $\alpha$  particles are deflected. Most pass through the relatively large region occupied by electrons, which are too light to deflect the rapidly moving particles. By: Rice University [Openstax CC BY NC SA](#)



## Link to Learning

[The Rutherford Scattering simulation](#) allows you to investigate the differences between a “plum pudding” atom and a Rutherford atom by firing  $\alpha$  particles at each type of atom.

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.

# ATOMIC STRUCTURE AND SYMBOLISM (2.3)

OpenStax

---

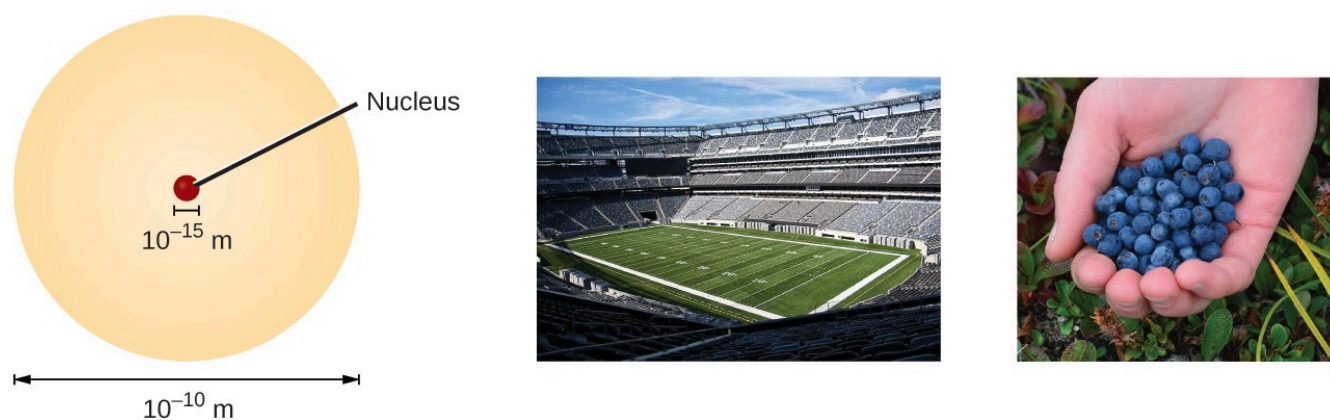
## Atomic Structure and Symbolism

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

- 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 2.13**).





**Figure 2.13** If an atom could be expanded to the size of a football stadium, the nucleus would be the size of a single blueberry. By: Rice University [Openstax CC BY NC SA](#)

Atoms—and the protons, neutrons, and electrons that compose them—are extremely small. For example, a carbon atom weighs less than  $2 \times 10^{-23}$  g, and an electron has a charge of less than  $2 \times 10^{-19}$  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  $\frac{1}{12}$  of the mass of one carbon-12 atom:  $1 \text{ amu} = 1.6605 \times 10^{-24}$  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  $e = 1.602 \times 10^{-19}$  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 of 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 2.2](#). (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 12.00 amu. This “missing” mass is known as the mass defect, and you will learn about it in the chapter on nuclear chemistry.)

**Table 2.2 Properties of Subatomic Particles By: Rice University [OpenStax CC BY-NC-SA 4.0](#)**

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

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:  $A - Z = \text{number of neutrons}$ .

$$\text{atomic number (Z)} = \text{number of protons}$$

$$\text{mass number (A)} = \text{number of protons} + \text{number of neutrons}$$

$$A - Z = \text{number of neutrons}$$

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:

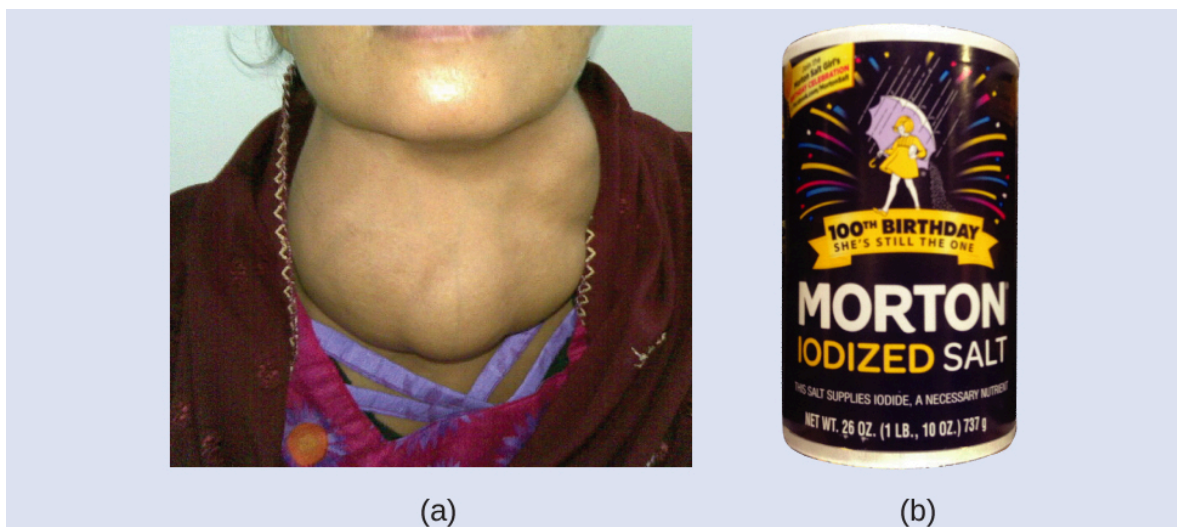
$$\text{Atomic charge} = \text{number of protons} - \text{number of electrons}$$

As will be discussed in more detail, 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

### Composition of an Atom

Iodine is an essential trace element in our diet; it is needed to produce the thyroid hormone. Insufficient iodine in the diet can lead to the development of a goiter, an enlargement of the thyroid gland (Figure 2.14).



**Figure 2.14** (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. By: Rice University [Openstax CC BY NC SA](#)

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 number 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 [ $53 - (1-) = 54$ ].

### Check Your Learning

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 2.15**). 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 2.15** The symbol Hg represents the element mercury regardless of the amount; it could represent one atom of mercury or a large amount of mercury. By: Rice University [Openstax CC BY NC SA](#)

The symbols for several common elements and their atoms are listed in [Table 2.3](#). Some symbols are derived from the common name of the element; others are abbreviations of the name in another language. Most symbols have one or two letters, but three-letter symbols have been used to describe some elements that have atomic numbers greater than 112. 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 in **Figure 3.37** (also found in **Figure 21.1**).

**Table 2.3 Some Common Elements and Their Symbols By: Rice University** [OpenStax CC BY-NC-SA 4.0](https://openstax.org/r/cc-by-nc-sa-4.0)

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

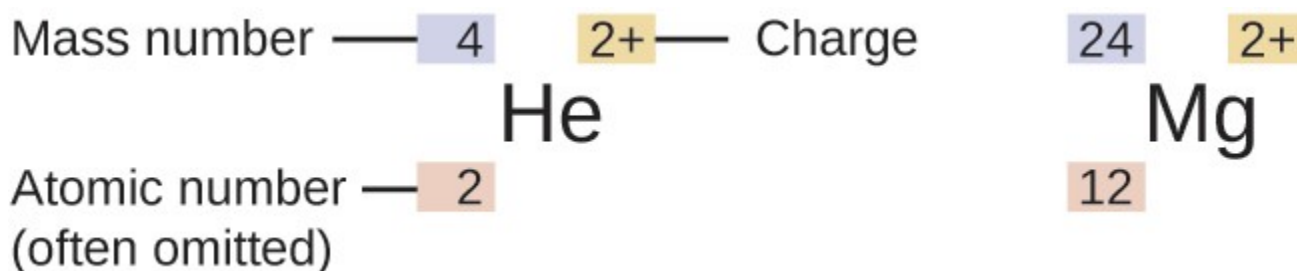


**Link to Learning**

[Visit this site](#) to learn more about IUPAC, the International Union of Pure and Applied Chemistry, and explore its periodic table.

## 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 2.16**). 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  $^{24}\text{Mg}$ ,  $^{25}\text{Mg}$ , and  $^{26}\text{Mg}$ . These isotope symbols are read as “element, mass number” and can be symbolized consistent with this reading. For instance,  $^{24}\text{Mg}$  is read as “magnesium 24” and can be written as “magnesium-24” or “Mg-24.”  $^{25}\text{Mg}$  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  $^{24}\text{Mg}$  atom has 12 neutrons in its nucleus, a  $^{25}\text{Mg}$  atom has 13 neutrons, and a  $^{26}\text{Mg}$  has 14 neutrons.



**Figure 2.16** 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. By: Rice University [Openstax CC BY NC SA](#)

Information about the naturally occurring isotopes of elements with atomic numbers 1 through 10 is given in [Table 2.4](#). 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  $2\text{H}$ , is also called deuterium and sometimes symbolized D. Hydrogen-3, symbolized  $3\text{H}$ , is also called tritium and sometimes symbolized T.

**Table 2.4 Nuclear Compositions of Atoms of the Very Light Elements By: Rice University [OpenStax CC BY-NC-SA 4.0](#)**

Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (amu)	% Natural Abundance
hydrogen	$^1_1\text{H}$ (protium)	1	1	0	1.0078	99.989
	$^2_1\text{H}$ (deuterium)	1	1	1	2.0141	0.0115
	$^3_1\text{H}$ (tritium)	1	1	2	3.01605	— (trace)
helium	$^3_2\text{He}$	2	2	1	3.01603	0.00013
	$^4_2\text{He}$	2	2	2	4.0026	100
lithium	$^6_3\text{Li}$	3	3	3	6.0151	7.59
	$^7_3\text{Li}$	3	3	4	7.0160	92.41
beryllium	$^9_4\text{Be}$	4	4	5	9.0122	100
boron	$^{10}_5\text{B}$	5	5	5	10.0129	19.9
	$^{11}_5\text{B}$	5	5	6	11.0093	80.1



carbon	$^{12}\text{C}_6$	6	6	6	12.0000	98.89
	$^{13}\text{C}_6$	6	6	7	13.0034	1.11
	$^{14}\text{C}_6$	6	6	8	14.0032	— (trace)
nitrogen	$^{14}\text{N}_7$	7	7	7	14.0031	99.63
	$^{15}\text{N}_7$	7	7	8	15.0001	0.37
oxygen	$^{16}\text{O}_8$	8	8	8	15.9949	99.757
	$^{17}\text{O}_8$	8	8	9	16.9991	0.038
	$^{18}\text{O}_8$	8	8	10	17.9992	0.205
fluorine	$^{19}\text{F}_9$	9	9	10	18.9984	100
neon	$^{20}\text{Ne}_{10}$	10	10	10	19.9924	90.48
	$^{21}\text{Ne}_{10}$	10	10	11	20.9938	0.27
	$^{22}\text{Ne}_{10}$	10	10	12	21.9914	9.25

---

## Link to Learning

Use this [Build an Atom simulator](#) to build atoms of the first 10 elements, see which isotopes exist, check nuclear stability, and gain experience with isotope symbols.

## 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  $^{10}\text{B}$  with a mass of 10.0129 amu, and the remaining 80.1% are  $^{11}\text{B}$  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 2.4

### 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%  $^{20}\text{Ne}$  (mass 19.9924 amu), 0.47%  $^{21}\text{Ne}$  (mass 20.9940 amu), and 7.69%  $^{22}\text{Ne}$  (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.)

### Check Your Learning

A sample of magnesium is found to contain 78.70% of  $^{24}\text{Mg}$  atoms (mass 23.98 amu), 10.13% of  $^{25}\text{Mg}$  atoms (mass 24.99 amu), and 11.17% of  $^{26}\text{Mg}$  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 2.5

### Calculation of Percent Abundance

Naturally occurring chlorine consists of  $^{35}\text{Cl}$  (mass 34.96885 amu) and  $^{37}\text{Cl}$  (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  $^{35}\text{Cl}$  times the mass of  $^{35}\text{Cl}$  plus the fraction that is  $^{37}\text{Cl}$  times the mass of  $^{37}\text{Cl}$ .

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

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

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

Substituting this into the average mass equation, we have:

$$35.453 \text{ amu} = (x \times 34.96885 \text{ amu}) + [(1.00 - x) \times 36.96590 \text{ amu}]$$

$$35.453 = 34.96885x + 36.96590 - 36.96590x$$

$$1.99705x = 1.513$$

$$x = \frac{1.513}{1.99705} = 0.7576$$

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

### Check Your Learning

Naturally occurring copper consists of  $^{63}\text{Cu}$  (mass 62.9296 amu) and  $^{65}\text{Cu}$  (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?

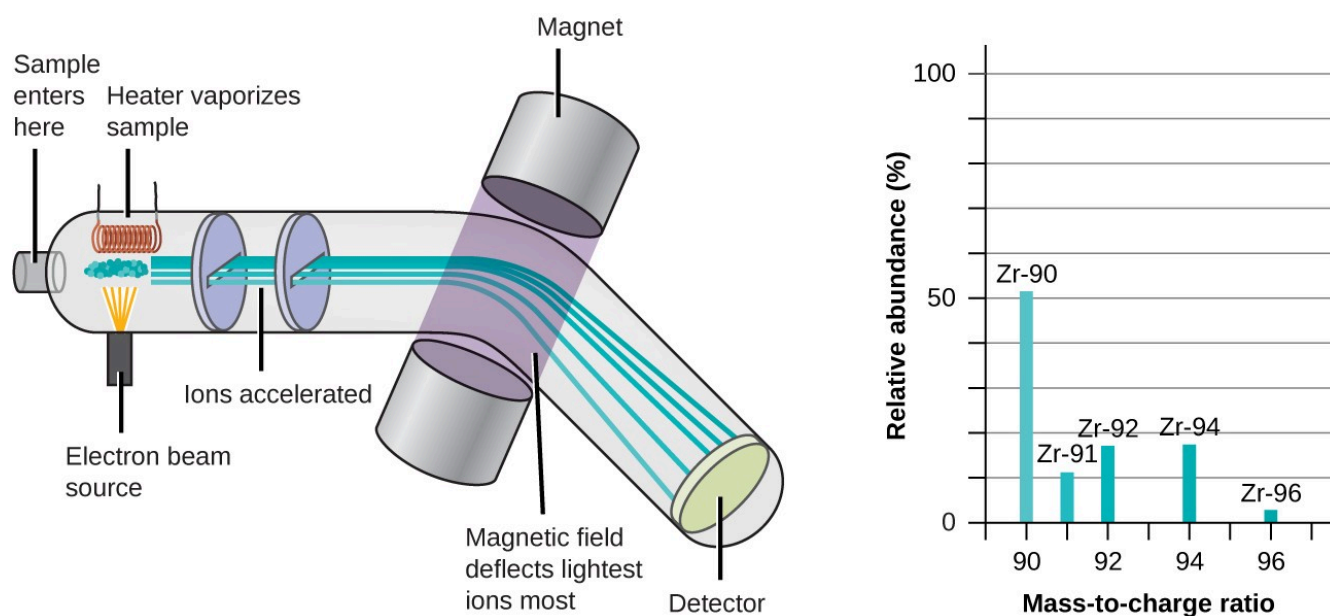
**Answer:** 69.15% Cu-63 and 30.85% Cu-65

### Link to Learning

[Visit this site](#) to make mixtures of the main isotopes of the first 18 elements, gain experience

with average atomic mass, and check naturally occurring isotope ratios using the Isotopes and Atomic Mass simulation.

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 2.17**), 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 than 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.



**Figure 2.17** Analysis of zirconium in a mass spectrometer produces a mass spectrum with peaks showing the different isotopes of Zr. By: Rice University [Openstax](#) CC BY NC SA

### Link to Learning

See [an animation](#) that explains mass spectrometry. Watch [this video](#) from the Royal Society for Chemistry for a brief description of the rudiments of mass spectrometry.

# CHEMICAL FORMULAS (2.4)

OpenStax

## 2.4 Chemical Formulas

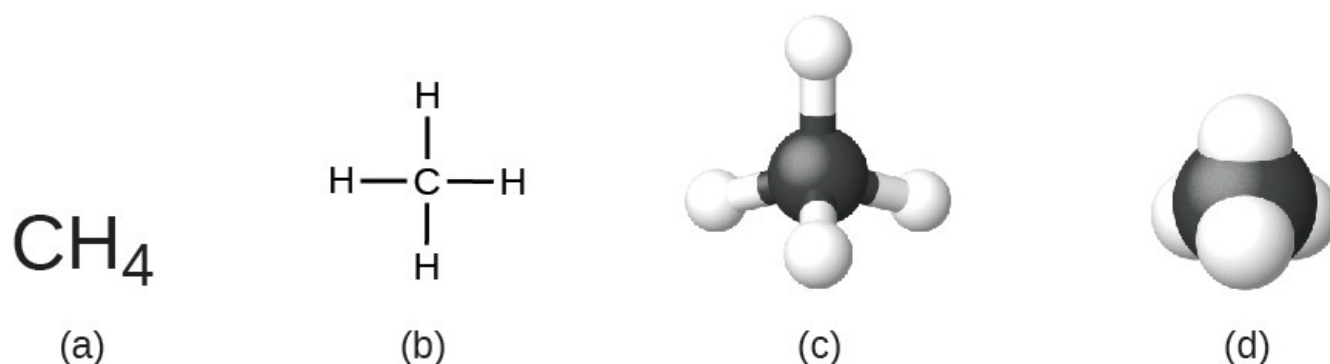
By the end of this section, you will be able to:

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

## Molecular and Empirical Formulas

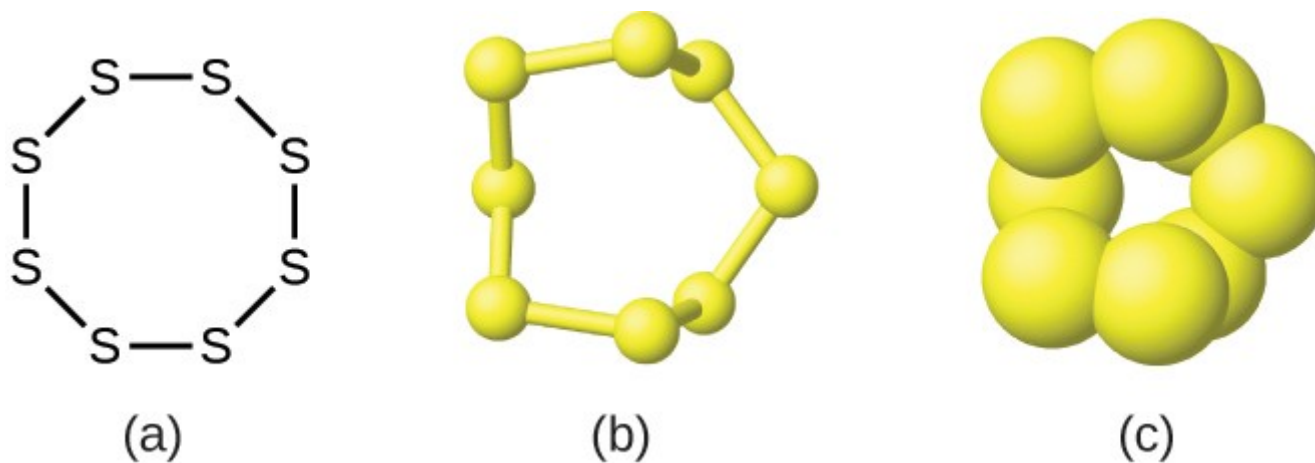
A **molecular formula** is a representation of a molecule that uses chemical symbols to indicate the types of atoms followed by subscripts to show the number of atoms of each type in the molecule. (A subscript is used only when more than one atom of a given type is present.) Molecular formulas are also 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 2.18**). 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 2.18** 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. By: Rice University [Openstax CC BY NC SA](#)

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  $\text{H}_2$ ,  $\text{O}_2$ , and  $\text{N}_2$ , respectively. Other elements commonly found as diatomic molecules are fluorine ( $\text{F}_2$ ), chlorine ( $\text{Cl}_2$ ), bromine ( $\text{Br}_2$ ), and iodine ( $\text{I}_2$ ). The most common form of the element sulfur is composed of molecules that consist of eight atoms of sulfur; its molecular formula is  $\text{S}_8$  (**Figure 2.19**).

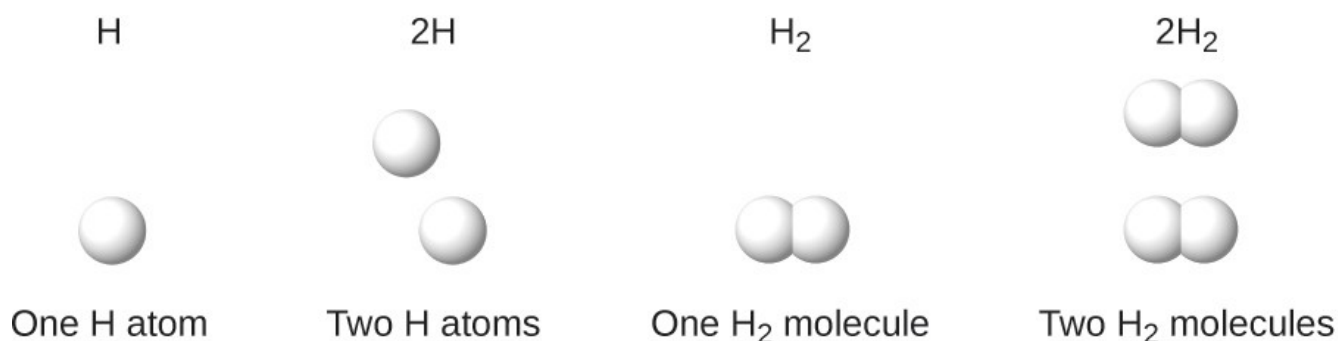


**Figure 2.19** A molecule of sulfur is composed of eight sulfur atoms and is therefore written as  $\text{S}_8$ . It can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. Sulfur atoms are represented by yellow spheres. By: Rice University [Openstax CC BY NC SA](#)

It is important to note that a subscript following a symbol and a number in front of a symbol does not represent the same thing; for example,  $\text{H}_2$  and  $2\text{H}$  represent distinctly different species.  $\text{H}_2$  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  $2\text{H}$ , on the other hand, indicates two separate hydrogen atoms



that are not combined as a unit. The expression  $2\text{H}_2$  represents two molecules of diatomic hydrogen (**Figure 2.20**).

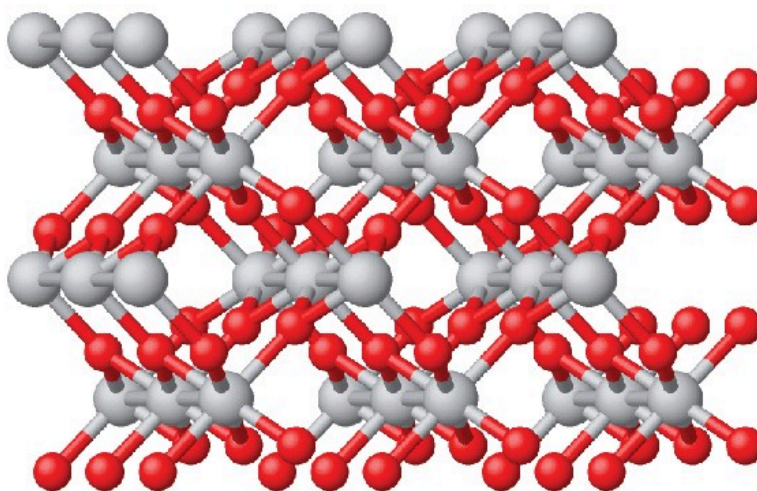


**Figure 2.20** The symbols  $\text{H}$ ,  $2\text{H}$ ,  $\text{H}_2$ , and  $2\text{H}_2$  represent very different entities. By: Rice University [Openstax](#) [CC BY NC SA](#)

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 a pigment in white paint and in the thick, white, blocking type of sunscreen) has an empirical formula of  $\text{TiO}_2$ . 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 2.21**).



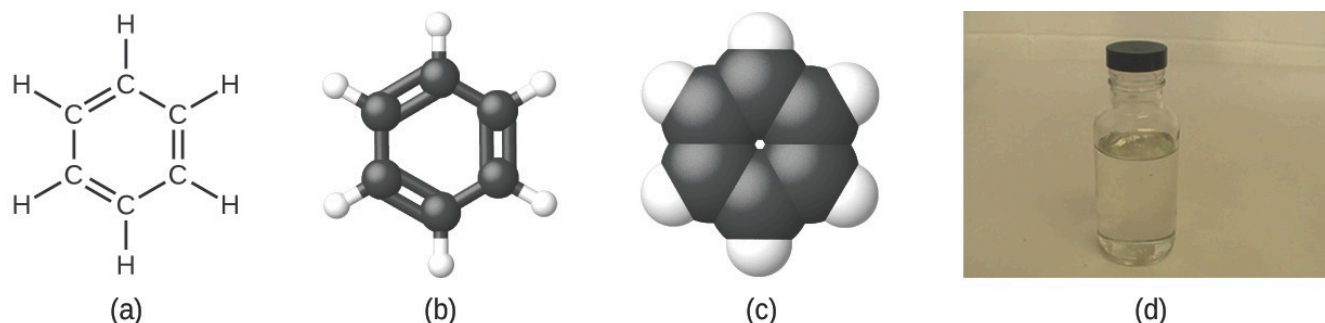
(a)



(b)

**Figure 2.21** (a) The white compound titanium dioxide provides effective protection from the sun. (b) A crystal of titanium dioxide,  $\text{TiO}_2$ , contains titanium and oxygen in a ratio of 1 to 2. The titanium atoms are gray, and the oxygen atoms are red. By: Rice University [Openstax](#) [CC BY NC SA](#)

As discussed previously, we can describe a compound with a molecular formula, in which the subscripts indicate the *actual number of atoms* of each element in a molecule of the compound. In many cases, the molecular formula of a substance is derived from the 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 2.22**).

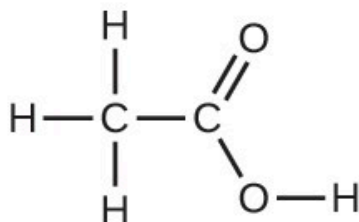


**Figure 2.22** Benzene,  $C_6H_6$ , is produced during oil refining and has many industrial uses. A benzene molecule can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. (d) Benzene is a clear liquid. By: Rice University [Openstax CC BY NC SA](#)

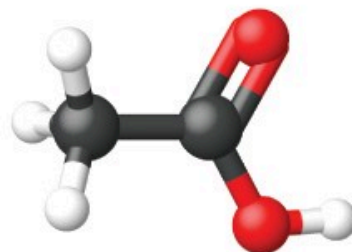
If we know a compound's formula, we can easily determine the empirical formula. (This is somewhat of an academic exercise; the reverse chronology is generally followed in actual practice.) For example, the molecular formula for acetic acid, the component that gives vinegar its sharp taste, is  $C_2H_4O_2$ . This formula indicates that a molecule of acetic acid (**Figure 2.23**) 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.



(a)



(b)



(c)

**Figure 2.23** (a) Vinegar contains acetic acid,  $\text{C}_2\text{H}_4\text{O}_2$ , which has an empirical formula of  $\text{CH}_2\text{O}$ . It can be represented as (b) a structural formula and (c) a ball-and-stick model. By: Rice University [Openstax CC BY NC SA](#)

## Example 2.6

### 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  $\text{C}_6\text{H}_{12}\text{O}_6$  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  $\text{CH}_2\text{O}$ .

#### Check Your Learning

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,  $\text{C}_8\text{H}_{16}\text{O}_4$ ; empirical formula,  $\text{C}_2\text{H}_4\text{O}$

### Link to Learning

You can explore molecule building using an online simulation.

### Portrait of a Chemist Lee Cronin

What is it that chemists do? According to Lee Cronin (**Figure 2.22**), chemists make very complicated molecules by “chopping up” small molecules and “reverse engineering” them. He wonders if we could “make a really cool universal chemistry set” by what he calls “app-ing” chemistry. Could we “app” chemistry? In a 2012 TED talk, Lee describes one fascinating possibility: Combining a collection of chemical “inks” with a 3D printer capable of fabricating a reaction apparatus (tiny test tubes, beakers, and the like) to fashion a “universal toolkit of chemistry.” This toolkit could be used to create custom-tailored drugs to fight a new superbug or to “print” medicine personally configured to your genetic makeup, environment, and health situation. Says Cronin, “What Apple did for music, I’d like to do for the discovery and distribution of prescription drugs.”<sup>1</sup>

View his [full talk](#) at the TED website.

---

1. TED. “Lee Cronin.” [https://www.ted.com/speakers/lee\\_cronin](https://www.ted.com/speakers/lee_cronin)

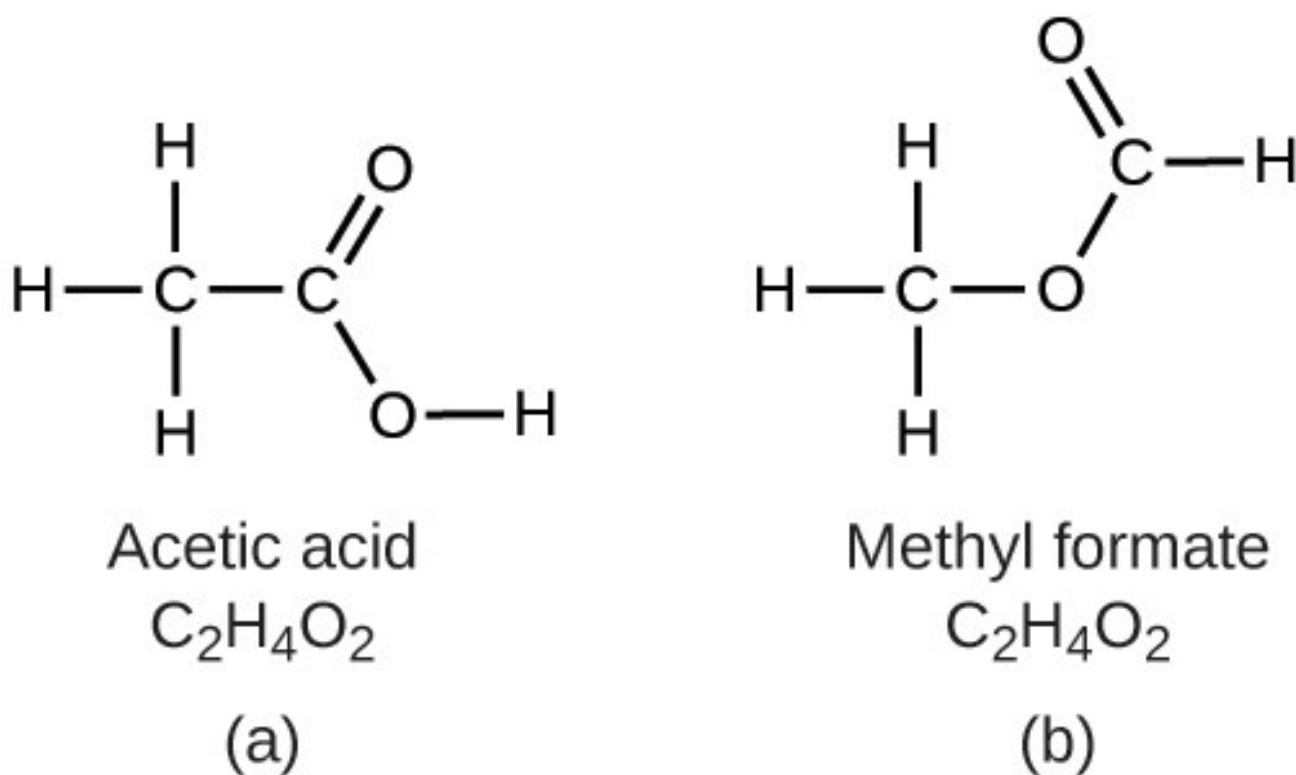


**Figure 2.24** Chemist Lee Cronin has been named one of the UK's 10 most inspirational scientists. The youngest chair at the University of Glasgow, Lee runs a large research group, collaborates with many scientists worldwide, has published over 250 papers in top scientific journals, and has given more than 150 invited talks. His research focuses on complex chemical systems and their potential to transform technology but also branches into nanoscience, solar fuels, synthetic biology, and even artificial life and evolution. By: Rice University [Openstax CC BY NC SA](#)

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,  $\text{C}_2\text{H}_4\text{O}_2$ ? And if so, what would be the structure of its molecules?

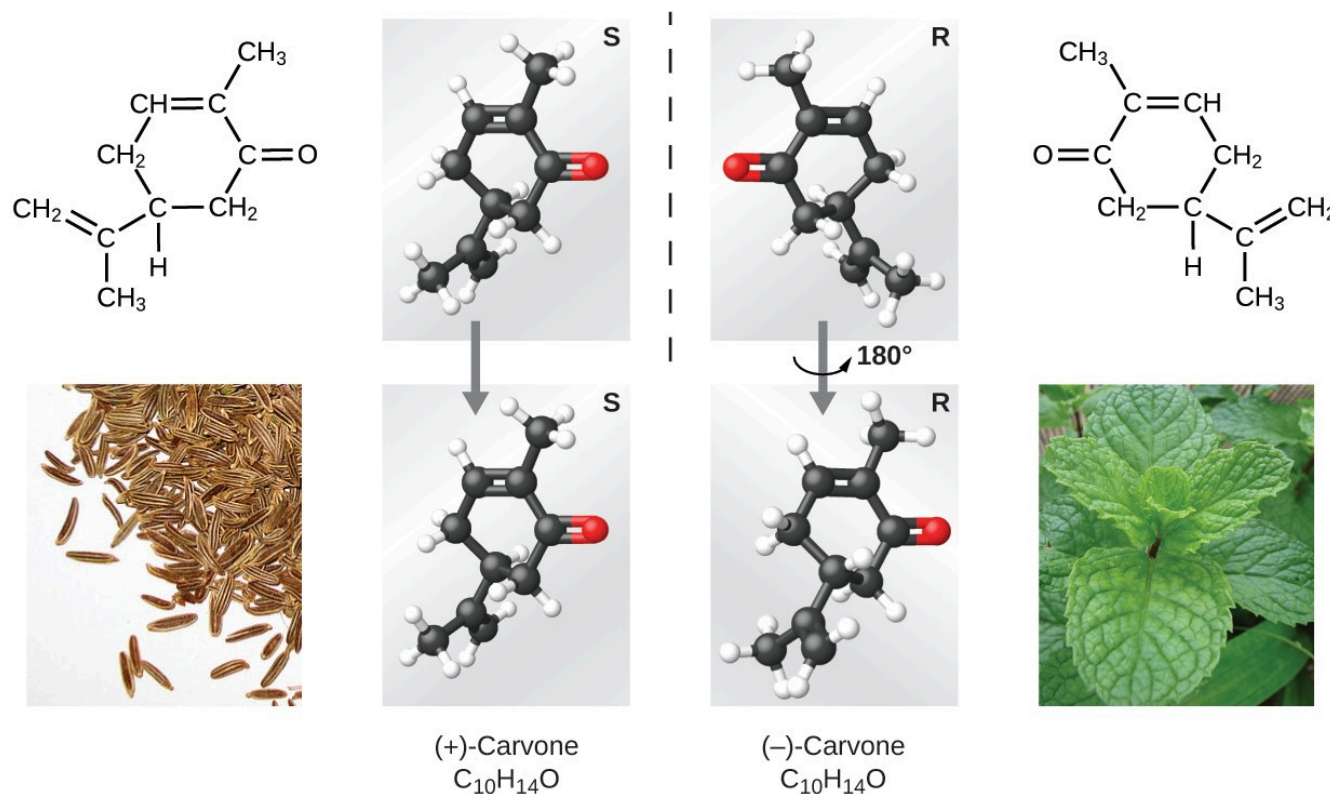
If you predict that another compound with the formula  $\text{C}_2\text{H}_4\text{O}_2$  could exist, then you demonstrated good chemical insight and are correct. Two C atoms, four H atoms, and two O atoms can also be arranged to form a methyl formate, which is used in manufacturing, as an insecticide, 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 2.25**). 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 2.25** Molecules of (a) acetic acid and (b) methyl formate are structural isomers; they have the same formula ( $\text{C}_2\text{H}_4\text{O}_2$ ) but different structures (and therefore different chemical properties). By: Rice University [Openstax CC BY NC SA](#)

Many types of isomers exist (**Figure 2.26**). 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 2.26** Molecules of carvone are spatial isomers; they only differ in the relative orientations of the atoms in space. By: Rice University [Openstax CC BY NC SA](#)

### Link to Learning

[Select this link](#) to view an explanation of isomers, spatial isomers, and why they have different smells (select the video titled “Mirror Molecule: Carvone”).

## The Mole

The identity of a substance is defined not only by the types of atoms or ions it contains but by the quantity of each type of atom or ion. For example, water,  $H_2O$ , and hydrogen peroxide,  $H_2O_2$ , are alike in that their respective molecules are composed of hydrogen and oxygen atoms. However, because a hydrogen peroxide molecule contains two oxygen atoms, as opposed to the water molecule, which has only one, the two substances exhibit very different properties. 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

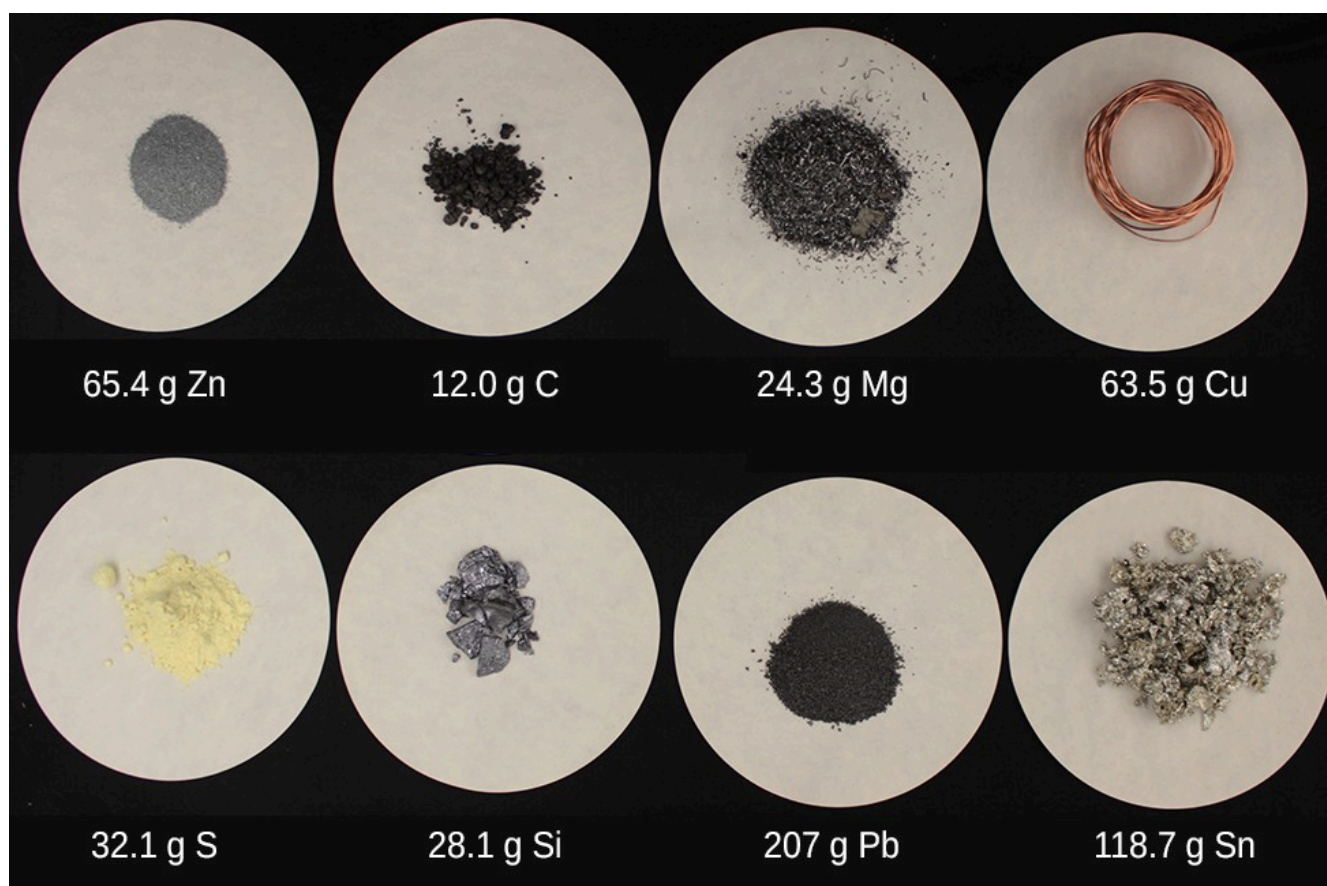
simple tools (balances and volumetric glassware). This experimental approach required the introduction of a new unit for the amount of substances, the *mole*, which remains indispensable in modern chemical science.

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  $^{12}\text{C}$  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  $6.02214179 \times 10^{23}$ , 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  $6.022 \times 10^{23}/\text{mol}$ .

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) (see **Figure 2.27**).





**Figure 2.27** Each sample contains  $6.022 \times 10^{23}$  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. By: Rice University [Openstax CC BY NC SA](#)

The molar mass of any substance is numerically equivalent to its atomic or formula weight in amu. Per the amu definition, a single  $^{12}\text{C}$  atom weighs 12 amu (its atomic mass is 12 amu). According to the definition of the mole, 12 g of  $^{12}\text{C}$  contains 1 mole of  $^{12}\text{C}$  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,  $^{12}\text{C}$ . Extending this principle, the molar mass of a compound in grams is likewise numerically equivalent to its formula mass in amu (**Figure 2.28**).



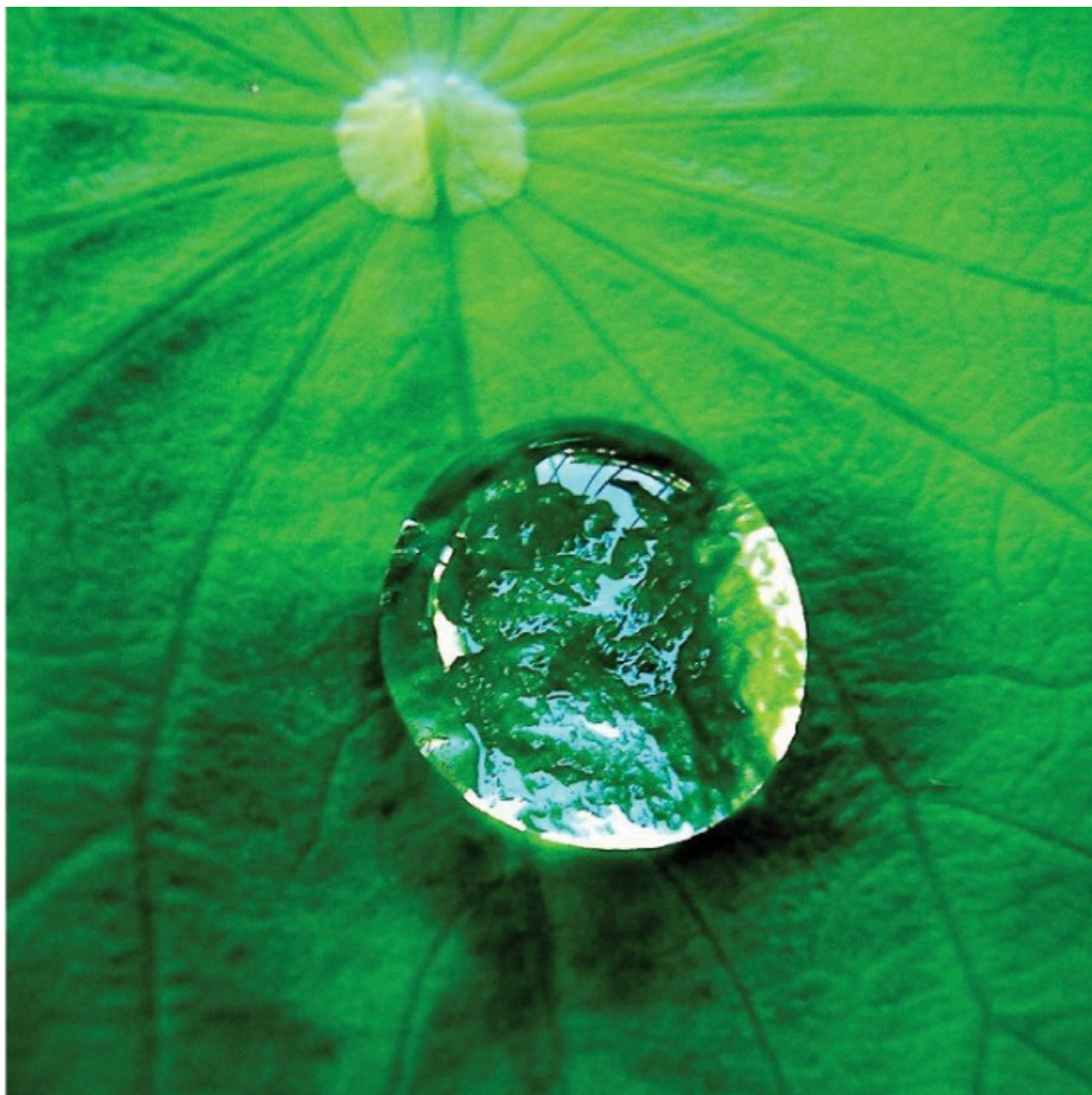
**Figure 2.28** Each sample contains  $6.02 \times 10^{23}$  molecules or formula units—1.00 mol of the compound or element. Clockwise from the upper left: 130.2 g of  $\text{C}_8\text{H}_{17}\text{OH}$  (1-octanol, formula mass 130.2 amu), 454.4 g of  $\text{HgI}_2$  (mercury(II) iodide, formula mass 454.4 amu), 32.0 g of  $\text{CH}_3\text{OH}$  (methanol, formula mass 32.0 amu) and 256.5 g of  $\text{S}_8$  (sulfur, formula mass 256.5 amu). Credit: Sahar Atwa. By: Rice University  
[Openstax CC BY NC SA](#)

**Table 2.5** By: Rice University [OpenStax CC BY-NC-SA 4.0](#)

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

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 weighing about 0.03 g (see **Figure 2.29**). 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.



**Figure 2.29** The number of molecules in a single droplet of water is roughly 100 billion times greater than the number of people on earth. By: Rice University [Openstax](#) [CC BY NC SA](#)

## LINK TO LEARNING

The mole is used in chemistry to represent  $6.022 \times 10^{23}$  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 the 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 2.7

### 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?

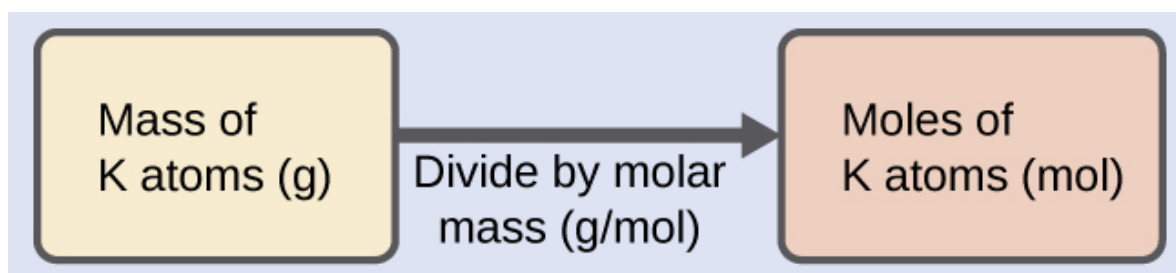
### Solution

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):





**Figure 2.30** By: Rice University [Openstax](#) [CC BY NC SA](#)

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

$$4.7\text{ g K} \times \frac{\text{mol K}}{39.0983\text{ g}} = 0.12 \text{ mol of potassium}$$

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

### Check Your Learning

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 2.8

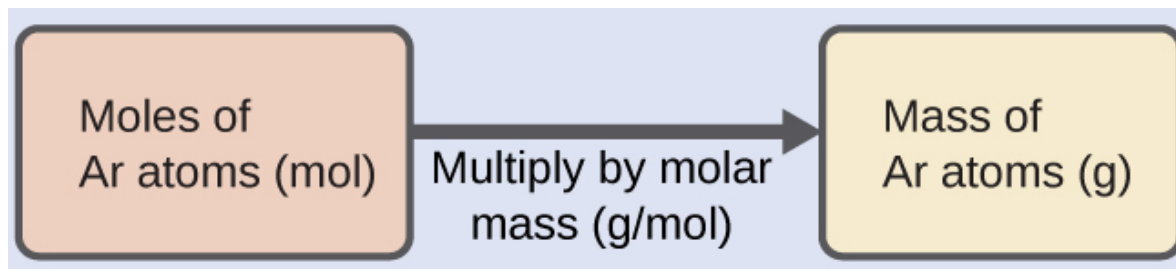
### Deriving Grams from Moles for an Element

A liter of air contains  $9.2 \times 10^{-4}$  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 ( $\sim 10^{-3}$ ) of a mole, and so the corresponding mass should be roughly one-one thousandth of the molar mass ( $\sim 0.04$  g):



**Figure 2.31** By: Rice University [Openstax CC BY NC SA](#)

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

$$9.2 \times 10^{-4} \text{ mol Ar} \times \frac{39.948 \text{ g}}{\text{mol Ar}} = 0.037 \text{ g of argon}$$

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

### Check Your Learning

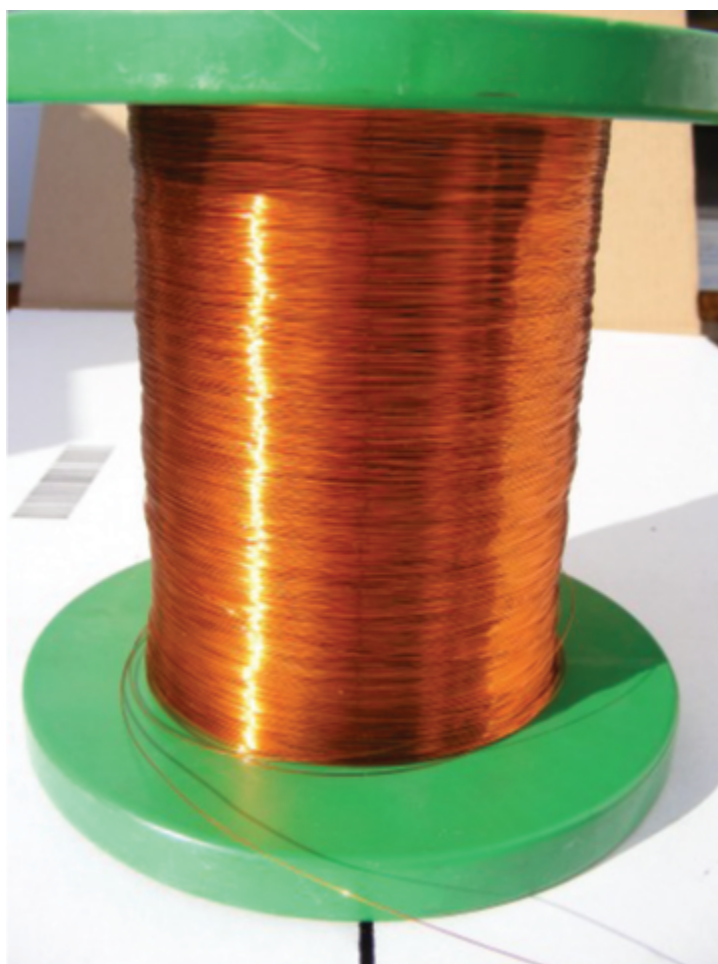
What is the mass of 2.561 mol of gold?

**Answer:** 504.4 g

## Example 2.9

### Deriving the Number of Atoms from Mass for an Element

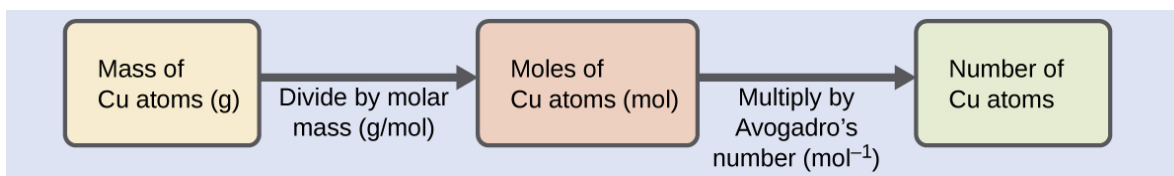
Copper is commonly used to fabricate electrical wire (Figure 2.32). How many copper atoms are in 5.00 g of copper wire?



**Figure 2.32** Copper wire is composed of many, many atoms of Cu. By: Rice University [Openstax CC BY NC SA](#)

### 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 the number of Cu atoms:



**Figure 2.33** By: Rice University [Openstax CC BY NC SA](#)

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:

$$5.00 \text{ g Cu} \times \frac{\cancel{\text{mol Cu}}}{63.546\text{g}} \times \frac{6.022 \times 10^{23} \text{ atoms}}{\cancel{\text{mol}}} = 4.74 \times 10^{22} \text{ atoms of copper}$$

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

### Check Your Learning

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:**  $4.586 \times 10^{22}$  Au atoms

## Example 2.10

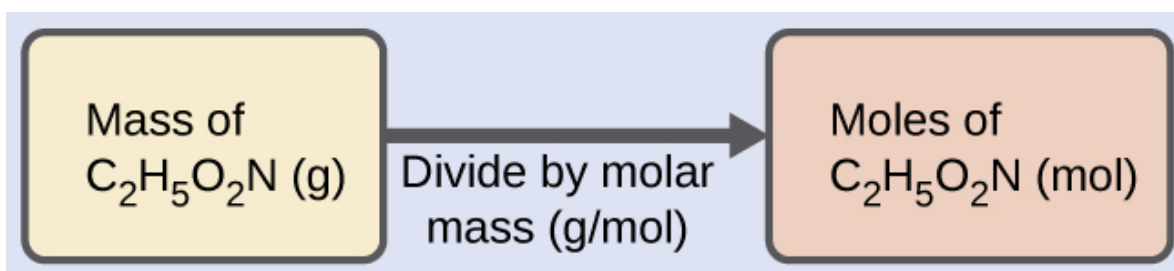
### Deriving Moles from Grams for a Compound

Our bodies synthesize protein from amino acids. One of these amino acids is glycine, which has the molecular formula  $\text{C}_2\text{H}_5\text{O}_2\text{N}$ . 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 Figure 2.34:

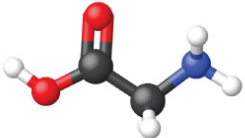




**Figure 2.34** By: Rice University [Openstax CC BY NC SA](#)

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,  $\text{C}_2\text{H}_5\text{O}_2\text{N}$ , 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



**Figure 2.35** By: Rice University [Openstax CC BY NC SA](#)

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:

$$28.35 \text{ g glycine} \times \frac{\text{mol glycine}}{75.067 \text{ g}} = 0.3777 \text{ mol of glycine}$$

This result is consistent with our rough estimate.

### Check Your Learning

How many moles of sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , are in a 25-g sample of sucrose?

**Answer:** 0.073 mol

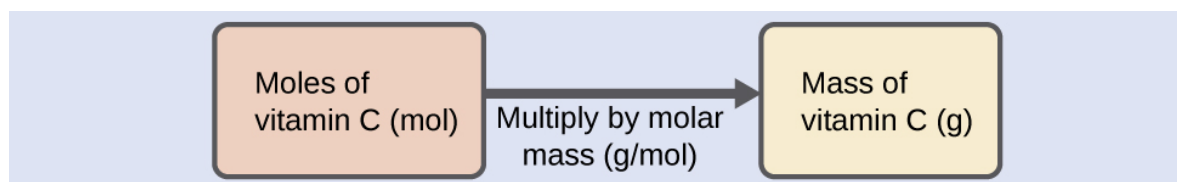
## Example 2.11

### Deriving Grams from Moles for a Compound

Vitamin C is a covalent compound with the molecular formula  $\text{C}_6\text{H}_8\text{O}_6$ . The recommended daily dietary allowance of vitamin C for children aged 4–8 years is  $1.42 \times 10^{-4}$  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:



**Figure 2.36** By: Rice University [Openstax CC BY NC SA](#)

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 ( $\sim 10^{-4}$  or one-ten thousandth); therefore, we would expect the corresponding mass to be about one-ten thousandth of the molar mass ( $\sim 0.02$  g). Performing the calculation, we get:

$$1.42 \times 10^{-4} \text{ mol vitamin C} \times \frac{176.126 \text{ g}}{\text{mol vitamin C}} = 0.0250 \text{ g of vitamin C}$$

This is consistent with the anticipated result.

### Check Your Learning

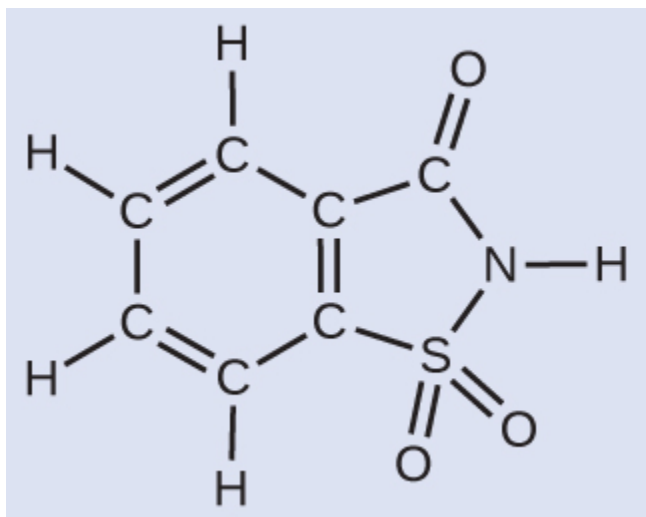
What is the mass of 0.443 mol of hydrazine,  $\text{N}_2\text{H}_4$ ?

**Answer:** 14.2 g

## Example 2.12

### Deriving the Number of Atoms and Molecules from the Mass of a Compound

A packet of an artificial sweetener contains 40.0 mg of saccharin ( $\text{C}_7\text{H}_5\text{NO}_3\text{S}$ ), which has the structural formula:



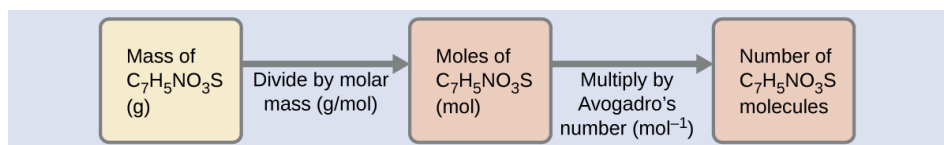
**Figure 2.37** By: Rice University [Openstax CC BY NC SA](#)

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 Figure 2.38, and then multiplying by Avogadro's number:

**Formula does not parse**



**Figure 2.38** By:  
Rice University  
Openstax CC BY  
NC SA

Using the provided mass and molar mass for saccharin yields:

$$0.0400 \text{ g C}_7\text{H}_5\text{NO}_3\text{S} \times \frac{\cancel{\text{mol C}_7\text{H}_5\text{NO}_3\text{S}}}{183.188 \text{ g C}_7\text{H}_5\text{NO}_3\text{S}} \times \frac{6.022 \times 10^{23} \text{ C}_7\text{H}_5\text{NO}_3\text{S molecules}}{1 \cancel{\text{mol C}_7\text{H}_5\text{NO}_3\text{S}}} \\ = \underline{1.3149} \times 10^{20} \text{ C}_7\text{H}_5\text{NO}_3\text{S molecules with 3 sig figs}$$

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

$$\underline{1.3149} \times 10^{20} \cancel{\text{molecules C}_7\text{H}_5\text{NO}_3\text{S}} \times \frac{7 \text{ C atoms}}{1 \cancel{\text{molecules C}_7\text{H}_5\text{NO}_3\text{S}}} \\ = \underline{9.2043} \times 10^{21} \text{ C molecules with 3 sig figs}$$

## Check Your Learning

How many  $\text{C}_4\text{H}_{10}$  molecules are contained in 9.213 g of this compound? How many hydrogen atoms?

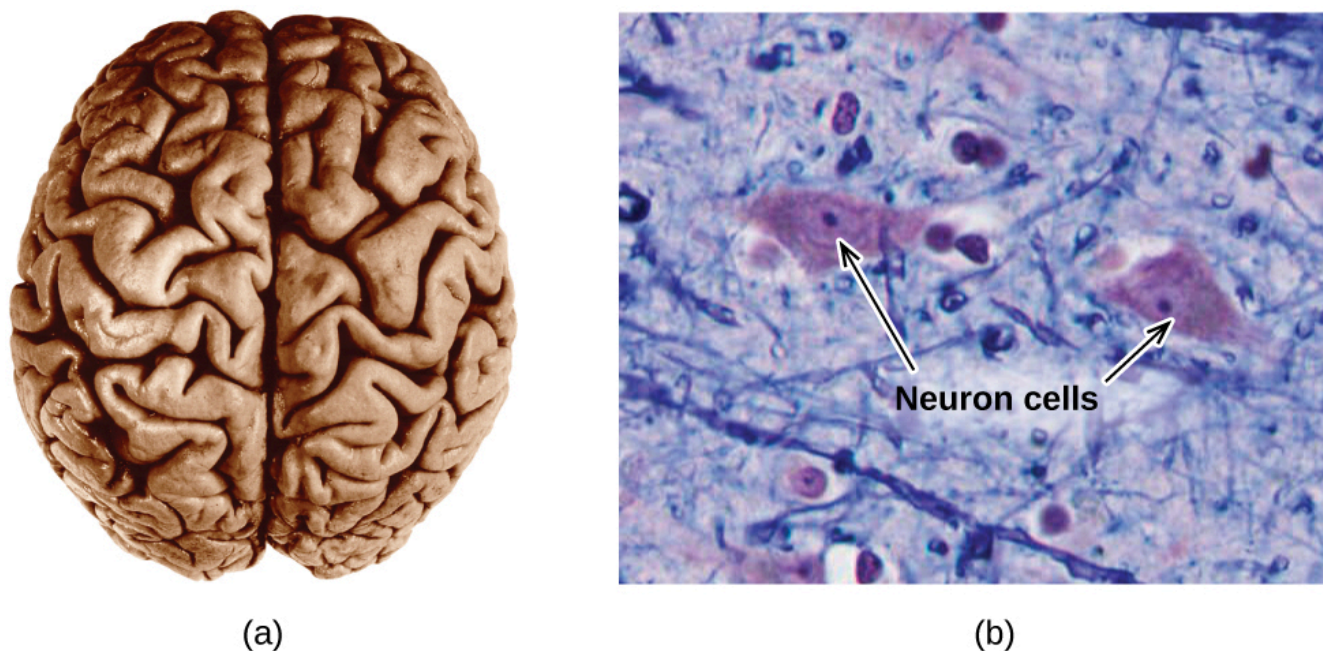
**Answer:**  $9.545 \times 10^{22}$  molecules  $\text{C}_4\text{H}_{10}$ ;  $9.545 \times 10^{23}$  atoms H

## HOW SCIENCES INTERCONNECT

### Counting Neurotransmitter Molecules in the Brain

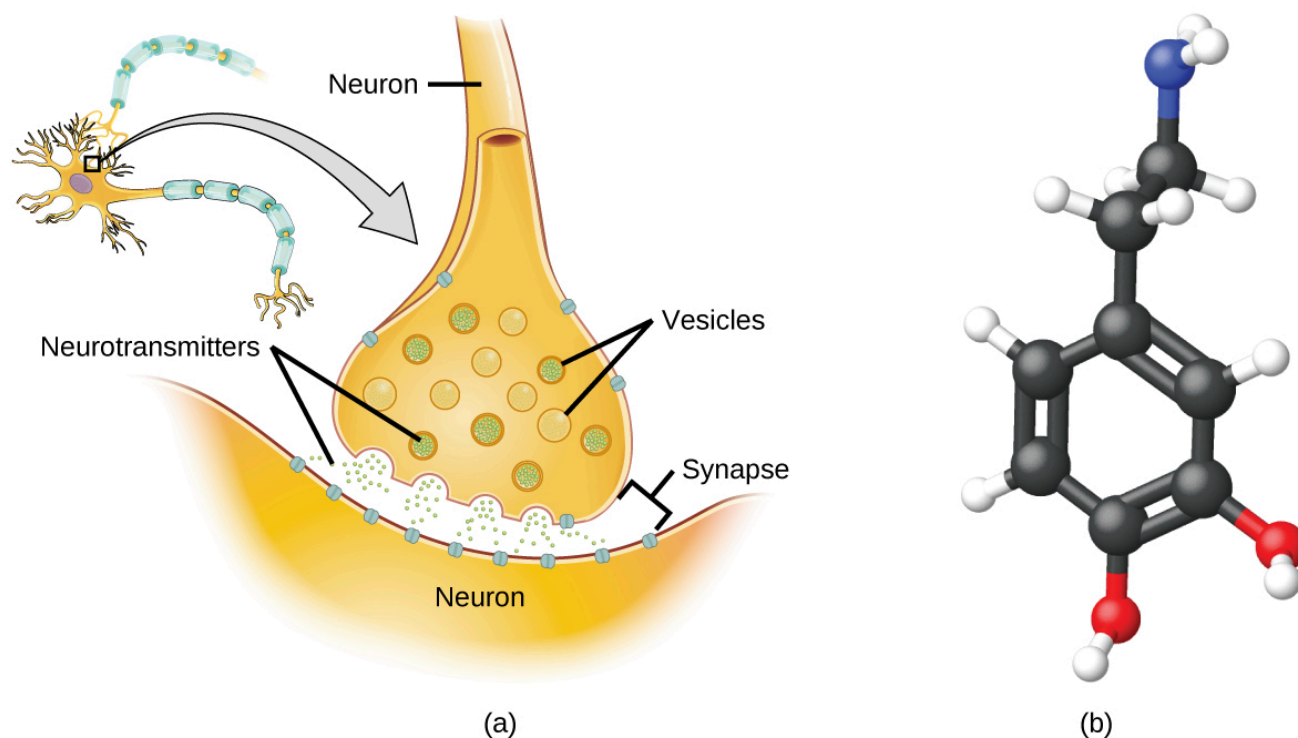
The brain is the control center of the central nervous system (**Figure 2.39**). It sends and receives signals to and from muscles and other internal organs to monitor and control their functions; it processes stimuli detected by

sensory organs to guide interactions with the external world; and it houses the complex physiological processes that give rise to our intellect and emotions. The broad field of neuroscience spans all aspects of the structure and function of the central nervous system, including research on the anatomy and physiology of the brain. Great progress has been made in brain research over the past few decades, and the BRAIN Initiative, a federal initiative announced in 2013, aims to accelerate and capitalize on these advances through the concerted efforts of various industrial, academic, and government agencies.



**Figure 2.39** (a) A typical human brain weighs about 1.5 kg and occupies a volume of roughly 1.1 L. (b) Information is transmitted in brain tissue and throughout the central nervous system by specialized cells called neurons (micrograph shows cells at 1600× magnification). By: Rice University [Openstax CC BY NC SA](#)

Specialized cells called neurons transmit information between different parts of the central nervous system by way of electrical and chemical signals. Chemical signaling occurs at the interface between different neurons when one of the cells releases molecules (called neurotransmitters) that diffuse across the small gap between the cells (called the synapse) and bind to the surface of the other cell. These neurotransmitter molecules are stored in small intracellular structures called vesicles that fuse to the cell wall and then break open to release their contents when the neuron is appropriately stimulated. This process is called exocytosis (see **Figure 2.40**). One neurotransmitter that has been very extensively studied is dopamine,  $\text{C}_8\text{H}_{11}\text{NO}_2$ . Dopamine is involved in various neurological processes that impact a wide variety of human behaviors. Dysfunctions in the dopamine systems of the brain underlie serious neurological diseases such as Parkinson's and schizophrenia.



**Figure 2.40** (a) Chemical signals are transmitted from neurons to other cells by the release of neurotransmitter molecules into the small gaps (synapses) between the cells. (b) Dopamine,  $C_8H_{11}NO_2$ , is a neurotransmitter involved in a number of neurological processes. By: Rice University [Openstax CC BY NC SA](#)

One important aspect of the complex processes related to dopamine signaling is the number of neurotransmitter molecules released during exocytosis. Since this number is a central factor in determining neurological response (and subsequent human thought and action), it is important to know how this number changes with certain controlled stimulations, such as the administration of drugs. It is also important to understand the mechanism responsible for any changes in the number of neurotransmitter molecules released—for example, some dysfunction in exocytosis, a change in the number of vesicles in the neuron, or a change in the number of neurotransmitter molecules in each vesicle.

Significant progress has been made recently in directly measuring the number of dopamine molecules stored in individual vesicles and the amount actually released when the vesicle undergoes exocytosis. Using miniaturized probes that can selectively detect dopamine molecules in very small amounts, scientists have determined that the vesicles of a certain type of mouse brain neuron contain an average of 30,000 dopamine molecules per vesicle (about  $5 \times 10^{-20}$  mol or 50 zmol). Analysis of these neurons from mice subjected to various drug therapies shows significant changes in the average number of dopamine molecules contained in individual vesicles, increasing or decreasing by up to three-fold, depending on the specific drug used. These

studies also indicate that not all of the dopamine in a given vesicle is released during exocytosis, suggesting that it may be possible to regulate the fraction released using pharmaceutical therapies.





# CHAPTER 3: ELECTRONIC STRUCTURE AND PERIODIC PROPERTIES OF ELEMENTS



Figure 3.1 The Crab Nebula consists of remnants of a supernova (the explosion of a star). NASA's Hubble Space Telescope produced this composite image. Measurements of the emitted light wavelengths enabled astronomers to identify the elements in the nebula, determining that it contains specific ions including  $S^+$  (green filaments) and  $O_2^+$  (red filaments). By: Rice University [Openstax CC BY NC SA](#)

## Chapter Outline

- 3.1 Electromagnetic Energy
- 3.2 The Bohr Model
- 3.3 Development of Quantum Theory
- 3.4 Electronic Structure of Atoms (Electron Configurations)
- 3.5 Periodic Variations in Element Properties
- 3.6 The Periodic Table
- 3.7 Molecular and Ionic Compounds

## Introduction

In 1054, Chinese astronomers recorded the appearance of a “guest star” in the sky, visible even during the day, which then disappeared slowly over the next two years. The sudden appearance was due to a supernova explosion, which was much brighter than the original star. Even though this supernova was observed almost a millennium ago, the remaining Crab Nebula (**Figure 3.1**) continues to release energy today. It emits not only visible light but also infrared light, X-rays, and other forms of electromagnetic radiation. The nebula emits both continuous spectra (the blue-white glow) and atomic emission spectra (the colored filaments). In this chapter, we will discuss light and other forms of electromagnetic radiation and how they are related to the electronic structure of atoms. We will also see how this radiation can be used to identify elements, even from thousands of light-years away.

# ELECTROMAGNETIC ENERGY (3.1)

OpenStax

---

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

- Explain the basic behavior of waves, including traveling waves and standing waves
- Describe the wave nature of light
- Use appropriate equations to calculate related light-wave properties such as period, frequency, wavelength, and energy
- Distinguish between line and continuous emission spectra
- Describe the particle nature of light

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

ultimately be resolved somehow within this framework. As we shall see, these paradoxes led to a contemporary framework that intimately connects particles and waves at a fundamental level called wave-particle duality, which has superseded the classical view.

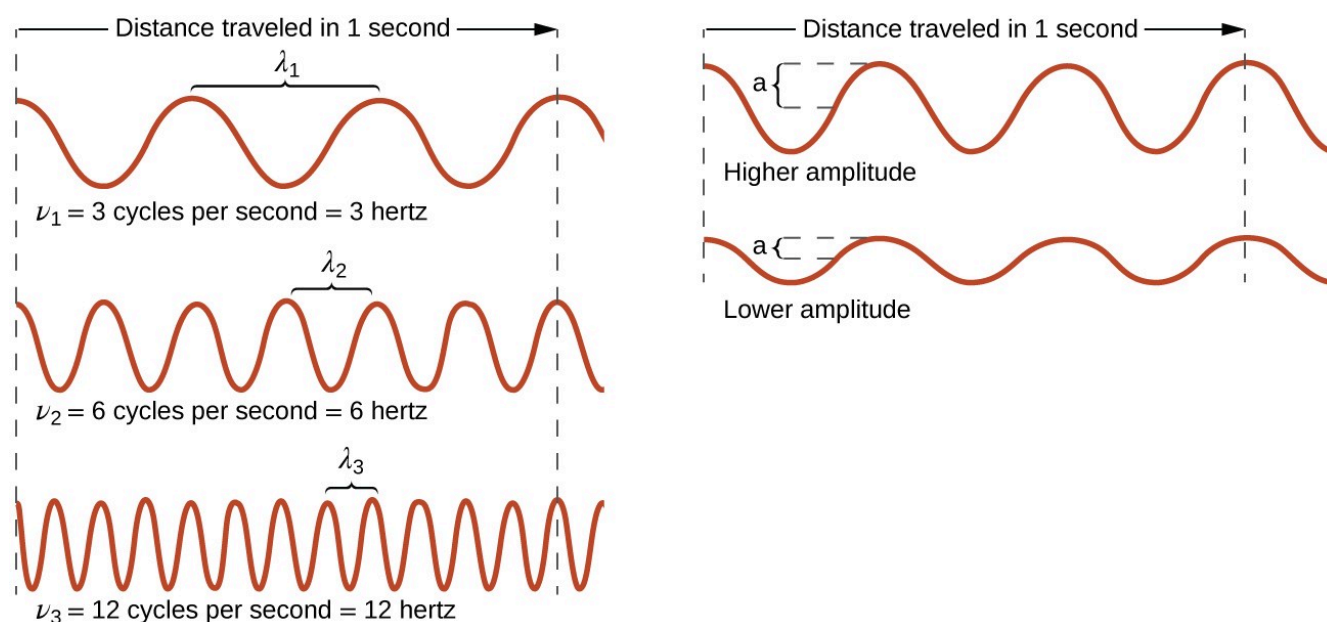
Visible light and other forms of electromagnetic radiation play important roles in chemistry, since they can be used to infer the energies of electrons within atoms and molecules. Much of modern technology is based on electromagnetic radiation. For example, radio waves from a mobile phone, X-rays used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

## 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  $2.998 \times 10^8$  m/s, the speed of light (denoted by  $c$ ).

All waves, including forms of electromagnetic radiation, are characterized by a **wavelength** (denoted by  $\lambda$ , the lowercase Greek letter lambda), a **frequency** (denoted by  $\nu$ , the lowercase Greek letter nu), and an **amplitude**. As can be seen in **Figure 3.2**, 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<sup>3</sup> m) to picometers (10<sup>−12</sup> 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<sup>−1</sup>], is the **hertz (Hz)**. Common multiples of this unit are megahertz (1 MHz =  $1 \times 10^6$  Hz) and gigahertz (1 GHz =  $1 \times 10^9$  Hz). The amplitude corresponds to the magnitude of the wave's displacement, and so in **Figure 3.2**, 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.

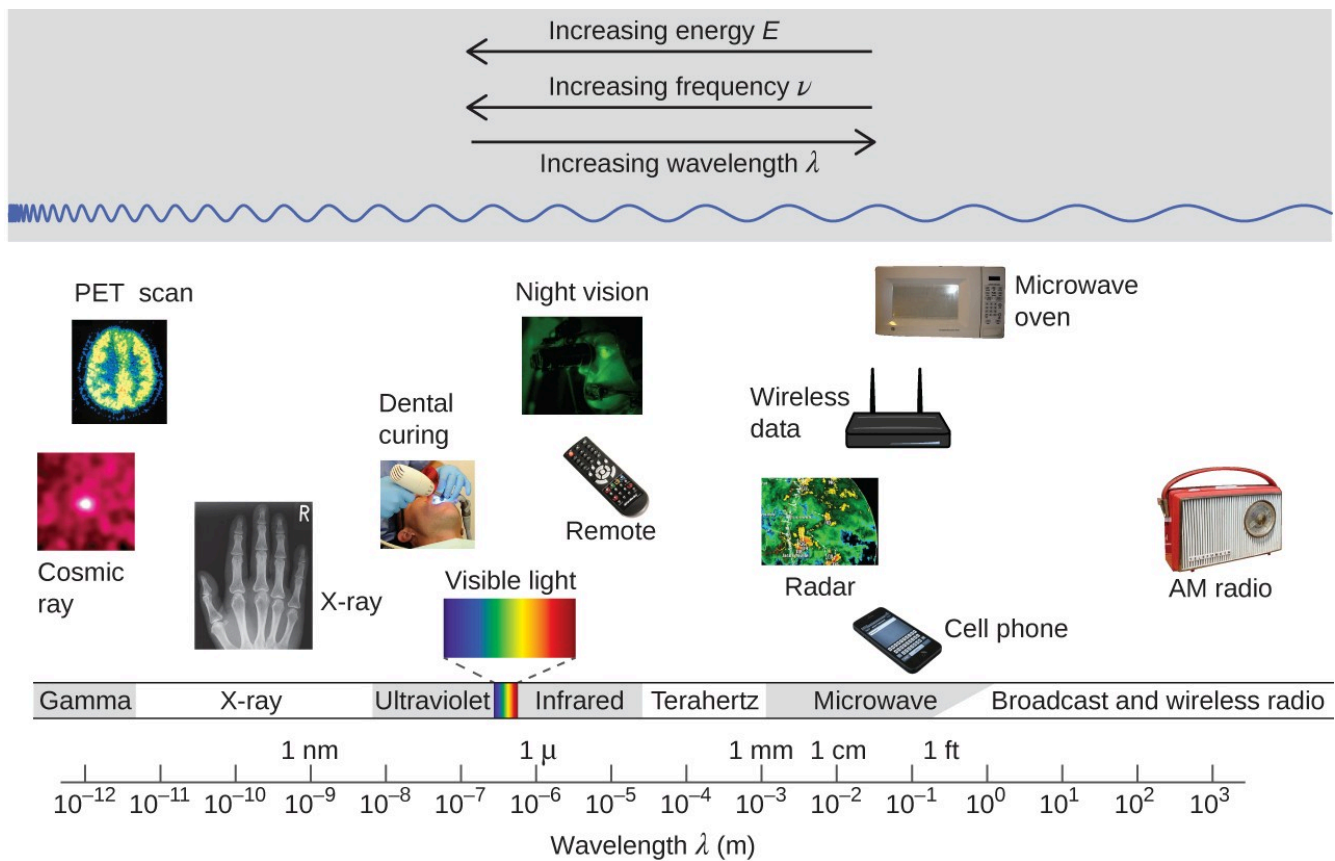


**Figure 3.2** One-dimensional sinusoidal waves show the relationship among wavelength, frequency, and speed. The wave with the shortest wavelength has the highest frequency. Amplitude is one-half the height of the wave from peak to trough. By: Rice University [Openstax CC BY NC SA](#)

The product of a wave's wavelength ( $\lambda$ ) and its frequency ( $\nu$ ),  $\lambda\nu$ , is the speed of the wave. Thus, for electromagnetic radiation in a vacuum, speed is equal to the fundamental constant,  $c$ :

$$c = 2.998 \times 10^8 \text{ ms}^{-1} = \lambda\nu$$

Wavelength and frequency are inversely proportional: As the wavelength increases, the frequency decreases. The inverse proportionality is illustrated in **Figure 3.3**. This figure also shows the electromagnetic spectrum, the range of all types of electromagnetic radiation. Each of the various colors of visible light has specific frequencies and wavelengths associated with them, and you can see that visible light makes up only a small portion of the electromagnetic spectrum. Because the technologies developed to work in various parts of the electromagnetic spectrum are different, for reasons of convenience and historical legacies, different units are typically used for different parts of the spectrum. For example, radio waves are usually specified as frequencies (typically in units of MHz), while the visible region is usually specified in wavelengths (typically in units of nm or angstroms).



**Figure 3.3** Portions of the electromagnetic spectrum are shown in order of decreasing frequency and increasing wavelength. By: Rice University [Openstax CC BY NC SA](#)

### Example 3.1

#### Determining the Frequency and Wavelength of Radiation

A sodium streetlight gives off yellow light that has a wavelength of 589 nm ( $1 \text{ nm} = 1 \times 10^{-9} \text{ m}$ ). What is the frequency of this light?

#### Solution

We can rearrange the equation  $c = \lambda \nu$  to solve for the frequency:

$$\nu = \frac{c}{\lambda}$$

Since  $c$  is expressed in meters per second, we must also convert 589 nm to meters.



$$\nu = \left( \frac{2.998 \times 10^8 \cancel{\text{m}} \text{s}^{-1}}{589 \cancel{\text{nm}}} \right) \left( \frac{1 \times 10^9 \cancel{\text{nm}}}{1 \cancel{\text{m}}} \right) = 5.09 \times 10^{14} \text{s}^{-1}$$

### Check Your Learning

One of the frequencies used to transmit and receive cellular telephone signals in the United States is 850 MHz. What is the wavelength in meters of these radio waves?

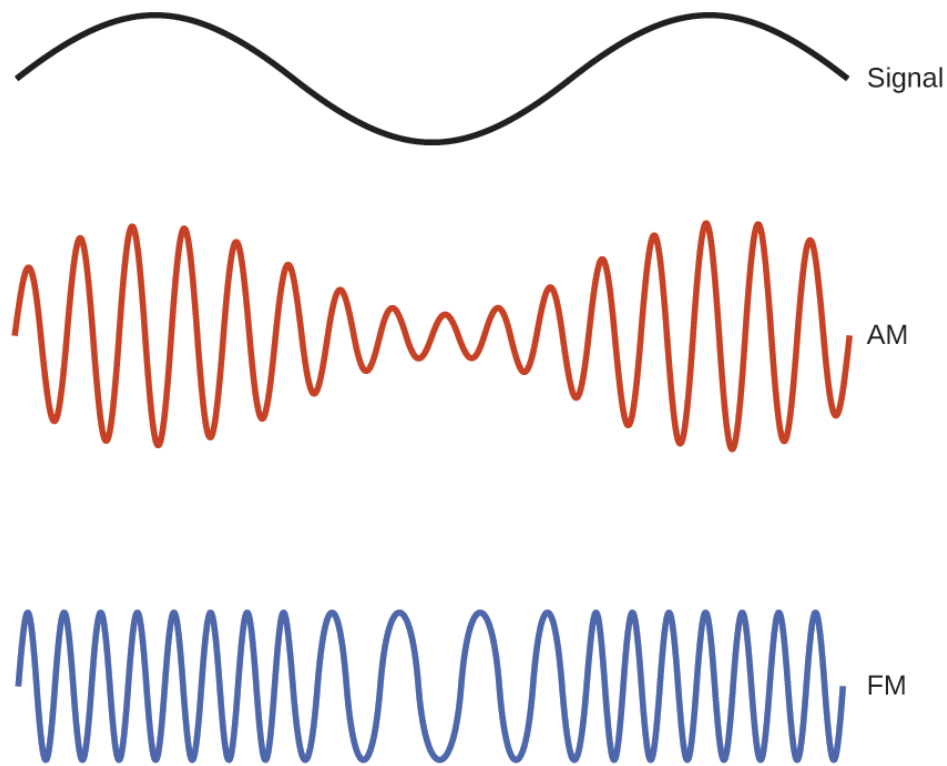
**Answer:** 0.353 m = 35.3 cm

## Chemistry in Everyday Life

### Wireless Communication



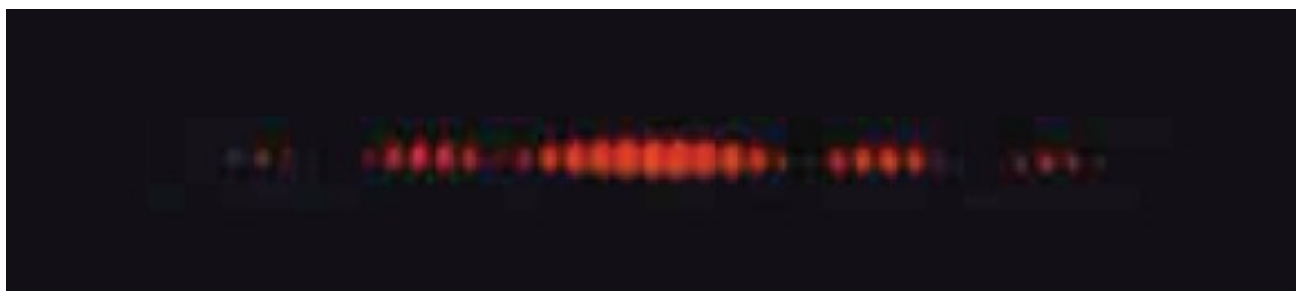
**Figure 3.4** Radio and cell towers are typically used to transmit long-wavelength electromagnetic radiation. Increasingly, cell towers are designed to blend in with the landscape, as with the Tucson, Arizona, cell tower (right) disguised as a palm tree. (Credit left: modification of work by Sir Mildred Pierce; credit middle: modification of work by M. O. Stevens.) Many valuable technologies operate in the radio (3 kHz–300 GHz) frequency region of the electromagnetic spectrum. At the low frequency (low energy, long wavelength) end of this region are AM (amplitude modulation) radio signals (540–2830 kHz) that can travel long distances. FM (frequency modulation) radio signals are used at higher frequencies (87.5–108.0 MHz). In AM radio, the information is transmitted by varying the amplitude of the wave (Figure 3.5). In FM radio, by contrast, the amplitude is constant, and the instantaneous frequency varies. By: Rice University [Openstax CC BY NC SA](#)



**Figure 3.5** This schematic depicts how amplitude modulation (AM) and frequency modulation (FM) can be used to transmit a radio wave. Other technologies also operate in the radio wave portion of the electromagnetic spectrum. For example, 4G cellular telephone signals are approximately 880 MHz, while Global Positioning System (GPS) signals operate at 1.228 and 1.575 GHz, local area wireless technology (Wi-Fi) networks operate at 2.4 to 5 GHz, and highway toll sensors operate at 5.8 GHz. The frequencies associated with these applications are convenient because such waves tend not to be absorbed much by common building materials. By: Rice University [Openstax CC BY NC SA](#)

One particularly characteristic phenomenon of waves results when two or more waves come into contact: They interfere with each other. **Figure 3.6** shows the **interference patterns** that arise when light passes through narrow slits closely spaced about a wavelength apart. The fringe patterns produced depend on the wavelength, with the fringes being more closely spaced for shorter wavelength light passing through a given set of slits. When the light passes through the two slits, each slit effectively acts as a new source, resulting in two closely spaced waves coming into contact at the detector (the camera in this case). The dark regions in Figure 3.6 correspond to regions where the peaks for the wave from one slit happen to coincide with the troughs for the wave from the other slit (destructive interference), while the brightest regions correspond to the regions where the peaks for the two waves (or their two troughs) happen to coincide (constructive interference). Likewise, when two stones are tossed close together into a pond, interference patterns are visible in the interactions between the waves produced by the stones. Such interference patterns cannot be explained by particles moving according to the laws of classical mechanics.





**Figure 3.6** Interference fringe patterns are shown for light passing through two closely spaced, narrow slits. The spacing of the fringes depends on the wavelength, with the fringes being more closely spaced for the shorter-wavelength blue light. By: Rice University [Openstax CC BY NC SA](#)

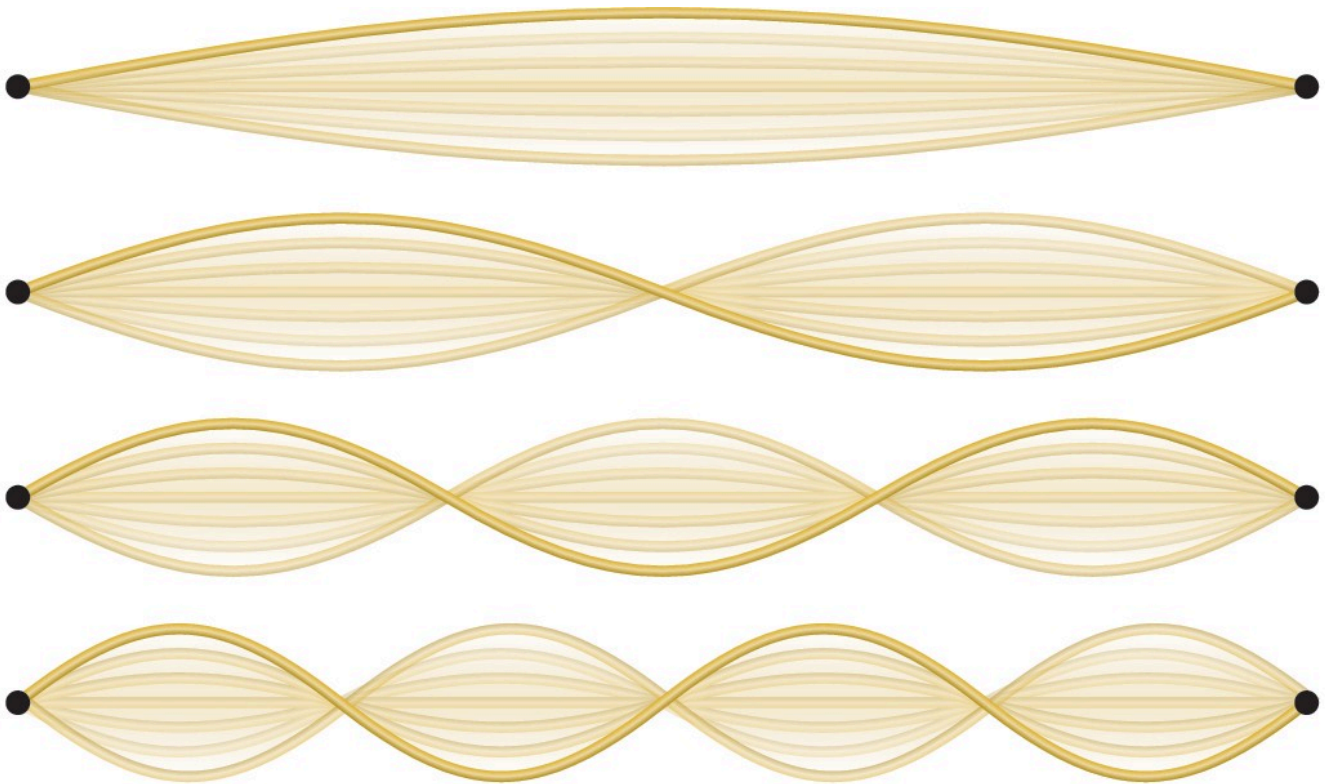
## Portrait of a Chemist

### Dorothy Hodgkin

Because the wavelengths of X-rays (10-10,000 picometers [pm]) are comparable to the size of atoms, X-rays can be used to determine the structure of molecules. When a beam of X-rays is passed through molecules packed together in a crystal, the X-rays collide with the electrons and scatter. Constructive and destructive interference of these scattered X-rays creates a specific diffraction pattern. Calculating backward from this pattern, the positions of each of the atoms in the molecule can be determined very precisely. One of the pioneers who helped create this technology was Dorothy Crowfoot Hodgkin. She was born in Cairo, Egypt, in 1910, where her British parents were studying archeology. Even as a young girl, she was fascinated with minerals and crystals. When she was a student at Oxford University, she began researching how X-ray crystallography could be used to determine the structure of biomolecules. She invented new techniques that allowed her and her students to determine the structures of vitamin B12, penicillin, and many other important molecules. Diabetes, a disease that affects 382 million people worldwide, involves the hormone insulin. Hodgkin began studying the structure of insulin in 1934, but it required several decades of advances in the field before she finally reported the structure in 1969. Understanding the structure has led to a better understanding of the disease and treatment options.

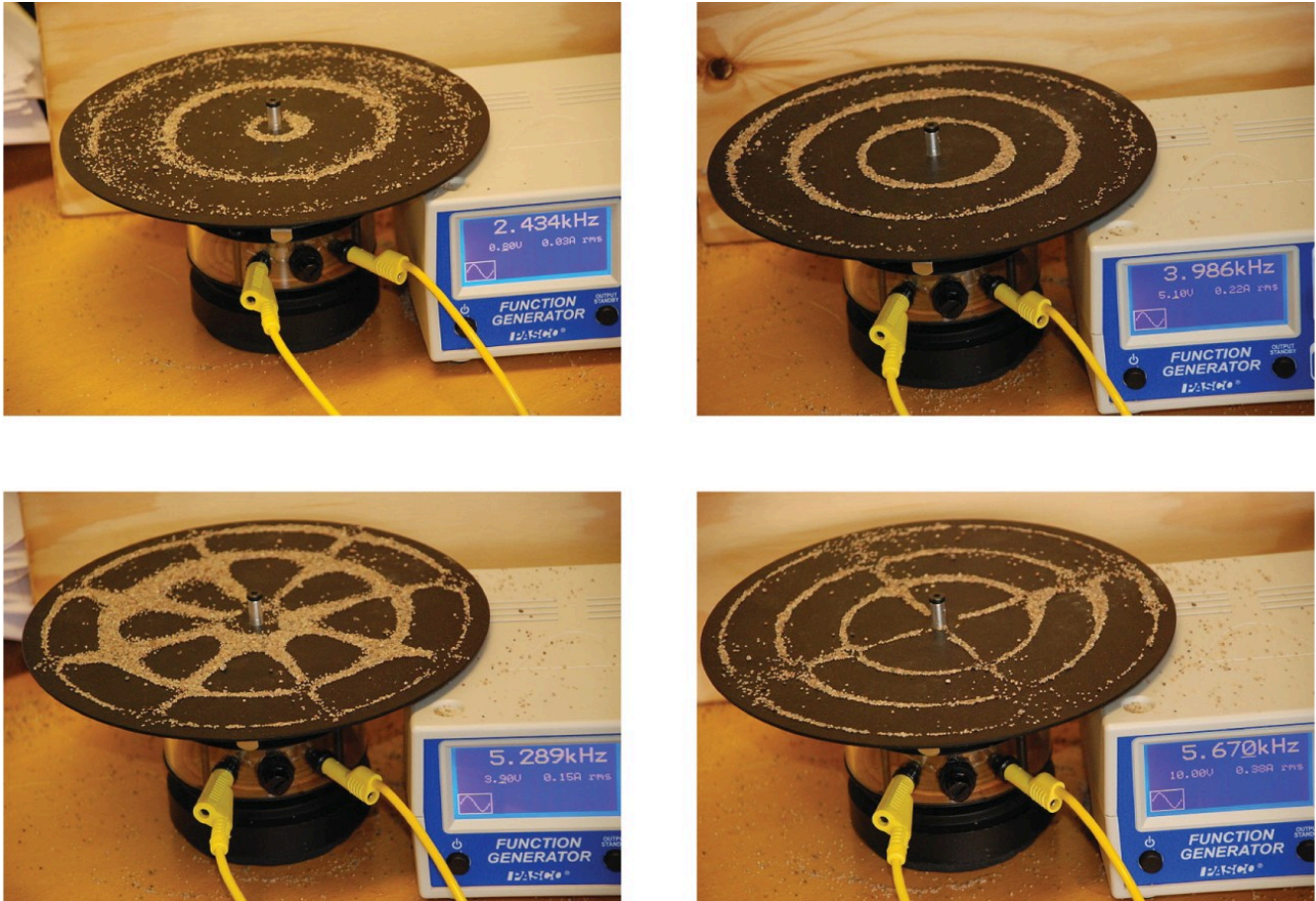
Not all waves are traveling waves. **Standing waves** (also known as **stationary waves**) remain constrained within some region of space. As we shall see, standing waves play an important role in our understanding of the electronic structure of atoms and molecules. The simplest example of a standing wave is a one-

dimensional wave associated with a vibrating string that is held fixed at its two end points. **Figure 3.7** shows the four lowest-energy standing waves (the fundamental wave and the lowest three harmonics) for a vibrating string at a particular amplitude. Although the string's motion lies mostly within a plane, the wave itself is considered to be one-dimensional, since it lies along the length of the string. The motion of string segments in a direction perpendicular to the string length generates the waves, and so the amplitude of the waves is visible as the maximum displacement of the curves seen in **Figure 3.7**. The key observation from the figure is *that only those waves having an integer number,  $n$ , of half-wavelengths between the end points can form*. A system with fixed end points such as this restricts the number and type of the possible waveforms. This is an example of **quantization**, in which only discrete values from a more general set of continuous values of some property are observed. Another important observation is that the harmonic waves (those waves displaying more than one-half wavelength) all have one or more points between the two end points that are not in motion. These special points are **nodes**. The energies of the standing waves with a given amplitude in a vibrating string increase with the number of half-wavelengths  $n$ . Since the number of nodes is  $n - 1$ , the energy can also be said to depend on the number of nodes, generally increasing as the number of nodes increases.



**Figure 3.7** A vibrating string shows some one-dimensional standing waves. Since the two end points of the string are held fixed, only waves having an integer number of half-wavelengths can form. The points on the string between the end points that are not moving are called the nodes. By: Rice University [Openstax](#) [CC BY NC SA](#)

An example of two-dimensional standing waves is shown in **Figure 3.8**, which shows the vibrational patterns on a flat surface. Although the vibrational amplitudes cannot be seen like they could in the vibrating string, the nodes have been made visible by sprinkling the drum surface with a powder that collects on the areas of the surface that have minimal displacement. For one-dimensional standing waves, the nodes were points on the line, but for two-dimensional standing waves, the nodes are lines on the surface (for three-dimensional standing waves, the nodes are two-dimensional surfaces within the three-dimensional volume).



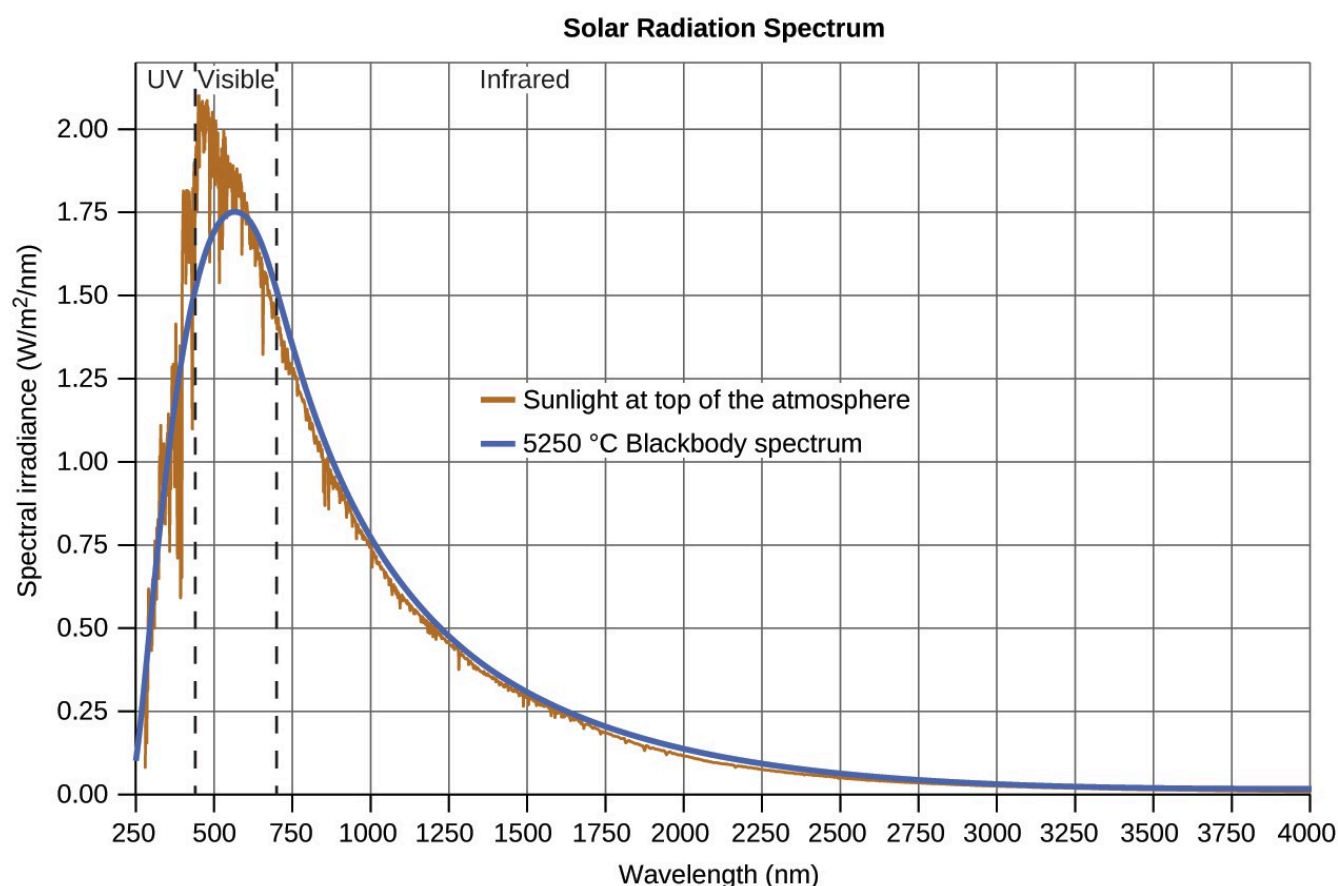
**Figure 3.8** Two-dimensional standing waves can be visualized on a vibrating surface. The surface has been sprinkled with a powder that collects near the nodal lines. There are two types of nodes visible: radial nodes (circles) and angular nodes (radii). By: Rice University [Openstax CC BY NC SA](#)

### Link to Learning

You can watch the formation of various radial nodes [here](#) as singer Imogen Heap projects her voice across a kettle drum.

## Blackbody Radiation and the Ultraviolet Catastrophe

The last few decades of the nineteenth century witnessed intense research activity in commercializing newly discovered electric lighting. This required obtaining a better understanding of the distributions of light emitted from various sources being considered. Artificial lighting is usually designed to mimic natural sunlight within the limitations of the underlying technology. Such lighting consists of a range of broadly distributed frequencies that form a **continuous spectrum**. **Figure 3.9** shows the wavelength distribution for sunlight. The most intense radiation is in the visible region, with the intensity dropping off rapidly for shorter wavelength ultraviolet (UV) light and more slowly for longer wavelength infrared (IR) light.



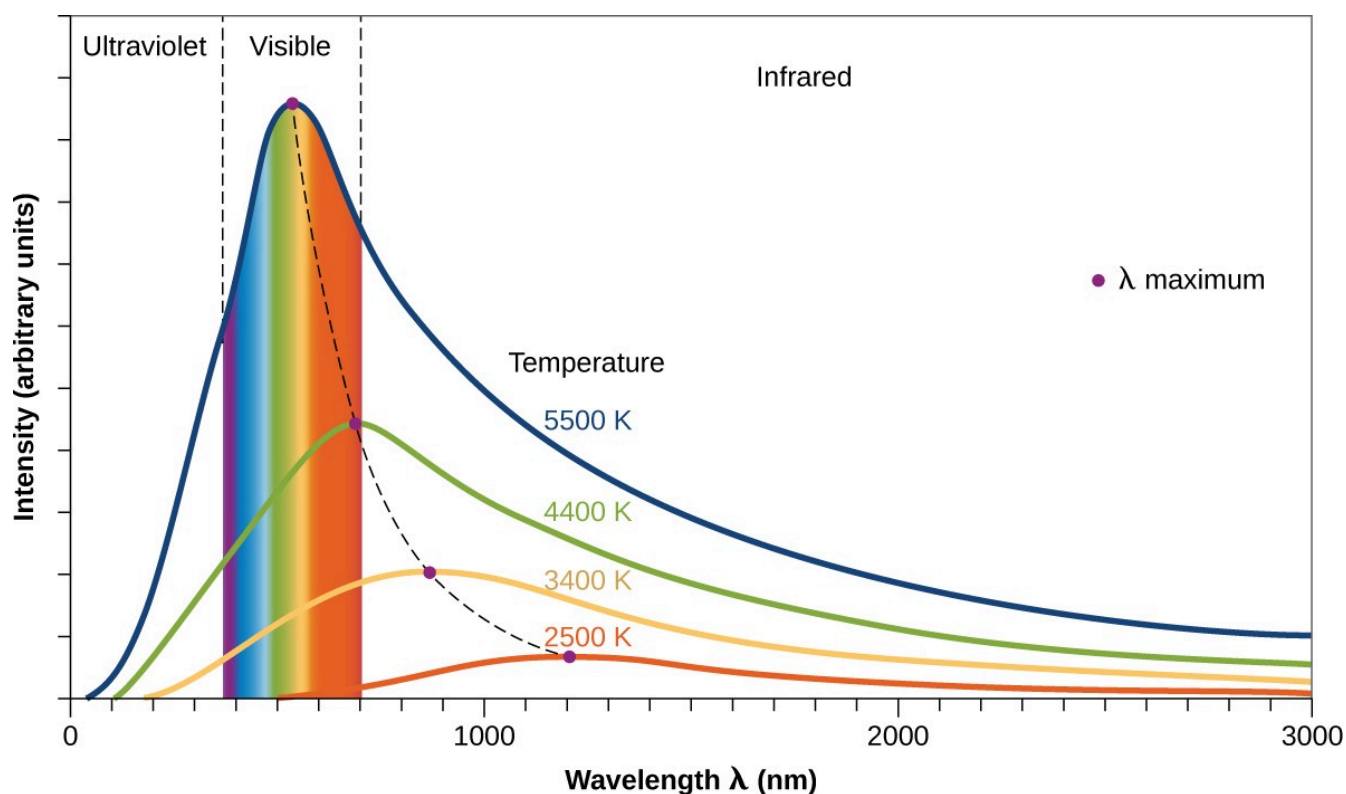
**Figure 3.9** The spectral distribution (light intensity vs. wavelength) of sunlight reaches the Earth's atmosphere as UV light, visible light, and IR light. The unabsorbed sunlight at the top of the atmosphere has a distribution that approximately matches the theoretical distribution of a blackbody at 5250 °C, represented by the blue curve. By: Rice University [Openstax CC BY NC SA](#)

In **Figure 3.9**, the solar distribution is compared to a representative distribution, called a blackbody spectrum, that corresponds to a temperature of 5250 °C. The blackbody spectrum matches the solar spectrum quite well. A **blackbody** is a convenient, ideal emitter that approximates the behavior of many materials when heated. It is “ideal” in the same sense that an ideal gas is a convenient, simple representation of real gases that works well, provided that the pressure is not too high nor the temperature too low. A good approximation of a blackbody that can be used to observe blackbody radiation is a metal oven that can be heated to very high temperatures. The oven has a small hole allowing for the light being emitted within the oven to be observed with a spectrometer so that the wavelengths and their intensities can be measured. **Figure 3.10** shows the resulting curves for some representative temperatures. Each distribution depends only on a single parameter: the temperature. The maxima in the blackbody curves,  $\lambda_{\text{max}}$ , shift to shorter wavelengths as the temperature increases, reflecting the observation that metals being heated to high temperatures begin to glow a darker red that becomes brighter as the temperature increases, eventually becoming white hot at very high temperatures as the intensities of all of the visible wavelengths become appreciable. This common observation was at the heart of the first paradox that showed the fundamental limitations of classical physics that we will examine.



Physicists derived mathematical expressions for the blackbody curves using well-accepted concepts from the theories of classical mechanics and classical electromagnetism. The theoretical expressions as functions of temperature fit the observed experimental blackbody curves well at longer wavelengths but showed significant discrepancies at shorter wavelengths. Not only did the theoretical curves not show a peak; they absurdly showed the intensity becoming infinitely large as the wavelength became smaller, which would imply that everyday objects at room temperature should be emitting large amounts of UV light. This became known as the “ultraviolet catastrophe” because no one could find any problems with the theoretical treatment that could lead to such unrealistic short-wavelength behavior. Finally, around 1900, Max Planck derived a theoretical expression for blackbody radiation that fit the experimental observations exactly (within experimental error). Planck developed his theoretical treatment by extending the earlier work that had been based on the premise that the atoms composing the oven vibrated at increasing frequencies (or decreasing wavelengths) as the temperature increased, with these vibrations being the source of the emitted electromagnetic radiation. But where the earlier treatments had allowed the vibrating atoms to have any energy values obtained from a continuous set of energies (perfectly reasonable, according to classical physics), Planck found that by restricting the vibrational energies to discrete values for each frequency, he could derive an expression for blackbody radiation that correctly had the intensity dropping rapidly for the short wavelengths in the UV region.

$E = nh\nu$ ,  $n = 1, 2, 3, \dots$ . The quantity  $h$  is a constant now known as Planck’s constant, in his honor. Although Planck was pleased he had resolved the blackbody radiation paradox, he was disturbed that to do so, he needed to assume the vibrating atoms required quantized energies, which he was unable to explain. The value of Planck’s constant is very small,  $6.626 \times 10^{-34}$  joule seconds (J s), which helps explain why energy quantization had not been observed previously in macroscopic phenomena.



**Figure 3.10** Blackbody spectral distribution curves are shown for some representative temperatures. By: Rice University [Openstax](#) [CC BY NC SA](#)

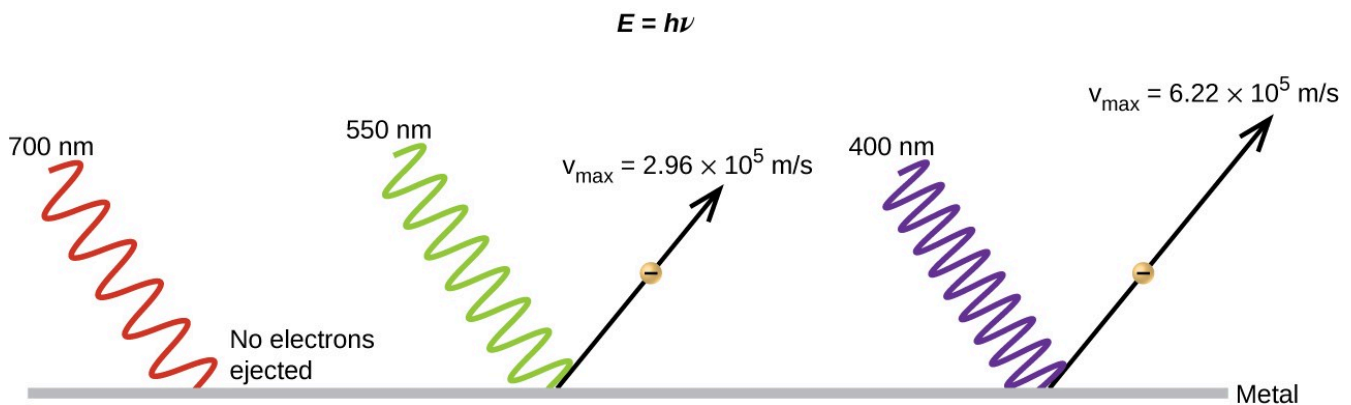
## The Photoelectric Effect

The next paradox in the classical theory to be resolved concerned the photoelectric effect (**Figure 3.11**). It had been observed that electrons could be ejected from the clean surface of a metal when light having a frequency greater than some threshold frequency was shone on it. Surprisingly, the kinetic energy of the ejected electrons did not depend on the brightness of the light but increased with increasing frequency of the light. Since the electrons in the metal had a certain amount of binding energy keeping them there, the incident light needed to have more energy to free the electrons. According to classical wave theory, a wave's energy depends on its intensity (which depends on its amplitude), not its frequency. One part of these observations was that the number of electrons ejected within a given time period was seen to increase as the brightness increased. In 1905, Albert Einstein was able to resolve the paradox by incorporating Planck's quantization findings into the discredited particle view of light (Einstein actually won his Nobel prize for this work and not for his theories of relativity for which he is most famous).

Einstein argued that the quantized energies that Planck had postulated in his treatment of blackbody radiation could be applied to the light in the photoelectric effect so that the light striking the metal surface should not be viewed as a wave but instead as a stream of particles (later called **photons**) whose energy depended on their frequency, according to Planck's formula,  $E = h\nu$  (or in terms of wavelength using  $c =$

$\nu\lambda$ ,  $E = \frac{hc}{\lambda}$ ). Electrons were ejected when hit by photons having sufficient energy (a frequency greater than the threshold). The greater the frequency, the greater the kinetic energy imparted to the escaping electrons by the collisions. Processes that increase the energy of an atom involve the absorption of light and are called **endothermic**. Processes that decrease the energy involve the emission of light and are called **exothermic**. Einstein also argued that the light intensity did not depend on the amplitude of the incoming wave but instead corresponded to the number of photons striking the surface within a given time period. This explains why the number of ejected electrons increased with increasing brightness, since the greater the number of incoming photons, the greater the likelihood that they would collide with some of the electrons.

With Einstein's findings, the nature of light took on a new air of mystery. Although many light phenomena could be explained either in terms of waves or particles, certain phenomena, such as the interference patterns obtained when light passed through a double slit, were completely contrary to a particle view of light, while other phenomena, such as the photoelectric effect, were completely contrary to a wave view of light. Somehow, at a deep fundamental level still not fully understood, light is both wavelike and particle-like. This is known as **wave-particle duality**.



**Figure 3.11** Photons with low frequencies do not have enough energy to cause electrons to be ejected via the photoelectric effect. For any frequency of light above the threshold frequency, the kinetic energy of an ejected electron will increase linearly with the energy of the incoming photon. By: Rice University [Openstax](#) CC BY NC SA



## Example 3.2

### Calculating the Energy of Radiation

When we see light from a neon sign, we are observing radiation from excited neon atoms. If this radiation has a wavelength of 640 nm, what is the energy of the photon being emitted?

### Solution

We use the part of Planck's equation that includes the wavelength,  $\lambda$ , and convert units of nanometers to meters so that the units of  $\lambda$  and  $c$  are the same.

$$E = \frac{hc}{\lambda}$$

$$E = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1})}{(640 \text{ nm})\left(\frac{1 \text{ m}}{10^9 \text{ nm}}\right)}$$

$$E = 3.10 \times 10^{-19} \text{ J}$$

### Check Your Learning

The microwaves in an oven are of a specific frequency that will heat the water molecules contained in food. (This is why most plastics and glass do not become hot in a microwave oven—they do not contain water molecules.) This frequency is about  $3 \times 10^9$  Hz. What is the energy of one photon in these microwaves?

**Answer:**  $2 \times 10^{-24} \text{ J}$

## Link to Learning

Use [this simulation program](#) to experiment with the photoelectric effect to see how intensity, frequency, type of metal, and other factors influence the ejected photons.

## Example 3.3

### Photoelectric Effect

Identify which of the following statements are false and, where necessary, change the italicized word or phrase to make them true, consistent with Einstein's explanation of the photoelectric effect.

- a. Increasing the brightness of incoming light *increases* the kinetic energy of the ejected electrons.
- b. Increasing the *wavelength* of incoming light increases the kinetic energy of the ejected electrons.
- c. Increasing the brightness of incoming light *increases* the number of ejected electrons.
- d. Increasing the *frequency* of incoming light can increase the number of ejected electrons.

### Solution

- a. False. Increasing the brightness of incoming light *has no effect* on the kinetic energy of the ejected electrons. Only energy, not the number or amplitude, of the photons influences the kinetic energy of the electrons.
- b. False. Increasing the *frequency* of incoming light increases the kinetic energy of the ejected electrons. Frequency is proportional to energy and inversely proportional to wavelength. Frequencies above the threshold value transfer the excess energy into the kinetic energy of the electrons.
- c. True. Because the number of collisions with photons increases with brighter light, the number of ejected electrons increases.

- d. True with regard to the threshold energy binding the electrons to the metal. Below this threshold, electrons are not emitted, and above it, they are. Once over the threshold value, further increasing the frequency does not increase the number of ejected electrons.

### Check Your Learning

Calculate the threshold energy in kJ/mol of electrons in aluminum, given that the lowest frequency photon for which the photoelectric effect is observed is  $9.87 \times 10^{14}$  Hz.

**Answer:** 394

## Line Spectra

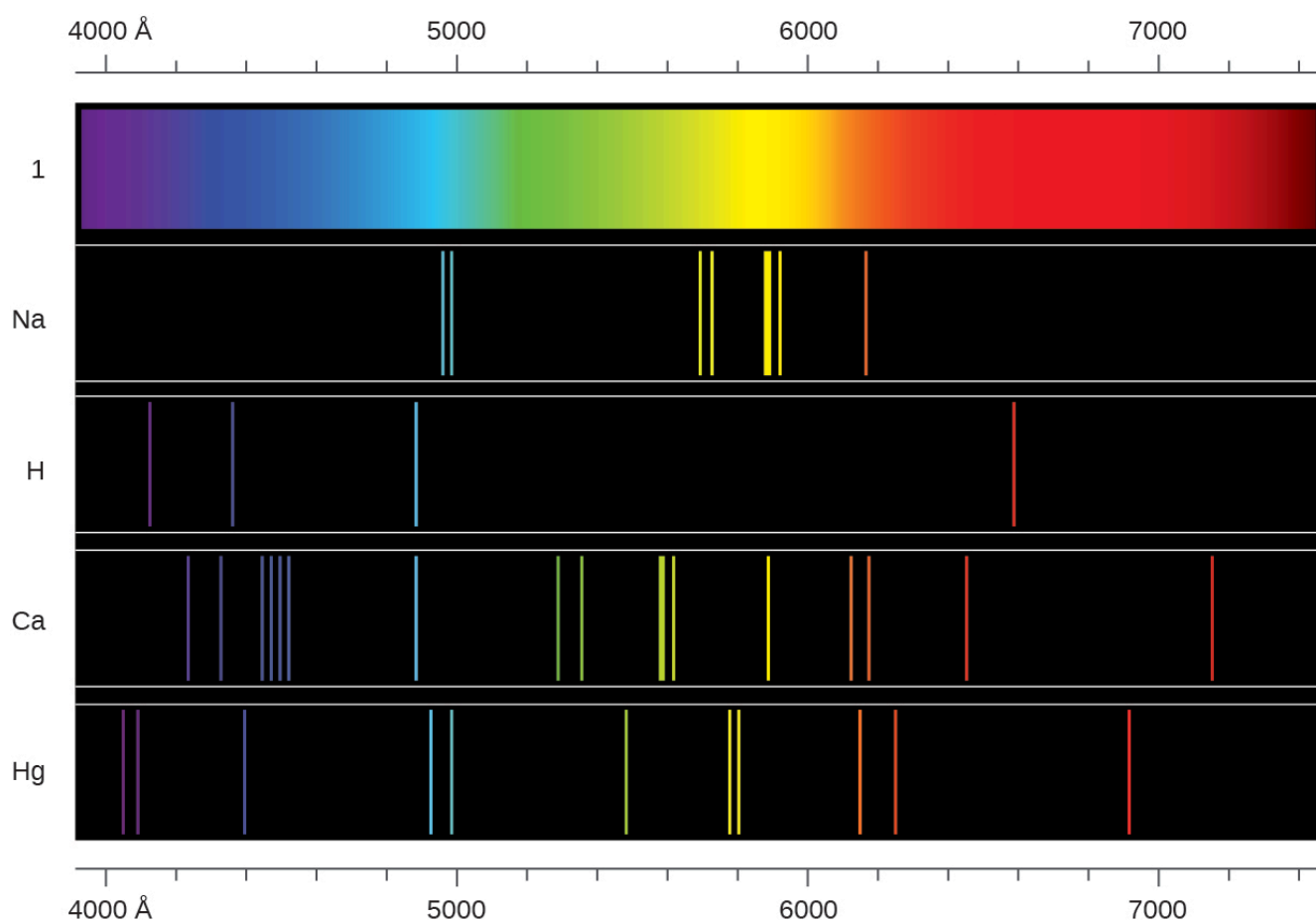
Another paradox within the classical electromagnetic theory that scientists in the late nineteenth century struggled with concerned the light emitted from atoms and molecules. When solids, liquids, or condensed gases are heated sufficiently, they radiate some of the excess energy as light. Photons produced in this manner have a range of energies and thereby produce a continuous spectrum in which an unbroken series of wavelengths is present. Most of the light generated from stars (including our sun) is produced in this fashion. You can see all the visible wavelengths of light present in sunlight by using a prism to separate them. As can be seen in **Figure 3.9**, sunlight also contains UV light (shorter wavelengths) and IR light (longer wavelengths) that can be detected using instruments but that are invisible to the human eye. Incandescent (glowing) solids such as tungsten filaments in incandescent lights also give off light that contains all wavelengths of visible light. These continuous spectra can often be approximated by blackbody radiation curves at some appropriate temperature, such as those shown in **Figure 3.10**.

In contrast to continuous spectra, light can also occur as discrete or **line spectra** having very narrow line widths interspersed throughout the spectral regions such as those shown in **Figure 3.13**. 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 3.12**). Each element displays its own characteristic set of lines, as do molecules, although their spectra are generally much more complicated.



**Figure 3.12** Neon signs operate by exciting a gas at low partial pressure using an electrical current. This sign shows the elaborate artistic effects that can be achieved. By: Rice University [Openstax CC BY NC SA](#)

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 3.13**.



**Figure 3.13** 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. By: Rice University Openstax CC BY NC SA

The origin of discrete spectra in atoms and molecules was extremely puzzling to scientists in the late nineteenth century, since according to classical electromagnetic theory, only continuous spectra should be observed. Even more puzzling, in 1885, Johann Balmer was able to derive an empirical equation that related the four visible wavelengths of light emitted by hydrogen atoms to whole integers. That equation is the following one, in which  $k$  is a constant:

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

Other discrete lines for the hydrogen atom were found in the UV and IR regions. Johannes Rydberg generalized Balmer's work and developed an empirical formula that predicted all of hydrogen's emission lines, not just those restricted to the visible range, where,  $n_1$  and  $n_2$  are integers,  $n_1 < n_2$ , and  $R_\infty$  is the Rydberg constant ( $1.097 \times 10^7 \text{ m}^{-1}$ ).

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

Even in the late nineteenth century, spectroscopy was a very precise science, and so the wavelengths of hydrogen were measured to very high accuracy, which implied that the Rydberg constant could be determined very precisely as well. That such a simple formula as the Rydberg formula could account for such precise measurements seemed astounding at the time, but it was the eventual explanation for emission spectra by Neils Bohr in 1913 that ultimately convinced scientists to abandon classical physics and spurred the development of modern quantum mechanics.

# THE BOHR MODEL (3.2)

OpenStax

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

- Describe the Bohr model of the hydrogen atom
- Use the Rydberg equation to calculate the energies of light emitted or absorbed by hydrogen atoms

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. This classical mechanics description of the atom is incomplete, however, since an electron moving in an elliptical orbit would be accelerating (by changing direction), and according to classical electromagnetism, it should continuously emit electromagnetic radiation. This loss in orbital energy should result in the electron’s orbit getting continually smaller until it spirals into the nucleus, implying that atoms are inherently unstable.

In 1913, Niels Bohr attempted to resolve the atomic paradox by ignoring classical electromagnetism’s prediction that the orbiting electron in hydrogen would continuously emit light. Instead, he incorporated into the classical mechanics description of the atom Planck’s ideas of quantization and Einstein’s finding that light consists of photons whose energy is proportional to their frequency. Bohr assumed that the electron orbiting the nucleus would not normally emit any radiation (the stationary state hypothesis), but it would emit or absorb a photon if it moved to a different orbit. The energy absorbed or emitted would reflect differences in the orbital energies according to this equation:

$$|\Delta E| = |E_f - E_i| = h\nu = \frac{hc}{\lambda}$$

In this equation,  $h$  is Planck’s constant, and  $E_i$  and  $E_f$  are the initial and final orbital energies, respectively.

The absolute value of the energy difference is used, since frequencies and wavelengths are always positive. Instead of allowing for continuous values of energy, Bohr assumed the energies of these electron orbitals were quantized:

$$E_n = -\frac{k}{n^2}, n = 1, 2, 3, \dots$$

In this expression,  $k$  is a constant comprising fundamental constants such as the electron mass and charge and Planck's constant. Inserting the expression for the orbit energies into the equation for  $\Delta E$  gives

$$\Delta E = k \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = \frac{hc}{\lambda}$$

or

$$\frac{1}{\lambda} = \frac{k}{hc} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

which is identical to the Rydberg equation in which  $R_\infty = \frac{k}{hc}$ . When Bohr calculated his theoretical value for the Rydberg constant,  $R_\infty$ , and compared it with the experimentally accepted value, he got an excellent agreement. Since the Rydberg constant was one of the most precisely measured constants at that time, this level of agreement was astonishing and meant that **Bohr's model** was taken seriously, despite the many assumptions that Bohr needed to derive it.

The lowest few energy levels are shown in **Figure 3.14**. 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. 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 3.15**).

Since Bohr's model involved only a single electron, it could also be applied to the single electron ions  $\text{He}^+$ ,  $\text{Li}^{2+}$ ,  $\text{Be}^{3+}$ , and so forth, which differ from hydrogen only in their nuclear charges, and so one-electron atoms and ions are collectively referred to as hydrogen-like atoms. The energy expression for hydrogen-like atoms is a generalization of the hydrogen atom energy, in which  $Z$  is the nuclear charge (+1 for hydrogen, +2 for He, +3 for Li, and so on), and  $k$  has a value of  $2.179 \times 10^{-18} \text{ J}$ .



$$E_n = -\frac{kZ^2}{n^2}$$

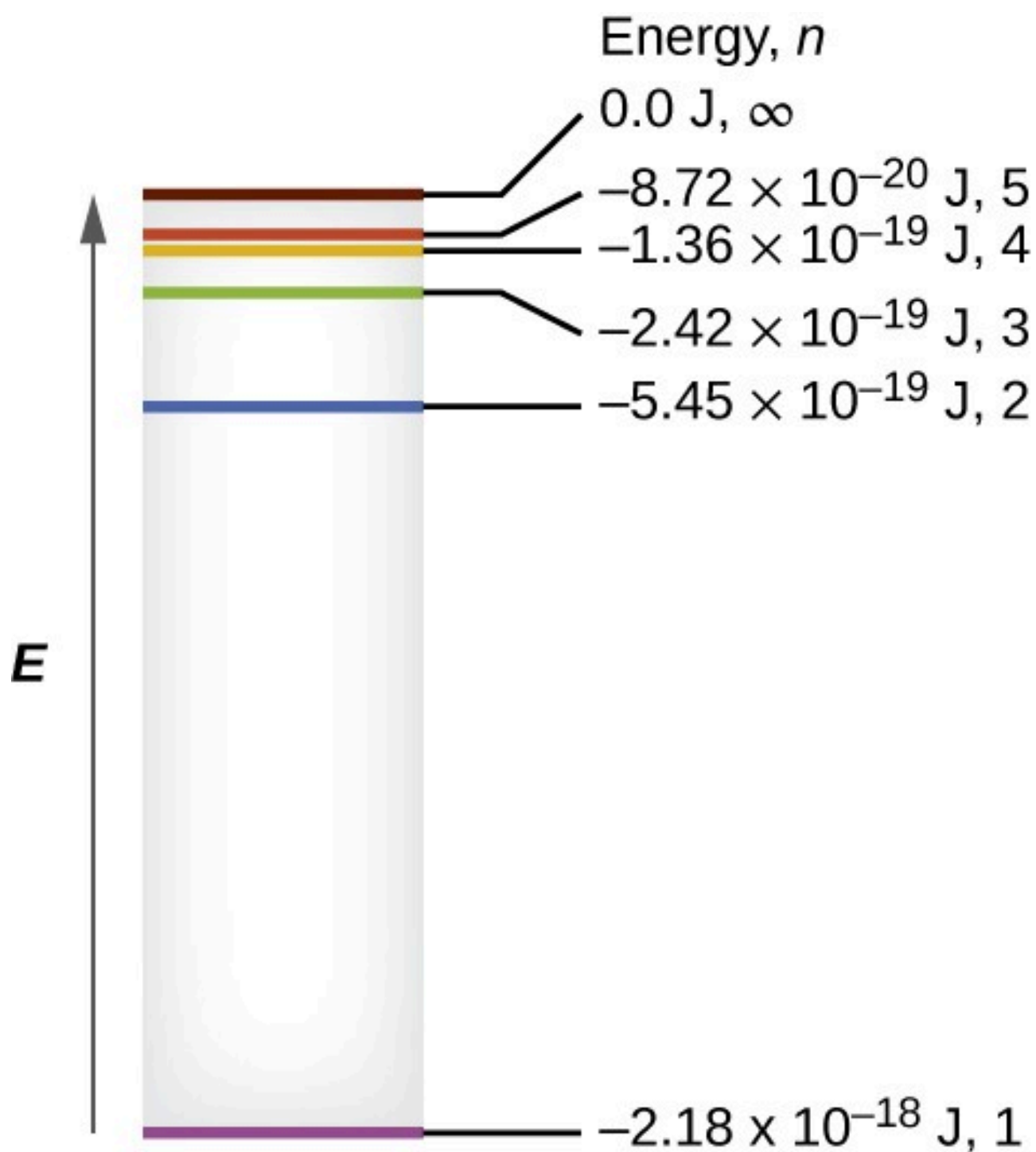
The sizes of the circular orbits for hydrogen-like atoms are given in terms of their radii by the following expression, in which  $a_0$  is a constant called the Bohr radius, with a value of  $5.292 \times 10^{-11}$  m:

$$r = \frac{n^2}{Z} a_0$$

The equation also shows us that as the electron's energy increases (as  $n$  increases), the electron is found at greater distances from the nucleus. This is implied by the inverse dependence of electrostatic attraction on distance, since, as the electron moves away from the nucleus, the electrostatic attraction between it and the nucleus decreases, and it is held less tightly in the atom. Note that as  $n$  gets larger and the orbits get larger, their energies get closer to zero, and so the limits  $n \rightarrow \infty$  and  $r \rightarrow \infty$  imply that  $E = 0$  corresponds to the ionization limit where the electron is completely removed from the nucleus. Thus, for hydrogen in the ground state  $n = 1$ , the ionization energy would be:

$$\Delta E = E_n \rightarrow \infty - E_1 = 0 + k = k$$

With three extremely puzzling paradoxes now solved (blackbody radiation, the photoelectric effect, and the hydrogen atom), and all involving Planck's constant in a fundamental manner, it became clear to most physicists at that time that the classical theories that worked so well in the macroscopic world were fundamentally flawed and could not be extended down into the microscopic domain of atoms and molecules. Unfortunately, despite Bohr's remarkable achievement in deriving a theoretical expression for the Rydberg constant, he was unable to extend his theory to the next simplest atom, He, which only has two electrons. Bohr's model was severely flawed, since it was still based on the classical mechanics notion of precise orbits, a concept that was later found to be untenable in the microscopic domain, when a proper model of quantum mechanics was developed to supersede classical mechanics.



**Figure 3.14** Quantum numbers and energy levels in a hydrogen atom. The more negative the calculated value, the lower the energy. By: Rice University [Openstax CC BY NC SA](#)

## EXAMPLE 3.4

## Calculating the Energy of an Electron in a Bohr Orbit

Early researchers were very excited when they were able to predict the energy of an electron at a particular distance from the nucleus in a hydrogen atom. If a spark promotes the electron in a hydrogen atom into an orbit with  $n = 3$ , what is the calculated energy, in joules, of the electron?

## Solution

The energy of the electron is given by this equation:

$$E = \frac{-kZ^2}{n^2}$$

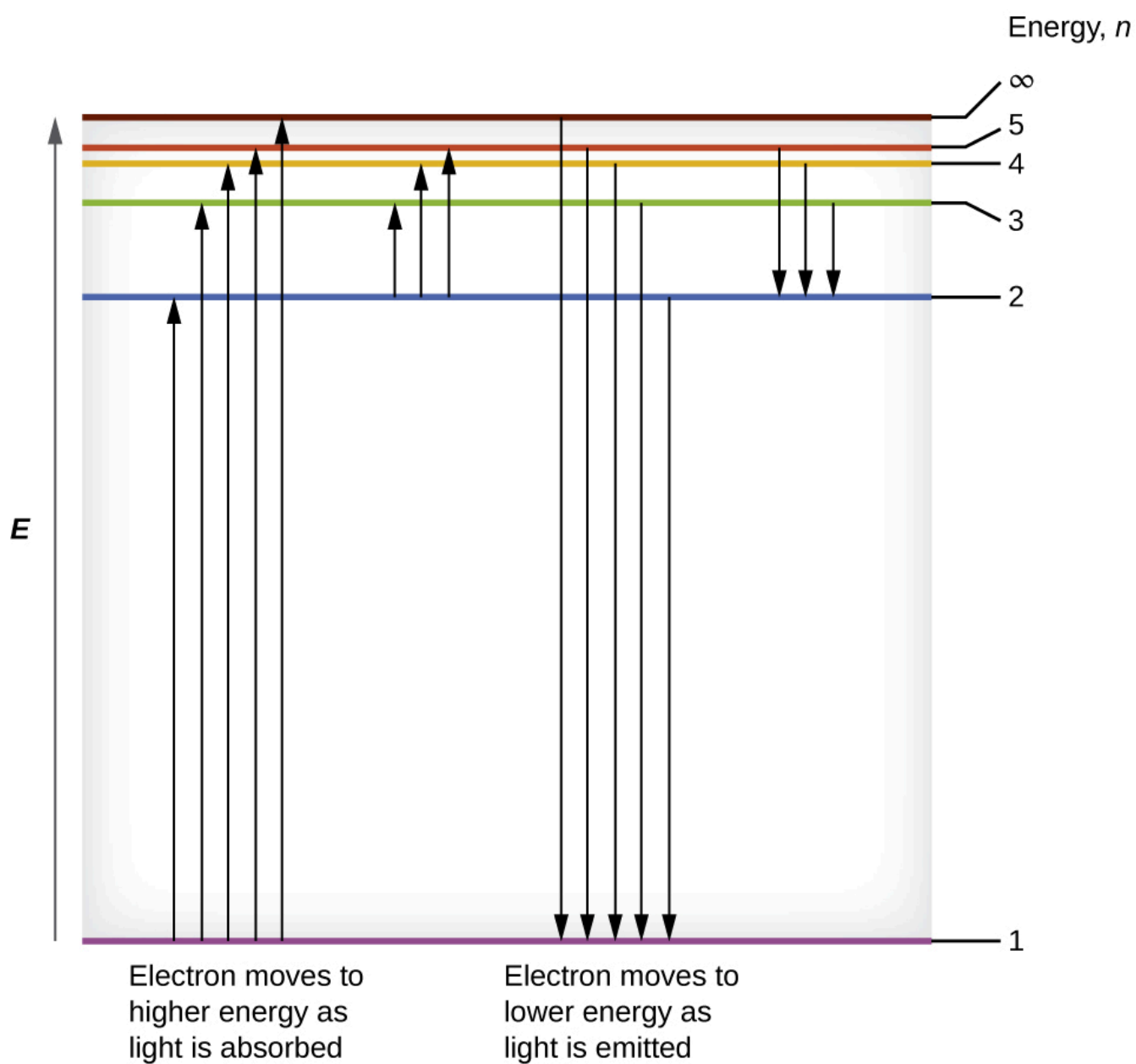
The atomic number,  $Z$ , of hydrogen is 1;  $k = 2.179 \times 10^{-18} \text{ J}$ ; and the electron is characterized by an  $n$  value of 3. Thus,

$$E = \frac{-(2.179 \times 10^{-18} \text{ J}) \times (1)^2}{(3)^2} = -2.421 \times 10^{-19} \text{ J}$$

## Check Your Learning

The electron in Figure 3.15 is promoted even further to an orbit with  $n = 6$ . What is its new energy?

**Answer:**  $-6.053 \times 10^{-20} \text{ J}$



**Figure 3.15** 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. By: Rice University [Openstax CC BY NC SA](#)

### Example 3.5

#### Calculating the Energy and Wavelength of Electron Transitions in a One-Electron (Bohr) System

What are the energy (in joules) and the wavelength (in meters) of the line in the spectrum of hydrogen that represent the movement of an electron from Bohr orbit with  $n = 4$  to the orbit with  $n = 6$ ? In what part of the electromagnetic spectrum do we find this radiation?

#### Solution

In this case, the electron starts out with  $n = 4$ , so  $n_1 = 4$ . It comes to rest in the  $n = 6$  orbit, so  $n_2 = 6$ . The difference in energy between the two states is given by this expression:

$$\Delta E = E_1 - E_2 = 2.179 \times 10^{-18} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\Delta E = 2.179 \times 10^{-18} \left( \frac{1}{4^2} - \frac{1}{6^2} \right) \text{ J}$$

$$\Delta E = 2.179 \times 10^{-18} \left( \frac{1}{16} - \frac{1}{36} \right) \text{ J}$$

$$\Delta E = 7.566 \times 10^{-20} \text{ J}$$

This energy difference is positive, indicating a photon enters the system (is absorbed) to excite the electron from the  $n = 4$  orbit up to the  $n = 6$  orbit. The wavelength of a photon with this energy is found by the expression  $E = \frac{hc}{\lambda}$ .

Rearrangement gives:

$$\lambda = \frac{hc}{E}$$

$$\begin{aligned} &= (6.626 \times 10^{-34} \text{ J} \cdot \text{s}) \times \frac{2.998 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{7.566 \times 10^{-20} \text{ J}} \\ &= 2.626 \times 10^{-6} \text{ m} \end{aligned}$$

From the illustration of the electromagnetic spectrum in Electromagnetic Energy, we can see that this wavelength is found in the infrared portion of the electromagnetic spectrum.

### Check Your Learning

What is the energy in joules and the wavelength in meters of the photon produced when an electron falls from the  $n = 5$  to the  $n = 3$  level in a  $\text{He}^+$  ion ( $Z = 2$  for  $\text{He}^+$ )?

**Answer:**  $6.198 \times 10^{-19} \text{ J}$ ;  $3.205 \times 10^{-7} \text{ m}$

Bohr's model of the hydrogen atom provides insight into the behavior of matter at the microscopic level, but it does not account for electron–electron interactions in atoms with more than one electron. It does introduce several important features of all models used to describe the distribution of electrons in an atom. These features include the following:

- The energies of electrons (energy levels) in an atom are quantized, described by **quantum numbers**: integer numbers having only specific allowed value and used to characterize the arrangement of electrons in an atom.
- An electron's energy increases with increasing distance from the nucleus.
- The discrete energies (lines) in the spectra of the elements result from quantized electronic energies.

Of these features, the most important is the postulate of quantized energy levels for an electron in an atom. As a consequence, the model laid the foundation for the quantum mechanical model of the atom. Bohr won a Nobel Prize in Physics for his contributions to our understanding of the structure of atoms and how that is related to line spectra emissions.

# DEVELOPMENT OF QUANTUM THEORY (3.3)

OpenStax

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

- Extend the concept of wave–particle duality that was observed in electromagnetic radiation to matter as well
- Understand the general idea of the quantum mechanical description of electrons in an atom and that it uses the notion of three-dimensional wave functions, or orbitals, that define the distribution of probability to find an electron in a particular part of space
- List and describe traits of the four quantum numbers that form the basis for completely specifying the state of an electron in an atom

Bohr's model explained the experimental data for the hydrogen atom and was widely accepted, but it also raised many questions. Why did electrons orbit at only fixed distances defined by a single quantum number  $n = 1, 2, 3$ , and so on, but never in between? Why did the model work so well describing hydrogen and one-electron ions, but could not correctly predict the emission spectrum for helium or any larger atoms? To answer these questions, scientists needed to completely revise the way they thought about matter.

## Behavior in the Microscopic World

We know how matter behaves in the macroscopic world—objects that are large enough to be seen by the naked eye follow the rules of classical physics. A billiard ball moving on a table will behave like a particle: It will continue in a straight line unless it collides with another ball or the table cushion, or is acted on by some other force (such as friction). The ball has a well-defined position and velocity (or a well-defined momentum,  $p = mv$ , defined by mass  $m$  and velocity  $v$ ) at any given moment. In other words, the ball is moving in a classical trajectory. This is the typical behavior of a classical object.

When waves interact with each other, they show interference patterns that are not displayed by macroscopic particles such as the billiard ball. For example, interacting waves on the surface of water can produce interference patterns similar to those shown in **Figure 3.16**. This is a case of wave behavior on the

macroscopic scale, and it is clear that particles and waves are very different phenomena in the macroscopic realm.



**Figure 3.16** An interference pattern on the water surface is formed by interacting waves. The waves are caused by the reflection of water from the rocks.  
By: Rice University [Openstax](#) [CC BY NC SA](#)

As technological improvements allowed scientists to probe the microscopic world in greater detail, it became increasingly clear by the 1920s that very small pieces of matter follow a different set of rules from those we observe for large objects. The unquestionable separation of waves and particles was no longer the case for the microscopic world.

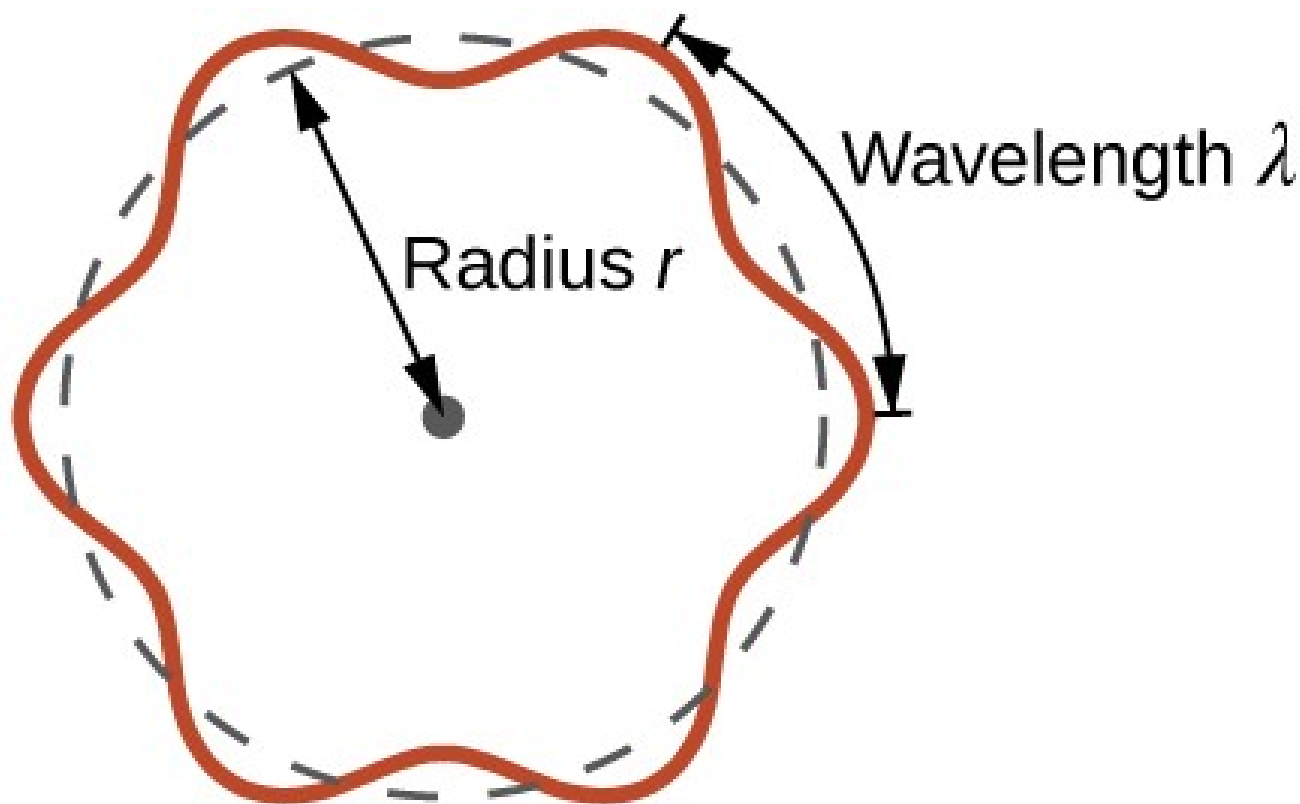
One of the first people to pay attention to the special behavior of the microscopic world was Louis de Broglie. He asked the question: If electromagnetic radiation can have a particle-like character, can electrons and other submicroscopic particles exhibit wavelike character? In his 1925 doctoral dissertation, de Broglie extended the wave–particle duality of light that Einstein used to resolve the photoelectric-effect paradox to material particles. He predicted that a particle with mass  $m$  and velocity  $v$  (that is, with linear momentum  $p$ ) should also exhibit the behavior of a wave with a wavelength value  $\lambda$ , given by this expression in which  $h$  is the familiar Planck’s constant:

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

This is called the *de Broglie wavelength*. Unlike the other values of  $\lambda$  discussed in this chapter, the de Broglie wavelength is a characteristic of particles and other bodies, not electromagnetic radiation (note that this equation involves velocity [ $v$ , m/s], not frequency [ $\nu$ , Hz]. Although these two symbols appear nearly identical, they mean very different things). Where Bohr had postulated the electron as being a particle orbiting the nucleus in quantized orbits, de Broglie argued that Bohr’s assumption of quantization can be



explained if the electron is considered not as a particle but rather as a circular standing wave such that only an integer number of wavelengths could fit exactly within the orbit (**Figure 3.17**).



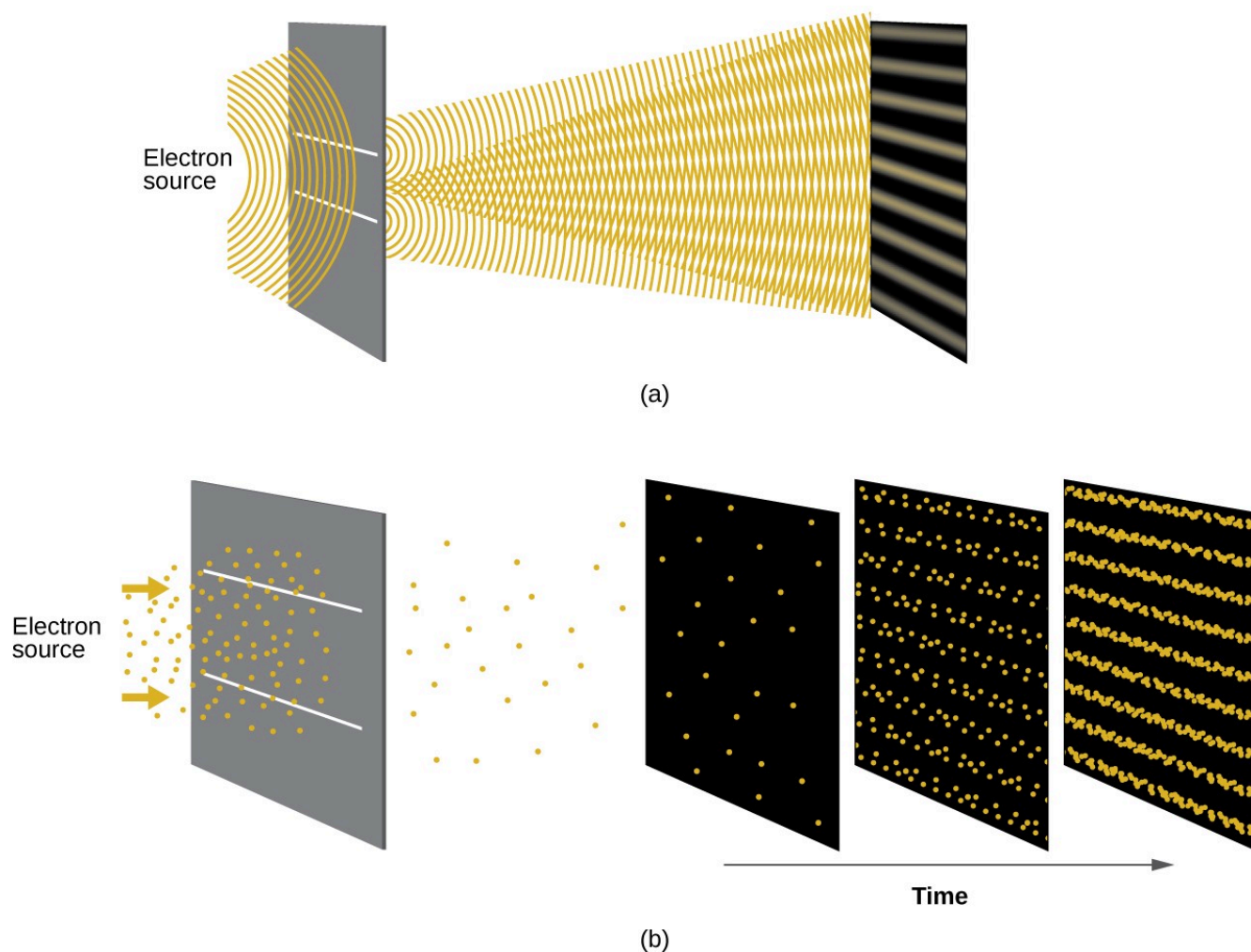
**Figure 3.17** If an electron is viewed as a wave circling around the nucleus, an integer number of wavelengths must fit into the orbit for this standing wave behavior to be possible. By: Rice University Openstax CC BY NC SA

For a circular orbit of radius  $r$ , the circumference is  $2\pi r$ , and so de Broglie's condition is:

$$2\pi r = n\lambda, \quad n = 1, 2, 3, \dots$$

Shortly after de Broglie proposed the wave nature of matter, two scientists at Bell Laboratories, C. J. Davisson and L. H. Germer, demonstrated experimentally that electrons can exhibit wavelike behavior by showing an interference pattern for electrons traveling through a regular atomic pattern in a crystal. The regularly spaced atomic layers served as slits, as used in other interference experiments. Since the spacing between the layers serving as slits needs to be similar in size to the wavelength of the tested wave for an interference pattern to form, Davisson and Germer used a crystalline nickel target for their "slits," since the spacing of the atoms within the lattice was approximately the same as the de Broglie wavelengths of the electrons that they used. **Figure 3.18** shows an interference pattern. It is strikingly similar to the interference patterns for light shown in Electromagnetic Energy for light passing through two closely spaced, narrow slits. The wave-particle duality of matter can be seen in **Figure 3.18** by observing what happens if electron collisions are recorded over a long period of time. Initially, when only a few electrons have been recorded, they

show clear particle-like behavior, having arrived in small localized packets that appear to be random. As more and more electrons arrived and were recorded, a clear interference pattern that is the hallmark of wavelike behavior emerged. Thus, it appears that while electrons are small localized particles, their motion does not follow the equations of motion implied by classical mechanics but instead is governed by some type of a wave equation. Thus the wave–particle duality first observed with photons is actually a fundamental behavior intrinsic to all quantum particles.



**Figure 3.18** (a) The interference pattern for electrons passing through very closely spaced slits demonstrates that quantum particles such as electrons can exhibit wavelike behavior. (b) The experimental results illustrated here demonstrate the wave–particle duality in electrons. By: Rice University [Openstax CC BY NC SA](#)

## Link to Learning

View the [Dr. Quantum – Double Slit Experiment cartoon](#) for an easy-to-understand description of wave-particle duality and the associated experiments.

## EXAMPLE 3.6

### Calculating the Wavelength of a Particle

If an electron travels at a velocity of  $1.000 \times 10^7 \text{ m s}^{-1}$  and has a mass of  $9.109 \times 10^{-28} \text{ g}$ , what is its wavelength?

### Solution

We can use de Broglie's equation to solve this problem, but we first must do a unit conversion of Planck's constant. You learned earlier that  $1 \text{ J} = 1 \text{ kg m}^2/\text{s}^2$ . Thus, we can write  $h = 6.626 \times 10^{-34} \text{ J s}$  as  $6.626 \times 10^{-34} \text{ kg m}^2/\text{s}$ .

$$\begin{aligned}\lambda &= \frac{h}{mv} \\ &= \frac{6.626 \times 10^{-34} \text{ kg m}^2/\text{s}}{(9.109 \times 10^{-31} \text{ kg})(1.000 \times 10^7 \text{ m/s})} \\ &= 7.274 \times 10^{-11} \text{ m}\end{aligned}$$

This is a small value, but it is significantly larger than the size of an electron in the classical (particle) view. This size is the same order of magnitude as the size of an atom. This means that electron wavelike behavior is going to be noticeable in an atom.

### Check Your Learning

Calculate the wavelength of a softball with a mass of  $100 \text{ g}$  traveling at a velocity of  $35 \text{ m s}^{-1}$ , assuming that it can be modeled as a single particle.

**Answer:**  $1.9 \times 10^{-34}$  m.

We never think of a thrown softball having a wavelength, since this wavelength is so small it is impossible for our senses or any known instrument to detect (strictly speaking, the wavelength of a real baseball would correspond to the wavelengths of its constituent atoms and molecules, which, while much larger than this value, would still be microscopically tiny). The de Broglie wavelength is only appreciable for matter that has a very small mass and/or a very high velocity.

Werner Heisenberg considered the limits of how accurately we can measure the properties of an electron or other microscopic particles. He determined that there is a fundamental limit to how accurately one can measure both a particle's position and its momentum simultaneously. The more accurately we measure the momentum of a particle, the less accurately we can determine its position at that time, and vice versa. This is summed up in what we now call the **Heisenberg uncertainty principle**: *It is fundamentally impossible to determine simultaneously and exactly both the momentum and the position of a particle.* For a particle of mass  $m$  moving with velocity  $v_x$  in the  $x$  direction (or equivalently with momentum  $p_x$ ), the product of the uncertainty in the position,  $\Delta x$ , and the uncertainty in the momentum,  $\Delta p_x$ , must be greater than or equal to  $\frac{h}{2}$  (where  $\hbar = \frac{h}{2\pi}$ , the value of Planck's constant divided by  $2\pi$ ).

$$\Delta x \times \Delta p_x = (\Delta x)(m\Delta v) \geq \frac{\hbar}{2}$$

This equation allows us to calculate the limit to how precisely we can know both the simultaneous position of an object and its momentum. For example, if we improve our measurement of an electron's position so that the uncertainty in the position ( $\Delta x$ ) has a value of, say, 1 pm ( $10^{-12}$  m, about 1% of the diameter of a hydrogen atom), then our determination of its momentum must have an uncertainty with a value of at least

$$\left[ \Delta p = m\Delta v = \frac{h}{(2\Delta x)} \right] = \frac{(1.055 \times 10^{-34} \text{ kgm}^2/\text{s})}{(2 \times 1 \times 10^{-12} \text{ m})} = 5 \times 10^{-23} \text{ kgm/s}$$

The value of  $\hbar$  is not large, so the uncertainty in the position or momentum of a macroscopic object like a baseball is too insignificant to observe. However, the mass of a microscopic object such as an electron is small enough that the uncertainty can be large and significant.

It should be noted that Heisenberg's uncertainty principle is not just limited to uncertainties in position and momentum, but it also links other dynamical variables. For example, when an atom absorbs a photon

and makes a transition from one energy state to another, the uncertainty in the energy and the uncertainty in the time required for the transition are similarly related, as  $\Delta E \Delta t \geq \frac{h}{2}$ .

Heisenberg's principle imposes ultimate limits on what is knowable in science. The uncertainty principle can be shown to be a consequence of wave–particle duality, which lies at the heart of what distinguishes modern quantum theory from classical mechanics.

### Link to Learning

[Read this article](#) that describes a recent macroscopic demonstration of the uncertainty principle applied to microscopic objects.

## The Quantum–Mechanical Model of an Atom

Shortly after de Broglie published his ideas that the electron in a hydrogen atom could be better thought of as being a circular standing wave instead of a particle moving in quantized circular orbits, Erwin Schrödinger extended de Broglie's work by deriving what is today known as the Schrödinger equation. When Schrödinger applied his equation to hydrogen-like atoms, he was able to reproduce Bohr's expression for the energy and, thus, the Rydberg formula governing hydrogen spectra. Schrödinger described electrons as three-dimensional stationary waves, or **wavefunctions**, represented by the Greek letter psi,  $\psi$ . A few years later, Max Born proposed an interpretation of the wavefunction  $\psi$  that is still accepted today: Electrons are still particles, and so the waves represented by  $\psi$  are not physical waves but, instead, are complex probability amplitudes. The square of the magnitude of a wavefunction  $|\psi|^2$  describes the probability of the quantum particle being present near a certain location in space. This means that wavefunctions can be used to determine the distribution of the electron's density with respect to the nucleus in an atom. In the most general form, the Schrödinger equation can be written as:

$$\widehat{H}\psi = E\psi$$

$\widehat{H}$  is the Hamiltonian operator, a set of mathematical operations representing the total energy of the quantum particle (such as an electron in an atom),  $\psi$  is the wavefunction of this particle that can be used to find the special distribution of the probability of finding the particle, and  $E$  is the actual value of the total energy of the particle.

Schrödinger's work, as well as that of Heisenberg and many other scientists following in their footsteps, is generally referred to as **quantum mechanics**.

### Link to Learning

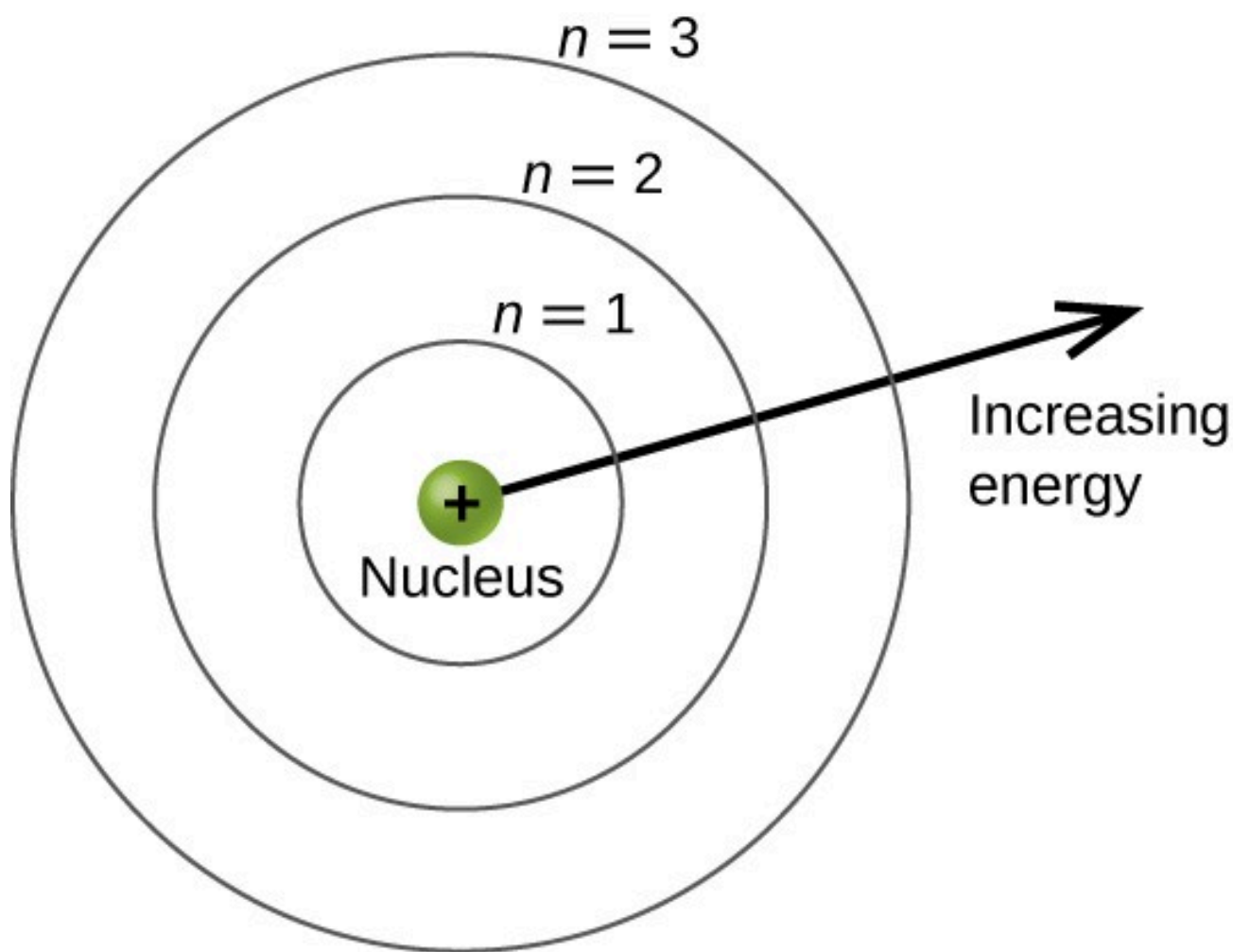
You may also have heard of Schrödinger because of his famous thought experiment. [This story](#) explains the concepts of superposition and entanglement as related to a cat in a box with poison.

## Understanding Quantum Theory of Electrons in Atoms

The goal of this section is to understand the electron orbitals (location of electrons in atoms), their different energies, and other properties. The use of quantum theory provides the best understanding of these topics. This knowledge is a precursor to chemical bonding.

As was described previously, electrons in atoms can exist only on discrete energy levels but not between them. It is said that the energy of an electron in an atom is quantized, that is, it can be equal only to certain specific values and can jump from one energy level to another but not transition smoothly or stay between these levels.

The energy levels are labeled with an  $n$  value, where  $n = 1, 2, 3, \dots$ . Generally speaking, the energy of an electron in an atom is greater for greater values of  $n$ . This number,  $n$ , is referred to as the principal quantum number. The **principal quantum number** defines the location of the energy level. It is essentially the same concept as the  $n$  in the Bohr atom description. Another name for the principal quantum number is the shell number. The **shells** of an atom can be thought of as concentric circles radiating out from the nucleus. The electrons that belong to a specific shell are most likely to be found within the corresponding circular area. The further we proceed from the nucleus, the higher the shell number and so the higher the energy level (**Figure 3.19**). The positively charged protons in the nucleus stabilize the electronic orbitals by electrostatic attraction between the positive charges of the protons and the negative charges of the electrons. So the further away the electron is from the nucleus, the greater the energy it has.



**Figure 3.19** Different shells are numbered by principal quantum numbers. By: Rice University [Openstax](#) CC BY NC SA

This quantum mechanical model for where electrons reside in an atom can be used to look at electronic transitions, the events when an electron moves from one energy level to another. If the transition is to a higher energy level, energy is absorbed, and the energy change has a positive value. To obtain the amount of energy necessary for the transition to a higher energy level, a photon is absorbed by the atom. A transition to a lower energy level involves a release of energy, and the energy change is negative. This process is accompanied by the emission of a photon by the atom. The following equation summarizes these relationships and is based on the hydrogen atom:

$$\begin{aligned}\Delta E &= E_{\text{final}} - E_{\text{initial}} \\ &= -2.18 \times 10^{-18} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \text{ J}\end{aligned}$$

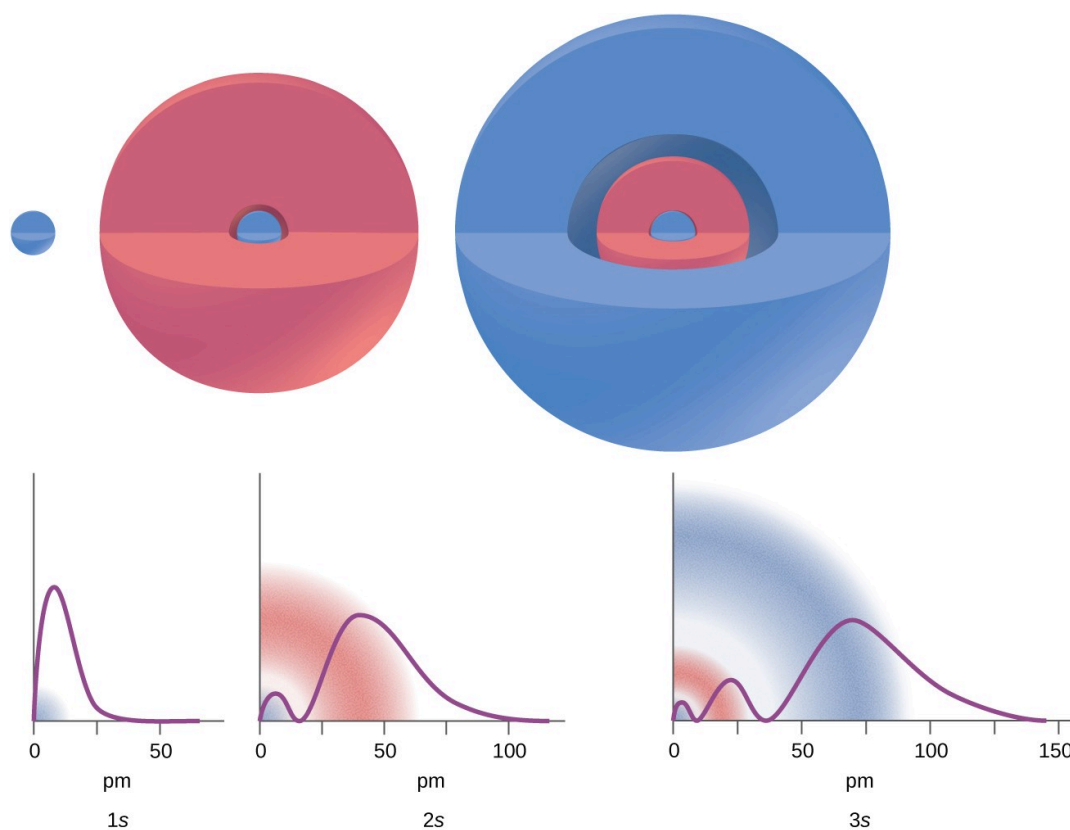
The values  $n_f$  and  $n_i$  are the final and initial energy states of the electron. **Example 3.5** in the previous section of the chapter demonstrates calculations of such energy changes.

The principal quantum number is one of three quantum numbers used to characterize an orbital. An **atomic orbital** is a general region in an atom within which an electron is most probable to reside. The quantum mechanical model specifies the probability of finding an electron in the three-dimensional space around the nucleus and is based on solutions of the Schrödinger equation. In addition, the principal quantum number defines the energy of an electron in a hydrogen or hydrogen-like atom or an ion (an atom or an ion with only one electron) and the general region in which discrete energy levels of electrons in multi-electron atoms and ions are located.

Another quantum number is  $l$ , the **secondary (angular momentum) quantum number**. It is an integer that may take the values  $l = 0, 1, 2, \dots, n - 1$ . This means that an orbital with  $n = 1$  can have only one value of  $l$ ,  $l = 0$ , whereas  $n = 2$  permits  $l = 0$  and  $l = 1$ , and so on. Whereas the principal quantum number,  $n$ , defines the general size and energy of the orbital, the secondary quantum number  $l$  specifies the shape of the orbital. Orbitals with the same value of  $l$  define a **subshell**.

Orbitals with  $l = 0$  are called **s orbitals**, and they make up the *s* subshells. The value  $l = 1$  corresponds to the *p* orbitals. For a given  $n$ , **p orbitals** constitute a *p* subshell (e.g.,  $3p$  if  $n = 3$ ). The orbitals with  $l = 2$  are called the **d orbitals**, followed by the *f*-, *g*-, and *h*-orbitals for  $l = 3, 4$ , and  $5$ .

There are certain distances from the nucleus at which the probability density of finding an electron located at a particular orbital is zero. In other words, the value of the wavefunction  $\psi$  is zero at this distance for this orbital. Such a value of radius  $r$  is called a radial node. The number of radial nodes in an orbital is  $n - l - 1$ .

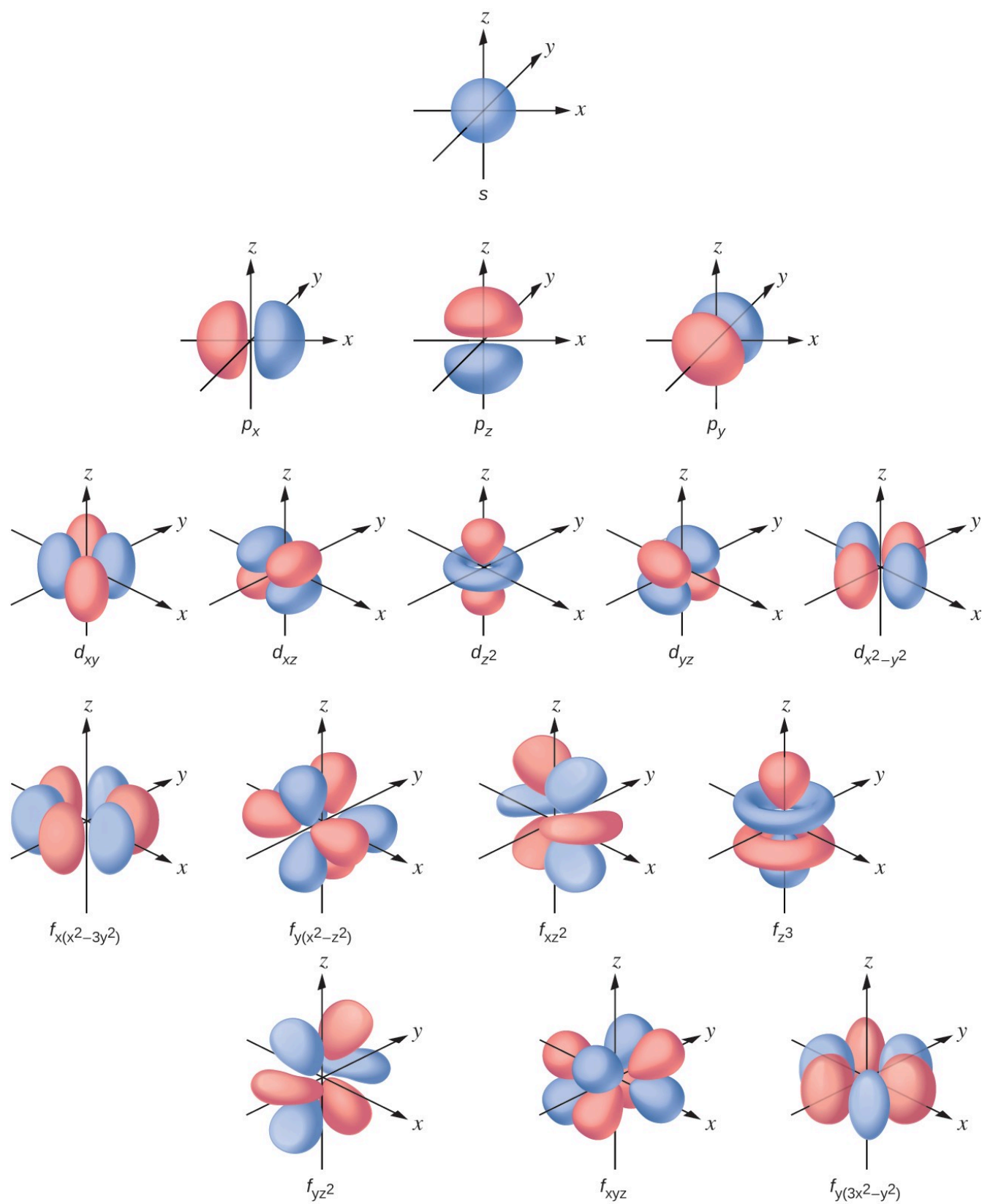


**Figure 3.20** The graphs show the probability (y axis) of finding an electron for the 1s, 2s, 3s orbitals as a function of distance from the nucleus. By: Rice University [Openstax CC BY NC SA](#)



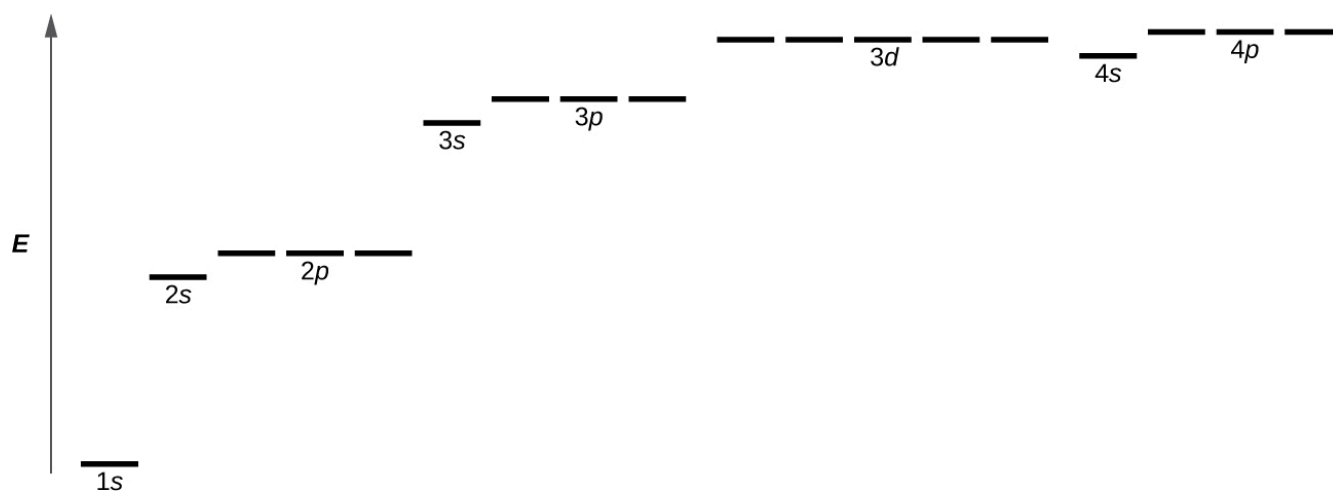
Consider the examples in **Figure 3.20**. The orbitals depicted are of the  $s$  type, thus  $l = 0$  for all of them. It can be seen from the graphs of the probability densities that there are  $1 - 0 - 1 = 0$  places where the density is zero (nodes) for  $1s$  ( $n = 1$ ),  $2 - 0 - 1 = 1$  node for  $2s$ , and  $3 - 0 - 1 = 2$  nodes for the  $3s$  orbitals.

The  $s$  subshell electron density distribution is spherical, and the  $p$  subshell has a dumbbell shape. The  $d$  and  $f$  orbitals are more complex. These shapes represent the three-dimensional regions within which the electron is likely to be found.



**Figure 3.21** Shapes of s, p, d, and f orbitals. By: Rice University [Openstax CC BY-NC-SA](https://openstax.org/r/chemistry-atoms-and-molecules)

The **magnetic quantum number**,  $m_l$ , specifies the relative spatial orientation of a particular orbital. Generally speaking,  $m_l$  can be equal to  $-l$ ,  $-(l-1)$ , ...,  $0$ , ...,  $(l-1)$ ,  $l$ . The total number of possible orbitals with the same value of  $l$  (that is, in the same subshell) is  $2l + 1$ . Thus, there is one  $s$ -orbital in an  $s$  subshell ( $l = 0$ ), there are three  $p$ -orbitals in a  $p$  subshell ( $l = 1$ ), five  $d$ -orbitals in a  $d$  subshell ( $l = 2$ ), seven  $f$ -orbitals in an  $f$  subshell ( $l = 3$ ), and so forth. The principal quantum number defines the general value of the electronic energy. The angular momentum quantum number determines the shape of the orbital. And the magnetic quantum number specifies the orientation of the orbital in space, as can be seen in **Figure 3.21**.



**Figure 3.22** The chart shows the energies of electron orbitals in a multi-electron atom. By: Rice University Openstax CC BY NC SA

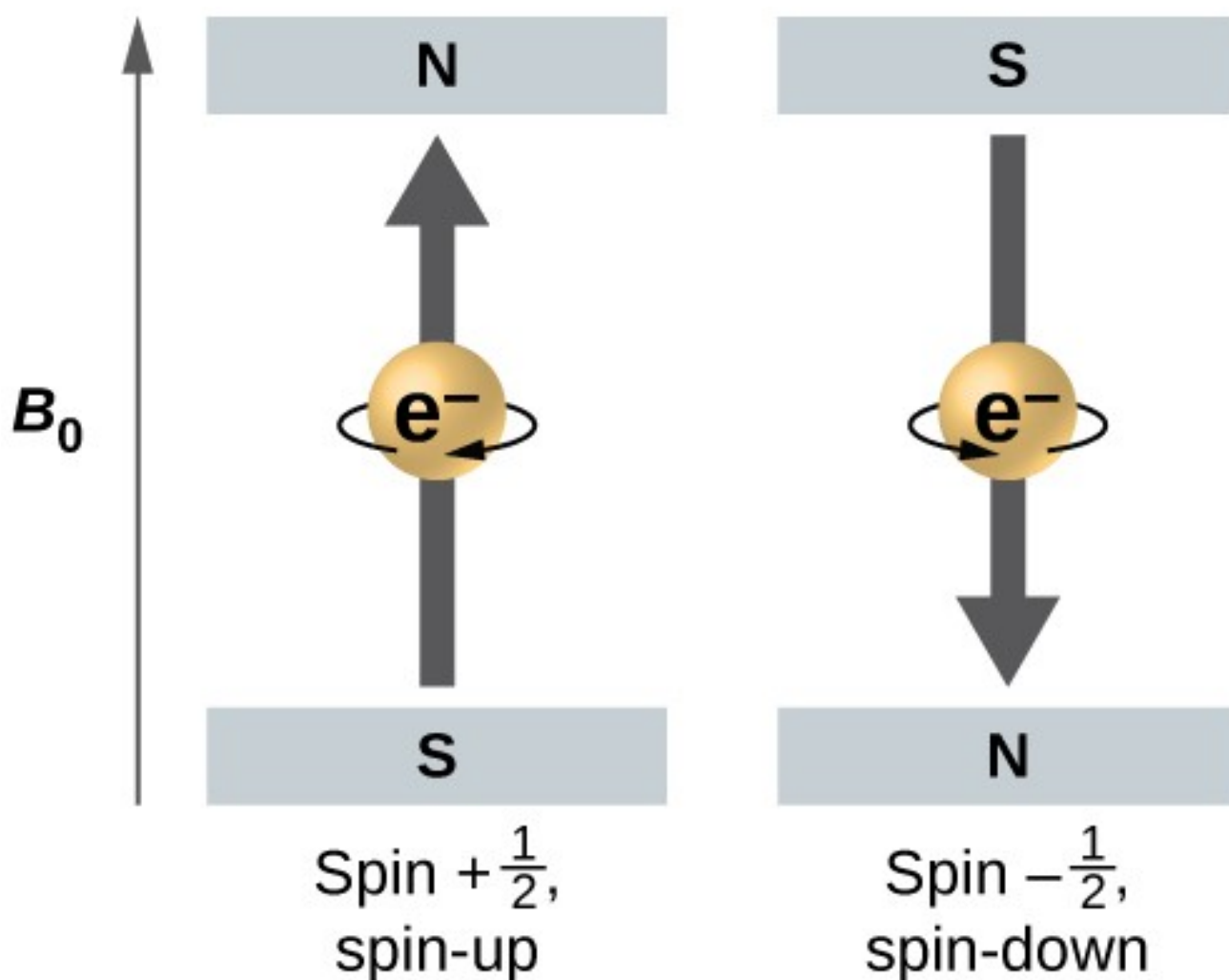
**Figure 3.22** illustrates the energy levels for various orbitals. The number before the orbital name (such as  $2s$ ,  $3p$ , and so forth) stands for the principal quantum number,  $n$ . The letter in the orbital name defines the subshell with a specific angular momentum quantum number  $l = 0$  for  $s$  orbitals,  $1$  for  $p$  orbitals,  $2$  for  $d$  orbitals. Finally, there is more than one possible orbitals for  $l \geq 1$ , each corresponding to a specific value of  $m_l$ . In the case of a hydrogen atom or a one-electron ion (such as  $\text{He}^+$ ,  $\text{Li}^{2+}$ , and so on), energies of all the orbitals with the same  $n$  are the same. This is called a degeneracy, and the energy levels for the same principal quantum number,  $n$ , are called **degenerate orbitals**. However, in atoms with more than one electron, this degeneracy is eliminated by the electron–electron interactions, and orbitals that belong to different subshells have different energies, as shown in **Figure 3.22**. Orbitals within the same subshell are still degenerate and have the same energy.

While the three quantum numbers discussed in the previous paragraphs work well for describing electron orbitals, some experiments showed that they were not sufficient to explain all observed results. It was demonstrated in the 1920s that when hydrogen-line spectra are examined at extremely high resolution, some lines are actually not single peaks but, rather, pairs of closely spaced lines. This is the so-called fine structure of the spectrum, and it implies that there are additional small differences in the energies of electrons even when they are located in the same orbital. These observations led Samuel Goudsmit and George Uhlenbeck

to propose that electrons have a fourth quantum number. They called this the **spin quantum number**, or  $m_s$ .

The other three quantum numbers,  $n$ ,  $l$ , and  $m_l$ , are properties of specific atomic orbitals that also define in what part of the space an electron is most likely to be located. Orbitals are a result of solving the Schrödinger equation for electrons in atoms. The electron spin is a different kind of property. It is a completely quantum phenomenon with no analogs in the classical realm. In addition, it cannot be derived from solving the Schrödinger equation and is not related to the normal spatial coordinates (such as the Cartesian  $x$ ,  $y$ , and  $z$ ). Electron spin describes an intrinsic electron “rotation” or “spinning.” Each electron acts as a tiny magnet or a tiny rotating object with an angular momentum, or as a loop with an electric current, even though this rotation or current cannot be observed in terms of spatial coordinates.

The magnitude of the overall electron spin can only have one value, and an electron can only “spin” in one of two quantized states. One is termed the  $\alpha$  state, with the  $z$  component of the spin being in the positive direction of the  $z$  axis. This corresponds to the spin quantum number  $m_s = \frac{1}{2}$ . The other is called the  $\beta$  state, with the  $z$  component of the spin being negative and  $m_s = -\frac{1}{2}$ . Any electron, regardless of the atomic orbital it is located in, can only have one of those two values of the spin quantum number. The energies of electrons having  $m_s = -\frac{1}{2}$  and  $m_s = \frac{1}{2}$  are different if an external magnetic field is applied.



**Figure 3.23** Electrons with spin values  $\pm \frac{1}{2}$  in an external magnetic field. By: Rice University [Openstax CC BY NC SA](#)

**Figure 3.23** illustrates this phenomenon. An electron acts like a tiny magnet. Its moment is directed up (in the positive direction of the  $z$  axis) for the  $\frac{1}{2}$  spin quantum number and down (in the negative  $z$  direction) for the spin quantum number of  $-\frac{1}{2}$ . A magnet has a lower energy if its magnetic moment is aligned with the external magnetic field (the left electron in **Figure 3.23**) and a higher energy for the magnetic moment being opposite to the applied field. This is why an electron with  $m_s = \frac{1}{2}$  has a slightly lower energy in an external field in the positive  $z$  direction, and an electron with  $m_s = -\frac{1}{2}$  has a slightly higher energy in the same field. This is true even for an electron occupying the same orbital in an atom. A spectral line corresponding to a transition for electrons from the same orbital but with different spin quantum numbers has two possible values of energy; thus, the line in the spectrum will show a fine structure splitting.

## The Pauli Exclusion Principle

An electron in an atom is completely described by four quantum numbers:  $n$ ,  $l$ ,  $m_l$ , and  $m_s$ . The first three quantum numbers define the orbital and the fourth quantum number describes the intrinsic electron property called spin. An Austrian physicist Wolfgang Pauli formulated a general principle that gives the last piece of information that we need to understand the general behavior of electrons in atoms. The **Pauli exclusion principle** can be formulated as follows: No two electrons in the same atom can have exactly the same set of all four quantum numbers. What this means is that two electrons can share the same orbital (the same set of the quantum numbers  $n$ ,  $l$ , and  $m_l$ ) only if their spin quantum numbers  $m_s$  have different values. Since the spin quantum number can only have two values  $\left(\pm \frac{1}{2}\right)$ , no more than two electrons can occupy the same orbital (and if two electrons are located in the same orbital, they must have opposite spins). Therefore, any atomic orbital can be populated by only zero, one, or two electrons.

The properties and meaning of the quantum numbers of electrons in atoms are briefly summarized in Table 3.1.

**Table 3.1 Quantum Numbers, Their Properties, and Significance** By: Rice University [OpenStax](#) [CC BY-NC-SA 4.0](#)

Name	Symbol	Allowed values	Physical meaning
principal quantum number	$n$	1, 2, 3, 4, ....	shell, the general region for the value of energy for an electron on the orbital
angular momentum or azimuthal quantum number	$l$	$0 \leq l \leq n - 1$	subshell, the shape of the orbital
magnetic quantum number	$m_l$	$-l \leq m_l \leq l$	orientation of the orbital
spin quantum number	$m_s$	$\frac{1}{2}, -\frac{1}{2}$	direction of the intrinsic quantum “spinning” of the electron

## EXAMPLE 3.7

**Working with Shells and Subshells**

Indicate the number of subshells, the number of orbitals in each subshell, and the values of  $l$  and  $m_l$  for the orbitals in the  $n = 4$  shell of an atom.

**Solution**

For  $n = 4$ ,  $l$  can have values of 0, 1, 2, and 3. Thus,  $s$ ,  $p$ ,  $d$ , and  $f$  subshells are found in the  $n = 4$  shell of an atom. For  $l = 0$  (the  $s$  subshell),  $m_l$  can only be 0. Thus, there is only one  $4s$  orbital. For  $l = 1$  ( $p$ -type orbitals),  $m$  can have values of  $-1$ ,  $0$ ,  $+1$ , so we find three  $4p$  orbitals. For  $l = 2$  ( $d$ -type orbitals),  $m_l$  can have values of  $-2$ ,  $-1$ ,  $0$ ,  $+1$ ,  $+2$ , so we have five  $4d$  orbitals. When  $l = 3$  ( $f$ -type orbitals),  $m_l$  can have values of  $-3$ ,  $-2$ ,  $-1$ ,  $0$ ,  $+1$ ,  $+2$ ,  $+3$ , and we can have seven  $4f$  orbitals. Thus, we find a total of 16 orbitals in the  $n = 4$  shell of an atom.

**Check Your Learning**

Identify the subshell in which electrons with the following quantum numbers are found: (a)  $n = 3$ ,  $l = 1$ ; (b)  $n = 5$ ,  $l = 3$ ; (c)  $n = 2$ ,  $l = 0$ .

**Answer:** (a)  $3p$ ; (b)  $5f$ ; (c)  $2s$

## EXAMPLE 3.8

**Maximum Number of Electrons**

Calculate the maximum number of electrons that can occupy a shell with (a)  $n = 2$ , (b)  $n = 5$ , and (c)  $n$  as a variable. Note you are only looking at the orbitals with the specified  $n$  value, not those at lower energies.

**Solution**

(a) When  $n = 2$ , there are four orbitals (a single  $2s$  orbital and three orbitals labeled  $2p$ ). These four orbitals can contain eight electrons.

(b) When  $n = 5$ , there are five subshells of orbitals that we need to sum

$$\begin{array}{r}
 1 \text{ orbital labeled } 5s \\
 3 \text{ orbitals labeled } 5p \\
 5 \text{ orbitals labeled } 5d \\
 7 \text{ orbitals labeled } 5f \\
 \underline{+ 9 \text{ orbitals labeled } 5g} \\
 25 \text{ orbitals total}
 \end{array}$$

Again, each orbital holds two electrons, so 50 electrons can fit in this shell.

(c) The number of orbitals in any shell  $n$  will equal  $n^2$ . There can be up to two electrons in each orbital, so the maximum number of electrons will be  $2 \times n^2$ .

**Check Your Learning**

If a shell contains a maximum of 32 electrons, what is the principal quantum number,  $n$ ?

**Answer:**  $n = 4$

**EXAMPLE 3.9****Working with Quantum Numbers**

Complete the following table for atomic orbitals:



Table 3.2 By: Rice University [OpenStax CC BY-NC-SA 4.0](#)

Orbital	$n$	$l$	$m_l$ degeneracy	Radial nodes (no.)
$4f$				
	4	1		
	7		7	3
$5d$				

### Solution

The table can be completed using the following rules:

- The orbital designation is  $nl$ , where  $l = 0, 1, 2, 3, 4, 5, \dots$  is mapped to the letter sequence  $s, p, d, f, g, h, \dots$
- The  $m_l$  degeneracy is the number of orbitals within an  $l$  subshell and so is  $2l + 1$  (there is one  $s$  orbital, three  $p$  orbitals, five  $d$  orbitals, seven  $f$  orbitals, and so forth).
- The number of radial nodes is equal to  $n - l - 1$ .

Table 3.3 By: Rice University [OpenStax CC BY-NC-SA 4.0](#)

Orbital	$n$	$l$	$m_l$ degeneracy	Radial nodes (no.)
$4f$	4	3	7	0
$4p$	4	1	3	2
$7f$	7	3	7	3
$5d$	5	2	5	2

### Check Your Learning

How many orbitals have  $l = 2$  and  $n = 3$ ?

**Answer:** The five degenerate  $3d$  orbitals

# ELECTRONIC STRUCTURE OF ATOMS (ELECTRON CONFIGURATIONS) (3.4)

OpenStax

---

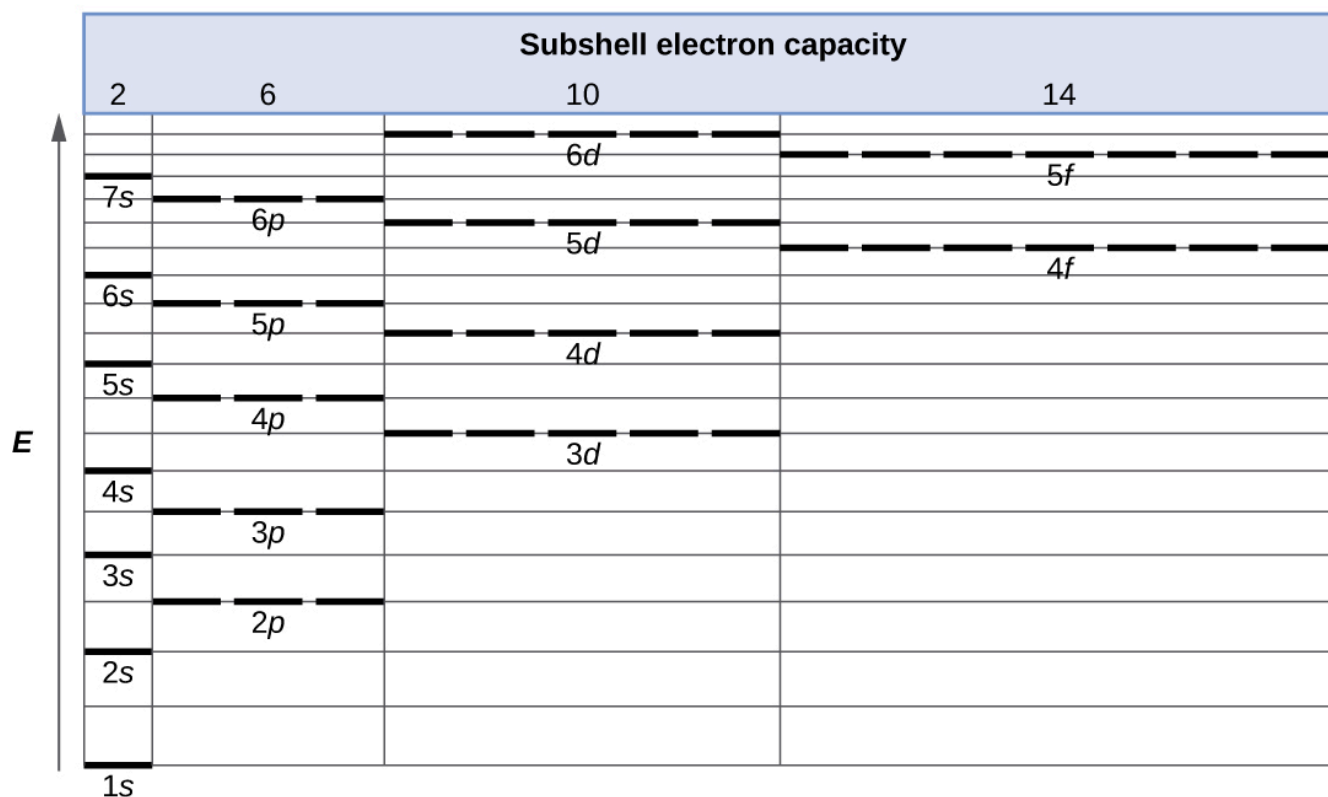
By the end of this section, you will be able to:

- 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 the 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 3.24** depicts how these two trends in increasing energy relate. The  $1s$  orbital at the bottom of the diagram is the orbital with electrons of the lowest energy. The energy increases as we move up to the  $2s$  and then  $2p$ ,  $3s$ , and  $3p$  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  $3d$  orbital is higher in energy than the  $4s$  orbital. Such overlaps continue to occur frequently as we move up the chart.



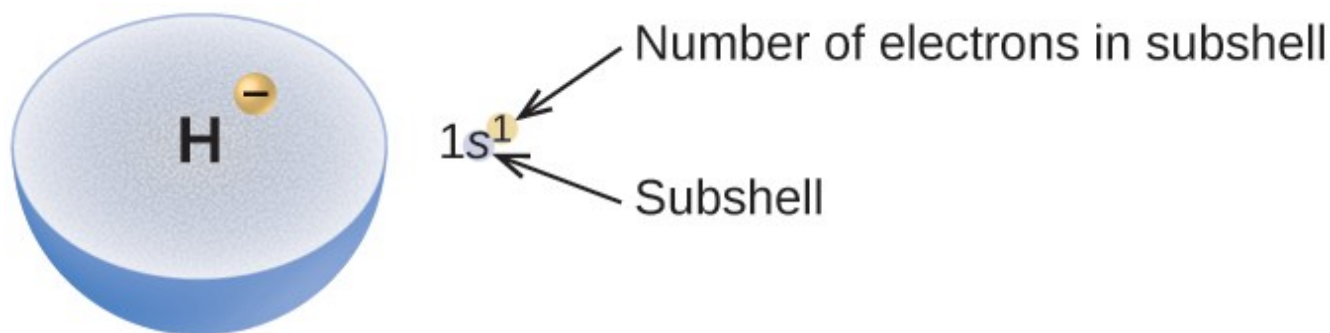
**Figure 3.24** Generalized energy-level diagram for atomic orbitals in an atom with two or more electrons (not to scale). By: Rice University [Openstax CC BY NC SA](#)

Electrons in successive atoms on the periodic table tend to fill low-energy orbitals first. Thus, many students find it confusing that, for example, the  $5p$  orbitals fill immediately after the  $4d$  and immediately before the  $6s$ . The filling order is based on observed experimental results and has been confirmed by theoretical calculations. As the principal quantum number,  $n$ , increases, the size of the orbital increases, and the electrons spend more time farther from the nucleus. Thus, the attraction to the nucleus is weaker and the energy associated with the orbital is higher (less stabilized). But this is not the only effect we have to take into account. Within each shell, as the value of  $l$  increases, the electrons are less penetrating (meaning there is less electron density found close to the nucleus), in the order  $s > p > d > f$ . Electrons that are closer to the nucleus slightly repel electrons that are farther out, offsetting the more dominant electron–nucleus attractions slightly (recall that all electrons have  $-1$  charges, but nuclei have  $+Z$  charges). This phenomenon is called shielding and will be discussed in more detail in the next section. Electrons in orbitals that experience more shielding are less stabilized and thus higher in energy. For small orbitals ( $1s$  through  $3p$ ), the increase in energy due to  $n$  is more significant than the increase due to  $l$ ; however, for larger orbitals, the two trends are comparable and cannot be simply predicted. We will discuss methods for remembering the observed order.

The arrangement of electrons in the orbitals of an atom is called the **electron configuration** of the atom. We describe an electron configuration with a symbol that contains three pieces of information (**Figure 3.25**):

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.

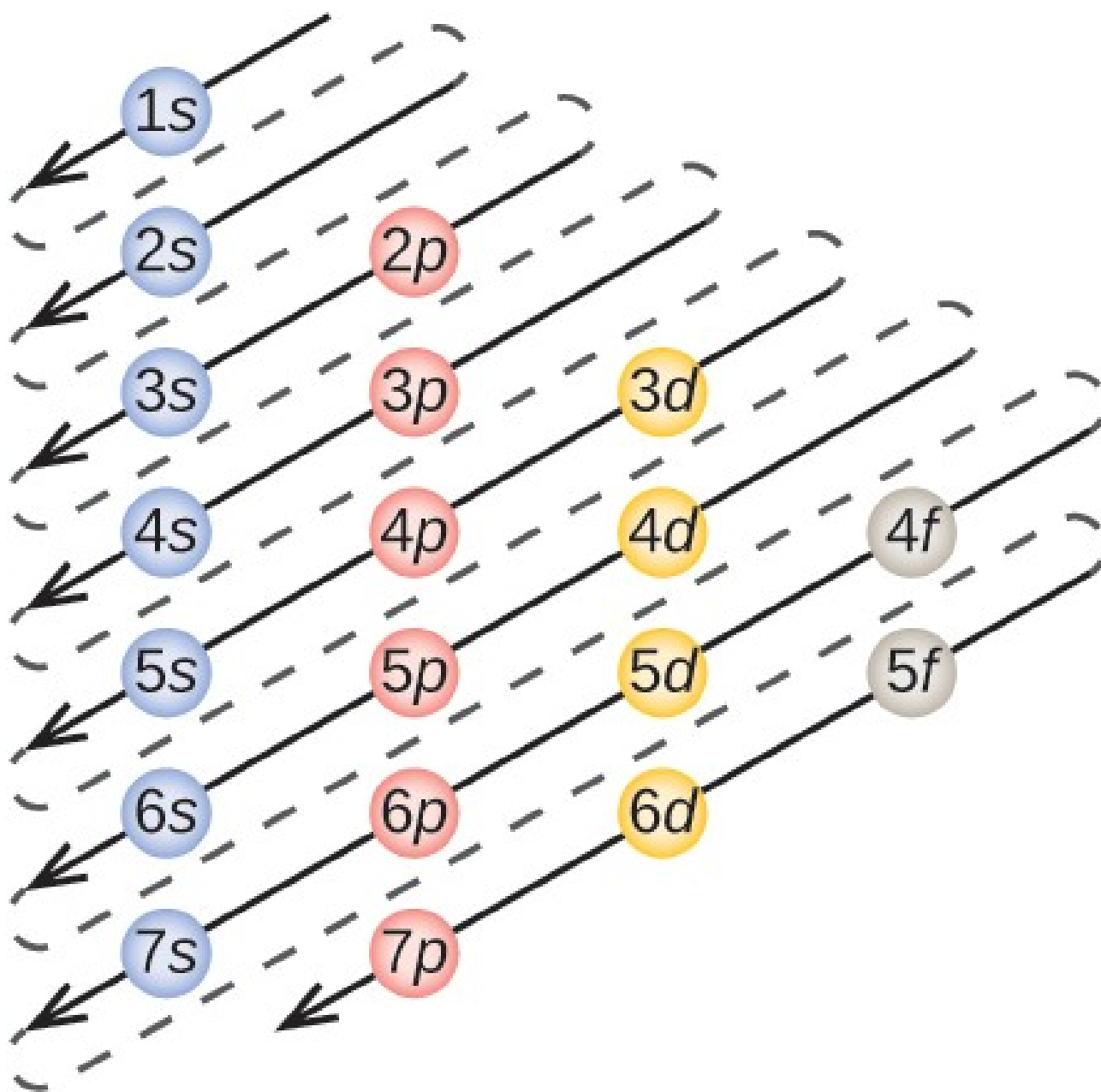
For example, the notation  $2p^4$  (read “two–p–four”) indicates four electrons in a  $p$  subshell ( $l = 1$ ) with a principal quantum number ( $n$ ) of 2. The notation  $3d^8$  (read “three–d–eight”) indicates eight electrons in the  $d$  subshell (i.e.,  $l = 2$ ) of the principal shell for which  $n = 3$ .



**Figure 3.25** The diagram of an electron configuration specifies the subshell ( $n$  and  $l$  value, with letter symbol) and superscript number of electrons. By: Rice University [Openstax CC BY NC SA](#)

## 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 the lowest energy available (in the order shown in **Figure 3.24**), 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 3.26** illustrates the traditional way to remember the filling order for atomic orbitals. Since the arrangement of the periodic table is based on the electron configurations, **Figure 3.27** 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  $3p$  block up to Ar, we see the orbital will be  $4s$  (K, Ca), followed by the  $3d$  orbitals.



**Figure 3.26** This diagram depicts the energy order for atomic orbitals and is useful for deriving ground-state electron configurations. By: Rice University [Openstax CC BY NC SA](#)

**Electron Configuration Table**

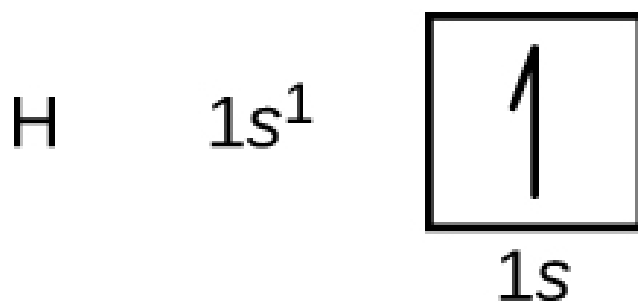
Period	Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1		H 1 1s																	He 1 1s
2		Li 1 2s	Be 2 2s											B 1 2p	C 2 2p	N 3 2p	O 4 2p	F 5 2p	Ne 6 2p
3		Na 1 3s	Mg 2 3s											Al 1 3p	Si 2 3p	P 3 3p	S 4 3p	Cl 5 3p	Ar 6 3p
4		K 1 4s	Ca 2 4s	Sc 1 3d	Ti 2 3d	V 3 3d	Cr 4 3d	Mn 5 3d	Fe 6 3d	Co 7 3d	Ni 8 3d	Cu 9 3d	Zn 10 3d	Ga 1 4p	Ge 2 4p	As 3 4p	Se 4 4p	Br 5 4p	Kr 6 4p
5		Rb 1 5s	Sr 2 5s	Y 1 4d	Zr 2 4d	Nb 3 4d	Mo 4 4d	Tc 5 4d	Ru 6 4d	Rh 7 4d	Pd 8 4d	Ag 9 4d	Cd 10 4d	In 1 5p	Sn 2 5p	Sb 3 5p	Te 4 5p	I 5 5p	Xe 6 5p
6		Cs 1 6s	Ba 2 6s	La *1 5d	Hf 2 5d	Ta 3 5d	W 4 5d	Re 5 5d	Os 6 5d	Ir 7 5d	Pt 8 5d	Au 9 5d	Hg 10 5d	Tl 1 6p	Pb 2 6p	Bi 3 6p	Po 4 6p	At 5 6p	Rn 6 6p
7		Fr 1 7s	Ra 2 7s	Ac **1 6d	Rf 2 6d	Db 3 6d	Sg 4 6d	Bh 5 6d	Hs 6 6d	Mt 7 6d	Ds 8 6d	Rg 9 6d	Cn 10 6d	Nh	Fl	Mc	Lv	Ts	Og
				* Ce 1 4f	Pr 2 4f	Nd 3 4f	Pm 4 4f	Sm 5 4f	Eu 6 4f	Gd 7 4f	Tb 8 4f	Dy 9 4f	Ho 10 4f	Er 11 4f	Tm 12 4f	Yb 13 4f	Lu 14 4f		
				** Th 1 5f	Pa 2 5f	U 3 5f	Np 4 5f	Pu 5 5f	Am 6 5f	Cm 7 5f	Bk 8 5f	Cf 9 5f	Es 10 5f	Fm 11 5f	Md 12 5f	No 13 5f	Lr 14 5f		

Name → **H** ← Electrons

**1s** ← Subshell

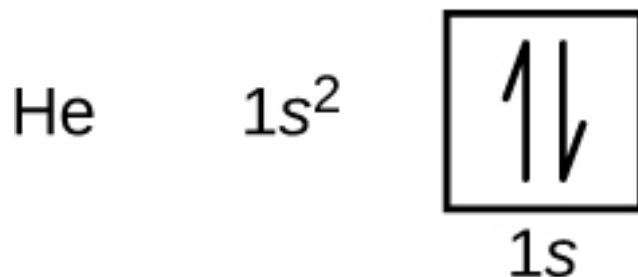
**Figure 3.27** This periodic table shows the electron configuration for each subshell. By “building up” from hydrogen, this table can be used to determine the electron configuration for any atom on the periodic table. By: Rice University [Openstax CC BY NC SA](#)

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 **Figure 3.26** or **Figure 3.27**, we would expect to find the electron in the 1s orbital. By convention, the  $m_s = +\frac{1}{2}$  value is usually filled first. The electron configuration and the orbital diagram are:



**Figure 3.28** By: Rice University [Openstax](#) [CC BY NC SA](#)

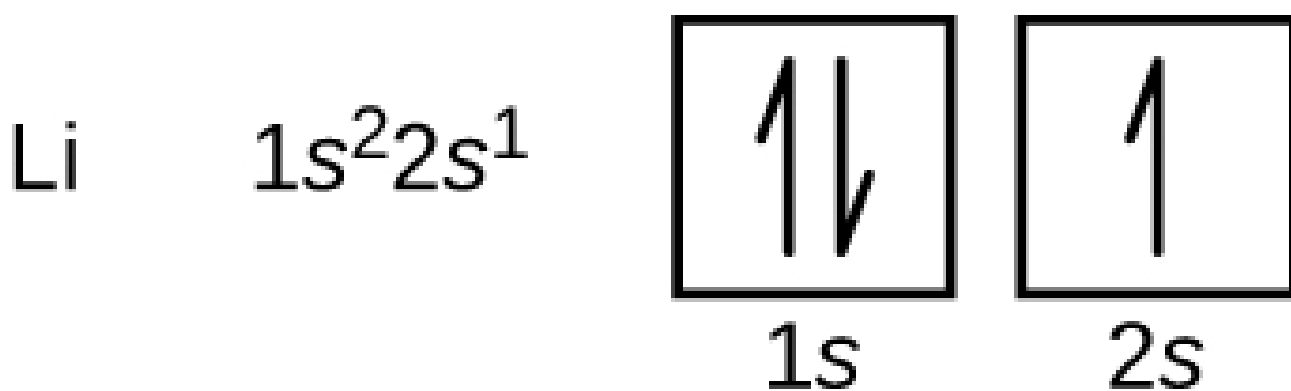
Following hydrogen is the noble gas helium, which has an atomic number of 2. The helium atom contains two protons and two electrons. The first electron has the same four quantum numbers as the hydrogen atom electron ( $n = 1$ ,  $l = 0$ ,  $m_l = 0$ ,  $m_s = +1$ ). The second electron also goes into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



**Figure 3.29** By: Rice University [Openstax](#) [CC BY NC SA](#)

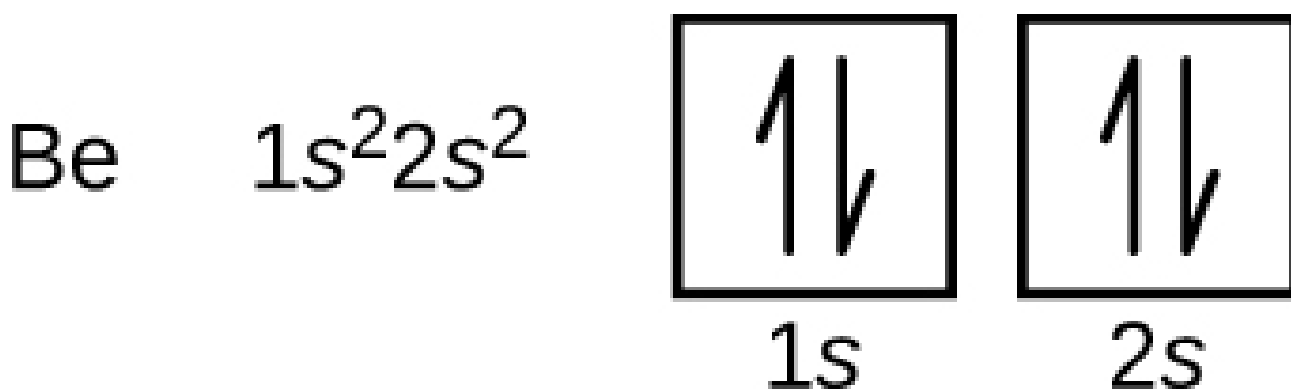
The  $n = 1$  shell is completely filled in a helium atom.

The next atom is the alkali metal lithium with an atomic number of 3. The first two electrons in lithium fill the  $1s$  orbital and have the same sets of four quantum numbers as the two electrons in helium. The remaining electron must occupy the orbital of the next lowest energy, the  $2s$  orbital (**Figure 3.26** or **Figure 3.27**). Thus, the electron configuration and orbital diagram of lithium are:



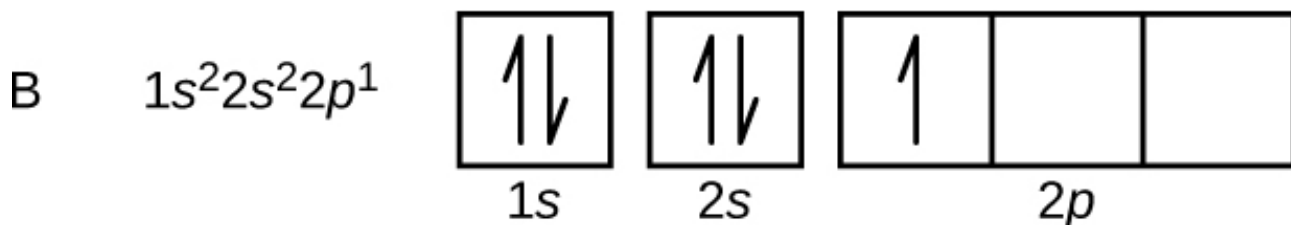
**Figure 3.30** By: Rice University [Openstax CC BY NC SA](#)

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  $2s$  orbital.



**Figure 3.31** By: Rice University [Openstax CC BY NC SA](#)

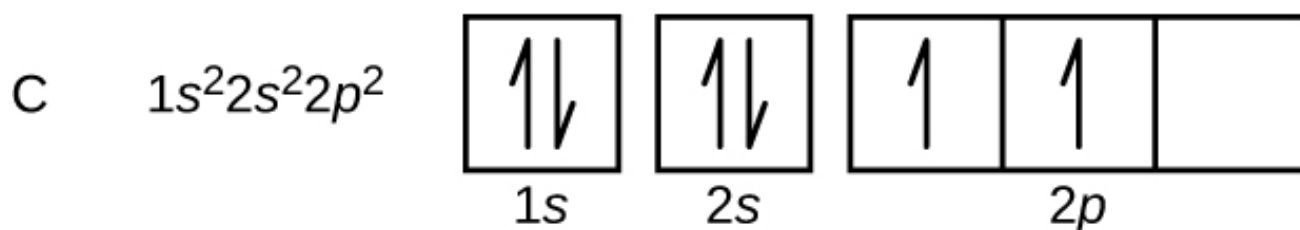
An atom of boron (atomic number 5) contains five electrons. The  $n = 1$  shell is filled with two electrons, and three electrons will occupy the  $n = 2$  shell. Because any  $s$  subshell can contain only two electrons, the fifth electron must occupy the next energy level, which will be a  $2p$  orbital.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



**Figure 3.32** By: Rice University [Openstax CC BY NC SA](#)

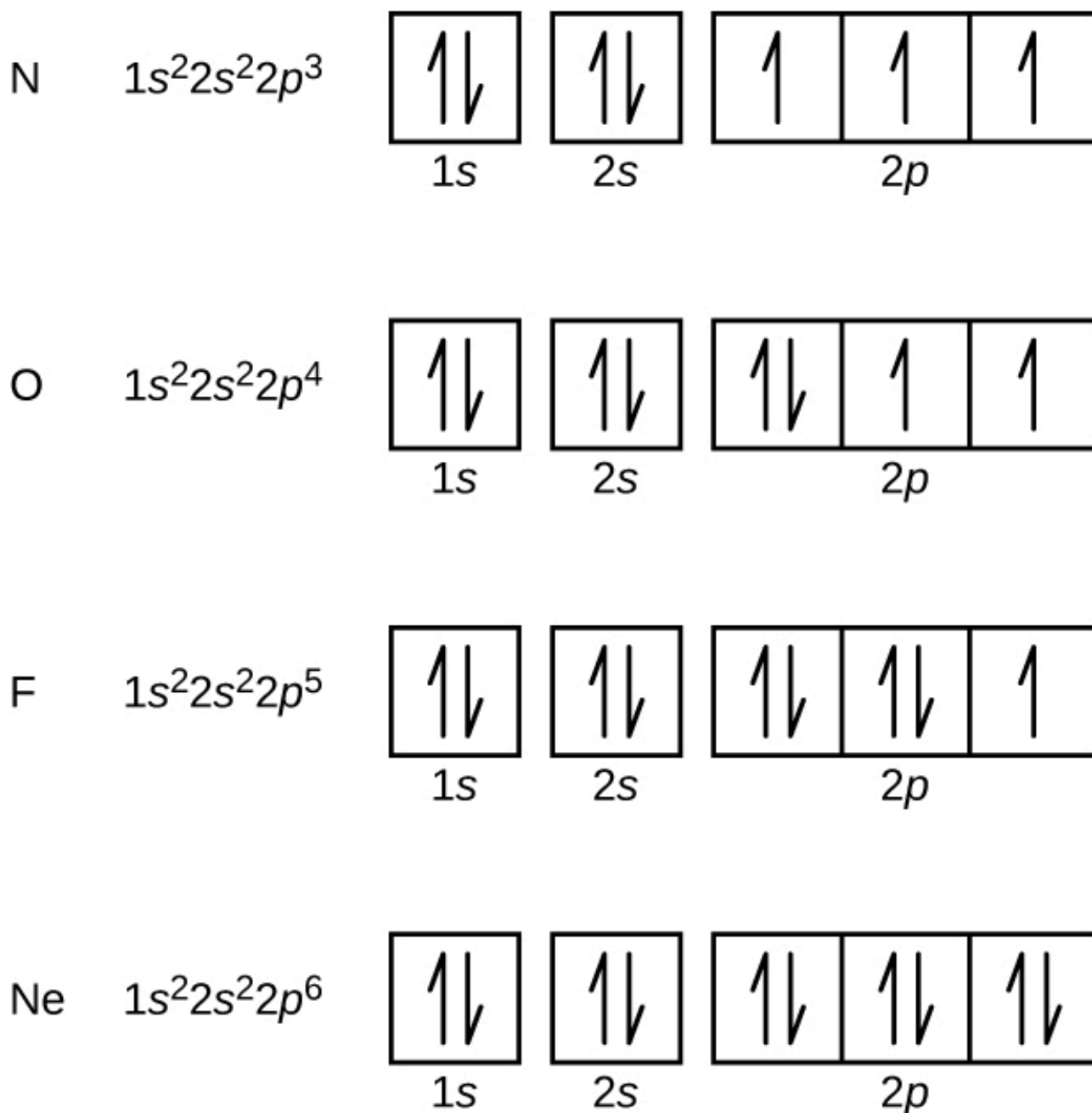


Carbon (atomic number 6) has six electrons. Four of them fill the  $1s$  and  $2s$  orbitals. The remaining two electrons occupy the  $2p$  subshell. We now have a choice of filling one of the  $2p$  orbitals and pairing the electrons or leaving the electrons unpaired in two different, but degenerate,  $p$  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 which has the maximum number of unpaired electrons. Thus, the two electrons in the carbon  $2p$  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:



**Figure 3.33** By: Rice University [Openstax CC BY NC SA](https://openstax.org/r/rice-university)

Nitrogen (atomic number 7) fills the  $1s$  and  $2s$  subshells and has one electron in each of the three  $2p$  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  $2p$  orbitals (the electrons have opposite spins) and a single electron in each of the other two. Fluorine (atomic number 9) has only one  $2p$  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 3.34** By: Rice University [Openstax CC BY-NC-SA](https://openstax.org/r/chemistry-atoms)

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  $3s$  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 3.35**). 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  $[\text{Ne}]3s^1$ .



**Figure 3.35** 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. By: Rice University [Openstax CC BY NC SA](#)

Similarly, the abbreviated configuration of lithium can be represented as  $[\text{He}]2s^1$ , 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.



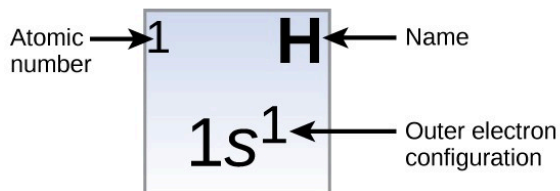
The alkaline earth metal magnesium (atomic number 12), with its 12 electrons in a  $[\text{Ne}]3s^2$  configuration, is analogous to its family member beryllium,  $[\text{He}]2s^2$ . Both atoms have a filled  $s$  subshell outside their filled inner shells. Aluminum (atomic number 13), with 13 electrons and the electron configuration  $[\text{Ne}]3s^2 3p^1$ , is analogous to its family member boron,  $[\text{He}]2s^2 2p^1$ .

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

**Electron Configuration Table**

Period	Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1		1 H 1s <sup>1</sup>																	2 He 1s <sup>2</sup>
2		3 Li 2s <sup>1</sup>	4 Be 2s <sup>2</sup>											5 B 2s <sup>2</sup> 2p <sup>1</sup>	6 C 2s <sup>2</sup> 2p <sup>2</sup>	7 N 2s <sup>2</sup> 2p <sup>3</sup>	8 O 2s <sup>2</sup> 2p <sup>4</sup>	9 F 2s <sup>2</sup> 2p <sup>5</sup>	10 Ne 2s <sup>2</sup> 2p <sup>6</sup>
3		11 Na 3s <sup>1</sup>	12 Mg 3s <sup>2</sup>											13 Al 3s <sup>2</sup> 3p <sup>1</sup>	14 Si 3s <sup>2</sup> 3p <sup>2</sup>	15 P 3s <sup>2</sup> 3p <sup>3</sup>	16 S 3s <sup>2</sup> 3p <sup>4</sup>	17 Cl 3s <sup>2</sup> 3p <sup>5</sup>	18 Ar 3s <sup>2</sup> 3p <sup>6</sup>
4		19 K 4s <sup>1</sup>	20 Ca 4s <sup>2</sup>	21 Sc 4s <sup>2</sup> 3d <sup>1</sup>	22 Ti 4s <sup>2</sup> 3d <sup>2</sup>	23 V 4s <sup>2</sup> 3d <sup>3</sup>	24 Cr 4s <sup>1</sup> 3d <sup>5</sup>	25 Mn 4s <sup>2</sup> 3d <sup>5</sup>	26 Fe 4s <sup>2</sup> 3d <sup>6</sup>	27 Co 4s <sup>2</sup> 3d <sup>7</sup>	28 Ni 4s <sup>2</sup> 3d <sup>8</sup>	29 Cu 4s <sup>1</sup> 3d <sup>10</sup>	30 Zn 4s <sup>2</sup> 3d <sup>10</sup>	31 Ga 4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>1</sup>	32 Ge 4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>2</sup>	33 As 4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>3</sup>	34 Se 4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>4</sup>	35 Br 4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>5</sup>	36 Kr 4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>6</sup>
5		37 Rb 5s <sup>1</sup>	38 Sr 5s <sup>2</sup>	39 Y 5s <sup>2</sup> 4d <sup>1</sup>	40 Zr 5s <sup>2</sup> 4d <sup>2</sup>	41 Nb 5s <sup>1</sup> 4d <sup>4</sup>	42 Mo 5s <sup>1</sup> 4d <sup>5</sup>	43 Tc 5s <sup>1</sup> 4d <sup>6</sup>	44 Ru 5s <sup>1</sup> 4d <sup>7</sup>	45 Rh 5s <sup>1</sup> 4d <sup>8</sup>	46 Pd 4d <sup>10</sup>	47 Ag 5s <sup>1</sup> 4d <sup>10</sup>	48 Cd 5s <sup>2</sup> 4d <sup>10</sup>	49 In 5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>1</sup>	50 Sn 5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>2</sup>	51 Sb 5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>3</sup>	52 Te 5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>4</sup>	53 I 5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>5</sup>	54 Xe 5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>6</sup>
6		55 Cs 6s <sup>1</sup>	56 Ba 6s <sup>2</sup>	57 La 6s <sup>2</sup> 5d <sup>1</sup>	72 Hf 6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>2</sup>	73 Ta 6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>3</sup>	74 W 6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>4</sup>	75 Re 6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>5</sup>	76 Os 6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>6</sup>	77 Ir 6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>7</sup>	78 Pt 6s <sup>1</sup> 4f <sup>14</sup> 5d <sup>9</sup>	79 Au 6s <sup>1</sup> 4f <sup>14</sup> 5d <sup>10</sup>	80 Hg 6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup>	81 Tl 6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup> 6p <sup>1</sup>	82 Pb 6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup> 6p <sup>2</sup>	83 Bi 6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup> 6p <sup>3</sup>	84 Po 6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup> 6p <sup>4</sup>	85 At 6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup> 6p <sup>5</sup>	86 Rn 6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup> 6p <sup>6</sup>
7		87 Fr 7s <sup>1</sup>	88 Ra 7s <sup>2</sup>	89 Ac 7s <sup>2</sup> 6d <sup>1</sup>	104 Rf 7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>2</sup>	105 Db 7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>3</sup>	106 Sg 7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>4</sup>	107 Bh 7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>5</sup>	108 Hs 7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>6</sup>	109 Mt 7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>7</sup>	110 Ds 7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>8</sup>	111 Rg 7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>9</sup>	112 Cn 7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>10</sup>	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
				* 58 Ce 6s <sup>2</sup> 4f <sup>2</sup>	59 Pr 6s <sup>2</sup> 4f <sup>3</sup>	60 Nd 6s <sup>2</sup> 4f <sup>4</sup>	61 Pm 6s <sup>2</sup> 4f <sup>5</sup>	62 Sm 6s <sup>2</sup> 4f <sup>6</sup>	63 Eu 6s <sup>2</sup> 4f <sup>7</sup>	64 Gd 6s <sup>2</sup> 4f <sup>7</sup> 5d <sup>1</sup>	65 Tb 6s <sup>2</sup> 4f <sup>9</sup>	66 Dy 6s <sup>2</sup> 4f <sup>10</sup>	67 Ho 6s <sup>2</sup> 4f <sup>11</sup>	68 Er 6s <sup>2</sup> 4f <sup>12</sup>	69 Tm 6s <sup>2</sup> 4f <sup>13</sup>	70 Yb 6s <sup>2</sup> 4f <sup>14</sup>	71 Lu 6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>1</sup>		
				** 90 Th 7s <sup>2</sup> 6d <sup>2</sup>	91 Pa 7s <sup>2</sup> 5f <sup>2</sup> 6d <sup>1</sup>	92 U 7s <sup>2</sup> 5f <sup>3</sup> 6d <sup>1</sup>	93 Np 7s <sup>2</sup> 5f <sup>4</sup> 6d <sup>1</sup>	94 Pu 7s <sup>2</sup> 5f <sup>6</sup>	95 Am 7s <sup>2</sup> 5f <sup>7</sup>	96 Cm 7s <sup>2</sup> 5f <sup>7</sup> 6d <sup>1</sup>	97 Bk 7s <sup>2</sup> 5f <sup>9</sup> 6d <sup>1</sup>	98 Cf 7s <sup>2</sup> 5f <sup>10</sup>	99 Es 7s <sup>2</sup> 5f <sup>11</sup>	100 Fm 7s <sup>2</sup> 5f <sup>12</sup>	101 Md 7s <sup>2</sup> 5f <sup>13</sup>	102 No 7s <sup>2</sup> 5f <sup>14</sup>	103 Lr 7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>1</sup>		



**Figure 3.36** 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. By: Rice University [Openstax CC BY NC SA](#)

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  $3d$  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  $3d$  level but is, instead, added to the  $4s$  level (**Figure 3.36**). As discussed previously, the  $3d$  orbital with no radial nodes is higher in energy because it is less penetrating and more shielded from the nucleus than the  $4s$ , which has three radial nodes. Thus, potassium has an electron configuration of  $[\text{Ar}]4s^1$ . Hence, potassium corresponds to Li and Na in its valence shell configuration. The next electron is added to complete the  $4s$  subshell, and calcium has an electron configuration of  $[\text{Ar}]4s^2$ . 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  $3d$  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  $4p$  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.

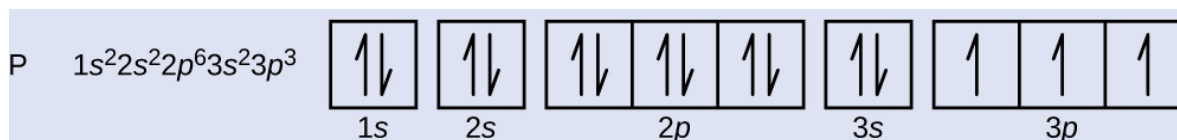
### Example 3.10

#### Quantum Numbers and Electron Configurations

What are 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  $1s$ ,  $2s$ ,  $2p$ ,  $3s$ ,  $3p$ ,  $4s$ ,  $\dots$ . The 15 electrons of the phosphorus atom will fill up to the  $3p$  orbital, which will contain three electrons:

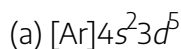


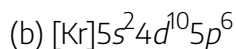
**Figure 3.37** By: Rice University [Openstax CC BY NC SA](#)

The last electron added is a  $3p$  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 are correct. For unpaired electrons, convention assigns the value of  $+\frac{1}{2}$  for the spin quantum number; thus,  $m_s = +\frac{1}{2}$ .

#### Check Your Learning

Identify the atoms from the electron configurations given:





**Answer:** (a) Mn (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 3.26** or **Figure 3.27**. For instance, the electron configurations (shown in **Figure 3.36**) of the transition metals chromium (Cr; atomic number 24) and copper (Cu; atomic number 29), among others, are not those we would expect. In general, such exceptions involve subshells with very similar energy, and small effects can lead to changes in the order of filling.

In the case of Cr and Cu, we find that half-filled and completely filled subshells apparently represent conditions of preferred stability. This stability is such that an electron shifts from the  $4s$  into the  $3d$  orbital to gain the extra stability of a half-filled  $3d$  subshell (in Cr) or a filled  $3d$  subshell (in Cu). Other exceptions also occur. For example, niobium (Nb, atomic number 41) is predicted to have the electron configuration  $[\text{Kr}]5s^24d^3$ . Experimentally, we observe that its ground-state electron configuration is actually  $[\text{Kr}]5s^14d^4$ . We can rationalize this observation by saying that the electron–electron repulsions experienced by pairing the electrons in the  $5s$  orbital are larger than the gap in energy between the  $5s$  and  $4d$  orbitals. There is no simple method to predict the exceptions for atoms where the magnitude of the repulsions between electrons is greater than the small differences in energy between subshells.

## 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 3.36**), 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 3.36**, 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 3.36** 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 3.36**. This category includes all the nonmetallic elements, as well as many metals and the metalloids. 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  $[\text{Ar}]\underline{4s^2}3d^{10}\underline{4p^1}$ , 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 3.36**) are not technically transition elements. However, the term is frequently used to refer to the entire  $d$  block (colored yellow in **Figure 3.36**), 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 3.36**. 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:
  - a. The lanthanide series: lanthanide (La) through lutetium (Lu)
  - b. 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

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 3.11

#### Predicting Electron Configurations of Ions

What is the electron configuration of:

- Na<sup>+</sup>
- P<sup>3-</sup>
- Al<sup>2+</sup>
- Fe<sup>2+</sup>
- Sm<sup>3+</sup>

#### 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.

- Na:  $1s^2 2s^2 2p^6 3s^1$ . Sodium cation loses one electron, so Na<sup>+</sup>:  $1s^2 2s^2 2p^6 3s^1 = \text{Na}^+ : 1s^2 2s^2 2p^6$ .
- P:  $1s^2 2s^2 2p^6 3s^2 3p^3$ . Phosphorus trianion gains three electrons, so P<sup>3-</sup>:  $1s^2 2s^2 2p^6 3s^2 3p^6$ .
- Al:  $1s^2 2s^2 2p^6 3s^2 3p^1$ . Aluminum dication loses two electrons Al<sup>2+</sup>:  $1s^2 2s^2 2p^6 3s^2 3p^1 = \text{Al}^{2+} : 1s^2 2s^2 2p^6 3s^1$ .
- Fe:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$ . Iron(II) loses two electrons, and since it is a transition metal, they are removed from the 4s orbital Fe<sup>2+</sup>:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6 = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ .
- Sm:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6$ . Samarium trication loses three electrons. The first two will be lost from the 6s orbital, and the final one will be removed from the 4f orbital. Sm<sup>3+</sup>:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6 = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 4f^5$ .



### Check Your Learning

Which ion with a +2 charge has the electron configuration  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^5$ ?

Which ion with a +3 charge has this configuration?

**Answer:**  $Tc^{2+}$ ,  $Ru^{3+}$

# PERIODIC VARIATIONS IN ELEMENT PROPERTIES (3.5)

OpenStax

---

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

- 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-gray 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.

Link to Learning

[Explore visualizations](#) of the periodic trends discussed in this section (and many more trends).

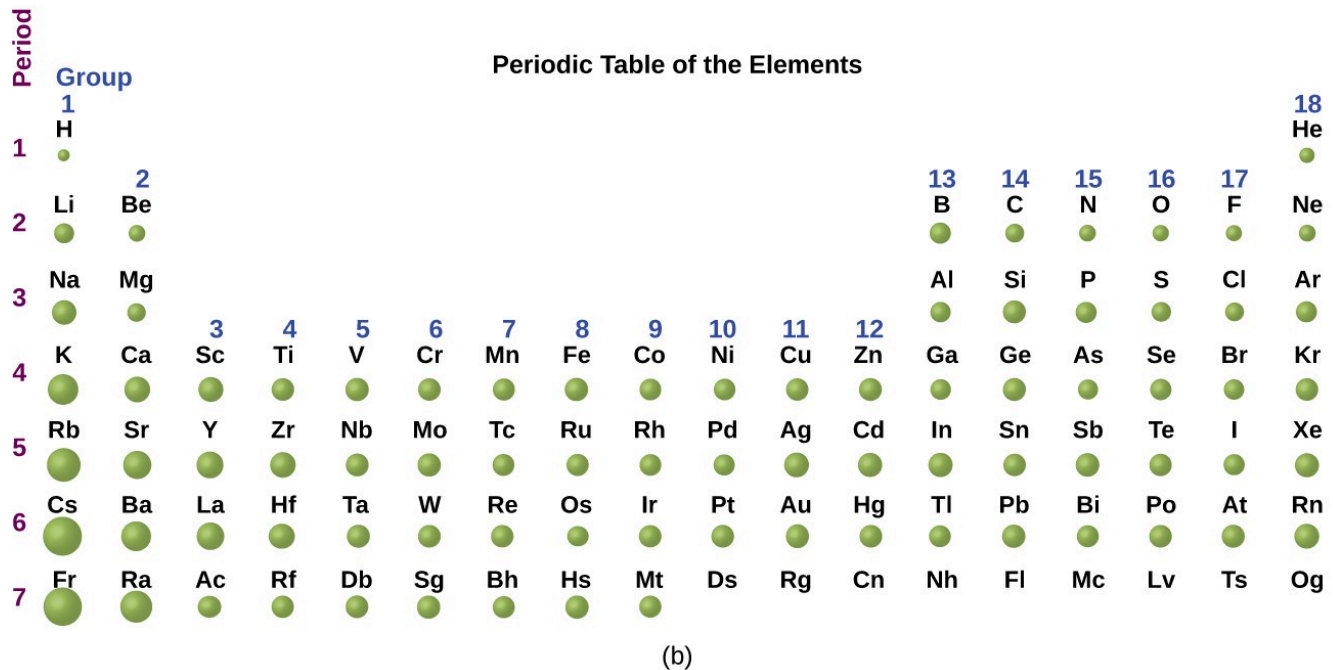
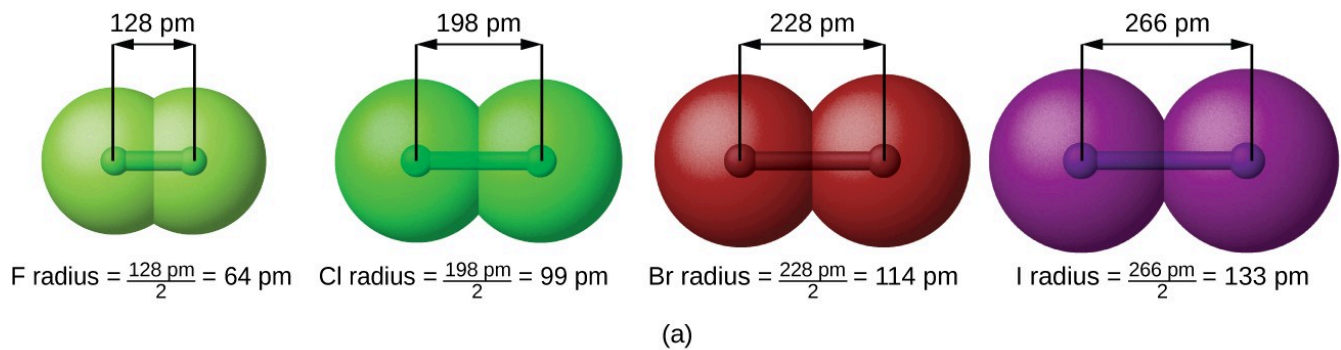
With just a few clicks, you can create three-dimensional versions of the periodic table showing atomic size or graphs of ionization energies from all measured elements.

## Variation in Covalent Radius

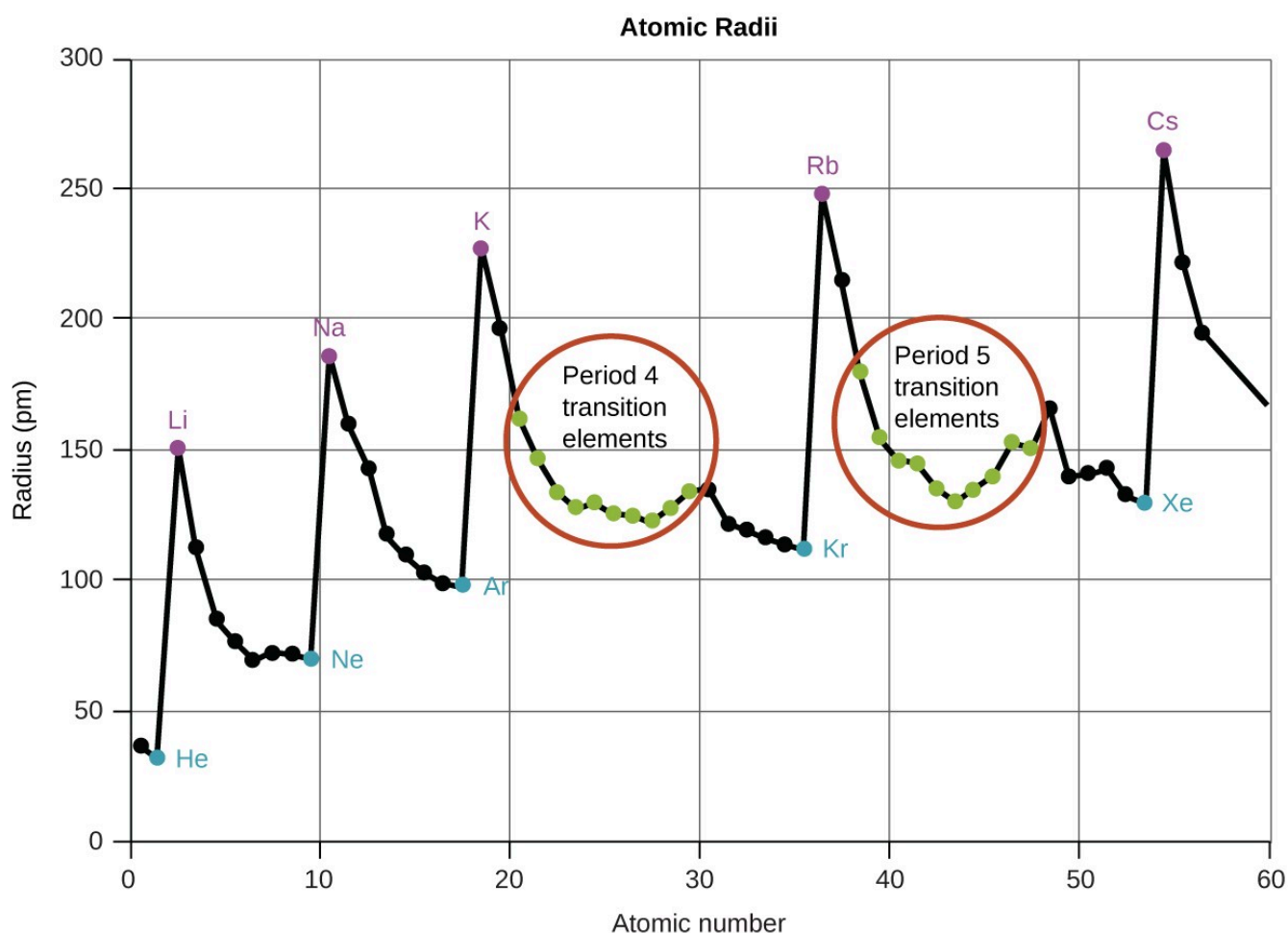
The quantum mechanical picture makes it difficult to establish a definite size of an atom. However, there are several practical ways to define the radius of atoms and, thus, to determine their relative sizes that give roughly similar values. We will use the **covalent radius** (**Figure 3.38**), which 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). 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 3.4](#) and **Figure 3.38**. The trends for the entire periodic table can be seen in **Figure 3.38**.

**Table 3.4 Covalent Radii of the Halogen Group Elements** By: Rice University [OpenStax CC BY-NC-SA 4.0](#)

Atom	Covalent radius (pm)	Nuclear charge
F	64	+9
Cl	99	+17
Br	114	+35
I	133	+53
At	148	+85



**Figure 3.38** (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. By: Rice University [Openstax CC BY NC SA](https://openstax.org/r/CC-BY-NC-SA)



**Figure 3.39** 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. By: Rice University [Openstax CC BY NC SA](#)

As shown in **Figure 3.39**, 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,  $Z_{\text{eff}}$** . 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 ( $Z_{\text{eff}}$ ) are equal. For all other atoms, the inner electrons partially *shield* the outer electrons from the pull of the nucleus, and thus:

$$Z_{\text{eff}} = Z - \text{shielding}$$

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,  $Z_{\text{eff}}$  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.

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 3.12

#### 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  $\text{Ge} < \text{Fl}$  (Note: Fl is the symbol for flerovium, element 114, NOT fluorine). Radius decreases as we move across a period, so  $\text{Kr} < \text{Br} < \text{Ge}$ . Putting the trends together, we obtain  $\text{Kr} < \text{Br} < \text{Ge} < \text{Fl}$ .

#### Check Your Learning

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 3.40**). 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  $\text{Al}^{3+}$  ( $1s^2 2s^2 2p^6$ ) 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  $Z_{\text{eff}}$  (as discussed) and are drawn even closer to the nucleus.



**Figure 3.40** 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. By: Rice University [Openstax](#) [CC BY NC SA](#)

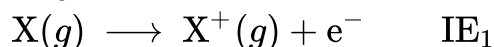
Cations with larger charges are smaller than cations with smaller charges (e.g.,  $V^{2+}$  has an ionic radius of 79 pm, while that of  $V^{3+}$  is 64 pm). Proceeding down the groups of the periodic table, we find that cations of successive elements with the same charge generally have larger radii, 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  $Z_{\text{eff}}$  per electron. Both effects (the increased number of electrons and the decreased  $Z_{\text{eff}}$ ) cause the radius of an anion to be larger than that of the parent atom (**Figure 3.40**). For example, a sulfur atom ( $[\text{Ne}]3s^23p^4$ ) has a covalent radius of 104 pm, whereas the ionic radius of the sulfide anion ( $[\text{Ne}]3s^23p^6$ ) is 170 pm. For consecutive elements proceeding down any group, anions have larger principal quantum numbers and, thus, larger radii.

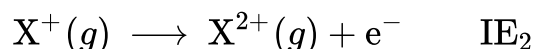
Atoms and ions that have the same electron configuration are said to be isoelectronic. Examples of isoelectronic species are  $\text{N}^{3-}$ ,  $\text{O}^{2-}$ ,  $\text{F}^-$ ,  $\text{Ne}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Al}^{3+}$  ( $1s^22s^22p^6$ ). Another isoelectronic series is  $\text{P}^{3-}$ ,  $\text{S}^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Ar}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Sc}^{3+}$  ( $[\text{Ne}]3s^23p^6$ ). 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** ( $\text{IE}_1$ ). The first ionization energy for an element, X, is the energy required to form a cation with +1 charge:



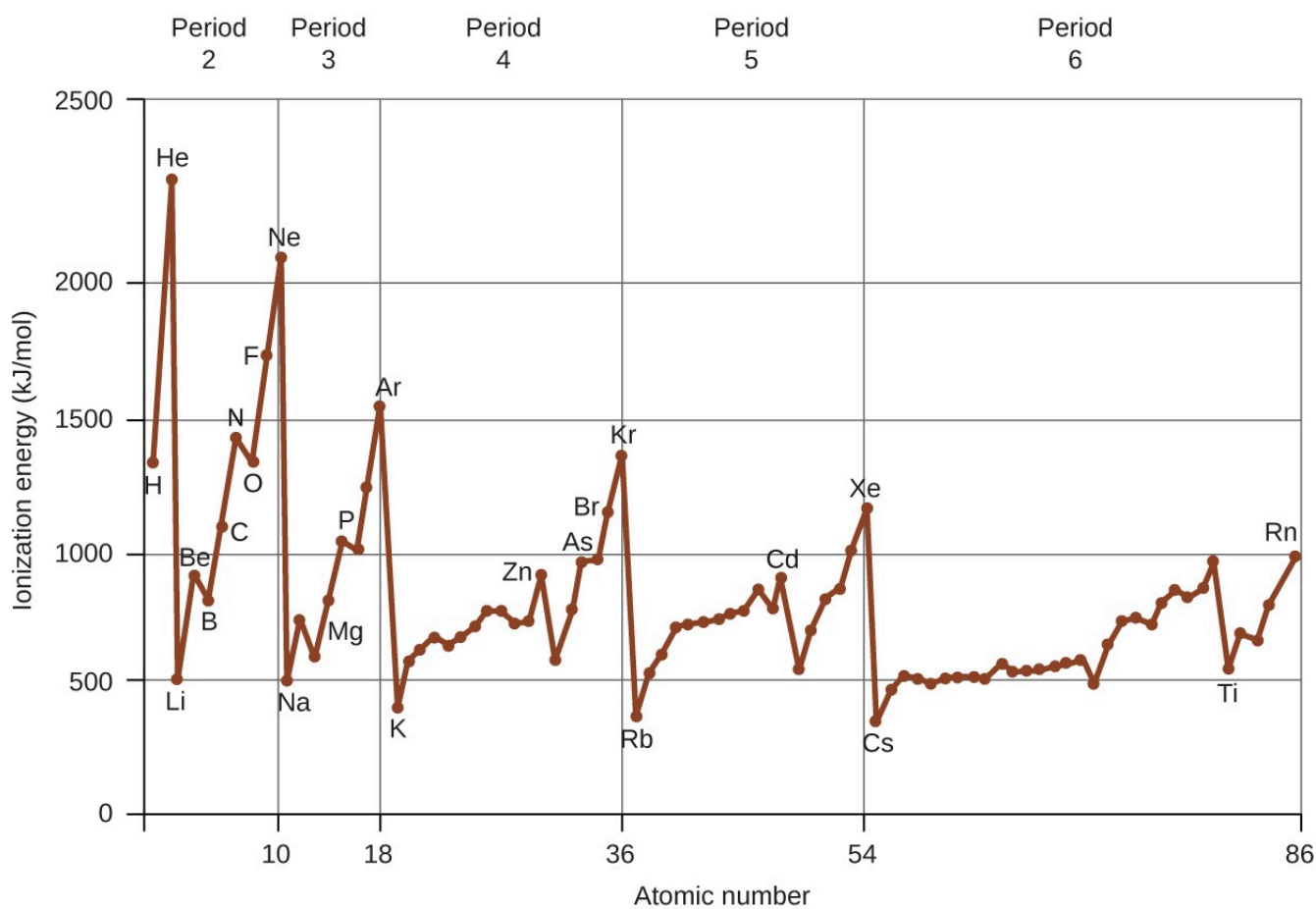
The energy required to remove the second most loosely bound electron is called the second ionization energy ( $\text{IE}_2$ ).



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 3.41** graphs the relationship between the first ionization energy and the atomic number of several elements. The values of the first ionization energy for the elements are given in **Figure 3.42**. Within a period, the  $IE_1$  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 ( $[\text{He}]2s^2$ ) is an  $s$  electron, whereas the electron removed during the ionization of boron ( $[\text{He}]2s^22p^1$ ) 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 3.41** The first ionization energies of the elements in the first five periods are plotted against their atomic number. By: Rice University [Openstax CC BY NC SA](https://openstax.org/r/chemistry-rice)





**Table 3.5 Successive Ionization Energies for Selected Elements (kJ/mol) By: Rice University [OpenStax CC BY-NC-SA 4.0](#)**

Element	IE <sub>1</sub>	IE <sub>2</sub>	IE <sub>3</sub>	IE <sub>4</sub>	IE <sub>5</sub>	IE <sub>6</sub>	IE <sub>7</sub>
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	6180.0	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 3.13

#### Ranking Ionization Energies

Predict the order of increasing energy for the following processes: IE<sub>1</sub> for Al, IE<sub>1</sub> for Tl, IE<sub>2</sub> for Na, IE<sub>3</sub> 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  $\text{IE}_1(\text{Tl}) < \text{IE}_1(\text{Al})$ . Ionizing the third electron from Al ( $\text{Al}^{2+} \rightarrow \text{Al}^{3+} + \text{e}^-$ ) requires more energy because the cation  $\text{Al}^{2+}$  exerts a stronger pull on the electron than the neutral Al atom, so  $\text{IE}_1(\text{Al}) < \text{IE}_3(\text{Al})$ . 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:  $\text{IE}_1(\text{Tl}) < \text{IE}_1(\text{Al}) < \text{IE}_3(\text{Al}) < \text{IE}_2(\text{Na})$ .

#### Check Your Learning

Which has the lowest value for IE<sub>1</sub>: 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).

$$\text{X}(g) + e^{-} \longrightarrow \text{X}^{-}(g) \quad \text{EA}_1$$
 This process can be either endothermic or exothermic, depending on the element. The EA of some of the elements is given in **Figure 3.44**. 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.

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 most negative 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 most negative EA. This 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 ( $\text{F}^{-}$ ), 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, resulting in a more negative EA.

**Electron Affinity Values for Selected Elements (kJ/mol)**

Period	Group 1	Group 2												13	14	15	16	17	18
1	H -72																		He +20*
2	Li -60	Be +240*												B -23	C -123	N 0	O -141	F -322	Ne -30
3	Na -53	Mg +230*												Al -44	Si -120	P -74	S -20	Cl -348	Ar +35*
4	K -48	Ca +150*	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn		Ga -40*	Ge -115	As -7	Se -195	Br -324	Kr +40*
5	Rb -46	Sr +160*	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd		In -40*	Sn -121	Sb -101	Te -190	I -295	Xe +40*
6	Cs -45	Ba +50*	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg		Tl -50	Pb -101	Bi -101	Po -170	At -270*	Rn +40*
7	Fr	Ra																	

\* Calculated value

**Figure 3.44** This version of the periodic table displays the electron affinity values (in kJ/mol) for selected elements. By: Rice University [Openstax CC BY NC SA](#)

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.

# THE PERIODIC TABLE (3.6)

OpenStax

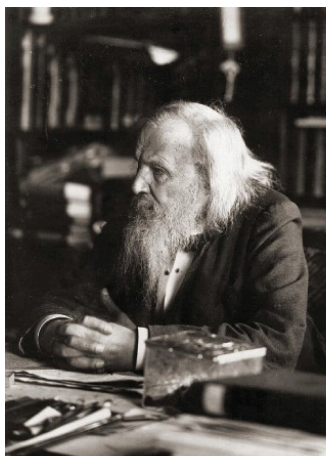
---

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

- 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 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 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 3.45**).



(a)

Reihen	Gruppe I. R <sup>0</sup>	Gruppe II. R <sup>0</sup>	Gruppe III. R <sup>0</sup> <sup>3</sup>	Gruppe IV. RH <sup>4</sup> R <sup>0</sup> <sup>4</sup>	Gruppe V. RH <sup>5</sup> R <sup>0</sup> <sup>5</sup>	Gruppe VI. RH <sup>6</sup> R <sup>0</sup> <sup>6</sup>	Gruppe VII. RH <sup>7</sup> R <sup>0</sup> <sup>7</sup>	Gruppe VIII. R <sup>0</sup> <sup>8</sup>
1	II=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	(Ca=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	?Co=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

(b)

**Figure 3.45** (a) Dimitri Mendeleev is widely credited with creating (b) the first periodic table of the elements. By: Rice University [Openstax CC BY NC SA](#)

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 3.46**). 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.



Period

Group

1

2

13

14

15

16

17

18

1	1	2																	2
1	H 1.008 hydrogen																		He 4.003 helium
2	3	4												5	6	7	8	9	10
	Li 6.94 lithium	Be 9.012 beryllium												B 10.81 boron	C 12.01 carbon	N 14.01 nitrogen	O 16.00 oxygen	F 19.00 fluorine	Ne 20.18 neon
3	11	12												13	14	15	16	17	18
	Na 22.99 sodium	Mg 24.31 magnesium												Al 26.98 aluminum	Si 28.09 silicon	P 30.97 phosphorus	S 32.06 sulfur	Cl 35.45 chlorine	Ar 39.95 argon
4	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	
	K 39.10 potassium	Ca 40.08 calcium	Sc 44.96 scandium	Ti 47.87 titanium	V 50.94 vanadium	Cr 52.00 chromium	Mn 54.94 manganese	Fe 55.85 iron	Co 58.93 cobalt	Ni 58.69 nickel	Cu 63.55 copper	Zn 65.38 zinc	Ga 69.72 gallium	Ge 72.63 germanium	As 74.92 arsenic	Se 78.97 selenium	Br 79.90 bromine	Kr 83.80 krypton	
5	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	
	Rb 85.47 rubidium	Sr 87.62 strontium	Y 88.91 yttrium	Zr 91.22 zirconium	Nb 92.91 niobium	Mo 95.95 molybdenum	Tc [97] technetium	Ru 101.1 ruthenium	Rh 102.9 rhodium	Pd 106.4 palladium	Ag 107.9 silver	Cd 112.4 cadmium	In 114.8 indium	Sn 118.7 tin	Sb 121.8 antimony	Te 127.6 tellurium	I 126.9 iodine	Xe 131.3 xenon	
6	55	56	57-71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	
	Cs 132.9 cesium	Ba 137.3 barium	La-Lu *	Hf 178.5 hafnium	Ta 180.9 tantalum	W 183.8 tungsten	Re 186.2 rhenium	Os 190.2 osmium	Ir 192.2 iridium	Pt 195.1 platinum	Au 197.0 gold	Hg 200.6 mercury	Tl 204.4 thallium	Pb 207.2 lead	Bi 209.0 bismuth	Po [209] polonium	At [210] astatine	Rn [222] radon	
7	87	88	89-103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	
	Fr [223] francium	Ra [226] radium	Ac-Lr **	Rf [267] rutherfordium	Db [270] dubnium	Sg [271] seaborgium	Bh [270] bohrium	Hs [277] hassium	Mt [276] meitnerium	Ds [281] darmstadtium	Rg [282] roentgenium	Cn [285] copernicium	Nh [285] nihonium	Fl [289] flerovium	Mc [288] moscovium	Lv [293] livermorium	Ts [294] tennessine	Og [294] oganesson	
			*	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	
				La 138.9 lanthanum	Ce 140.1 cerium	Pr 140.9 praseodymium	Nd 144.2 neodymium	Pm [145] promethium	Sm 150.4 samarium	Eu 152.0 europium	Gd 157.3 gadolinium	Tb 158.9 terbium	Dy 162.5 dysprosium	Ho 164.9 holmium	Er 167.3 erbium	Tm 168.9 thulium	Yb 173.1 ytterbium	Lu 175.0 lutetium	
			**	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	
				Ac [227] actinium	Th 232.0 thorium	Pa 231.0 protactinium	U 238.0 uranium	Np [237] neptunium	Pu [244] plutonium	Am [243] americium	Cm [247] curium	Bk [247] berkelium	Cf [251] californium	Es [252] einsteinium	Fm [257] fermium	Md [258] mendelevium	No [259] nobelium	Lr [262] lawrencium	

Atomic number

1

H

1.008

hydrogen

Symbol

Atomic mass

Color Code

Metal

Metalloid

Nonmetal

Solid

Liquid

Gas

**Figure 3.46** Elements in the periodic table are organized according to their properties. By: Rice University Openstax CC BY NC SA

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;<sup>1</sup> 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 3.47**). 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.

# Periodic Table of the Elements

<b>Group</b> <b>1</b>																	<b>18</b>
<b>Main group elements</b>																	
	<b>2</b>											<b>13</b>	<b>14</b>	<b>15</b>	<b>16</b>	<b>17</b>	
<b>A l k a l i m e t a l s</b>	<b>e a r t h A l k a l i m e t a l s</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>	<b>9</b>	<b>10</b>	<b>11</b>	<b>12</b>		<b>P n i c t o g e n s</b>	<b>C h a l c o g e n s</b>	<b>H a l o g e n s</b>	<b>N o b l e g a s e s</b>	
<b>Transition metals</b>																	
<b>Lanthanides</b>																	
<b>Actinides</b>																	

**Figure 3.47** The periodic table organizes elements with similar properties into groups. By: Rice University Openstax CC BY NC SA

1. Per the IUPAC definition, group 12 elements are not transition metals, though they are often referred to as such. Additional details on this group's elements are provided in a chapter on transition metals and coordination chemistry.



## Link to Learning

[Click on this link](#) for an interactive periodic table, which you can use to explore the properties of the elements (includes podcasts and videos of each element). You may also want to [try this one](#) that shows photos of all the elements.

## EXAMPLE 3.14

### 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

### Check Your Learning

Give the group name for each of the following elements:

- (a) krypton

(b) selenium

(c) barium

(d) lithium

**Answer:**(a) noble gas; (b) chalcogen; (c) alkaline earth metal; (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.

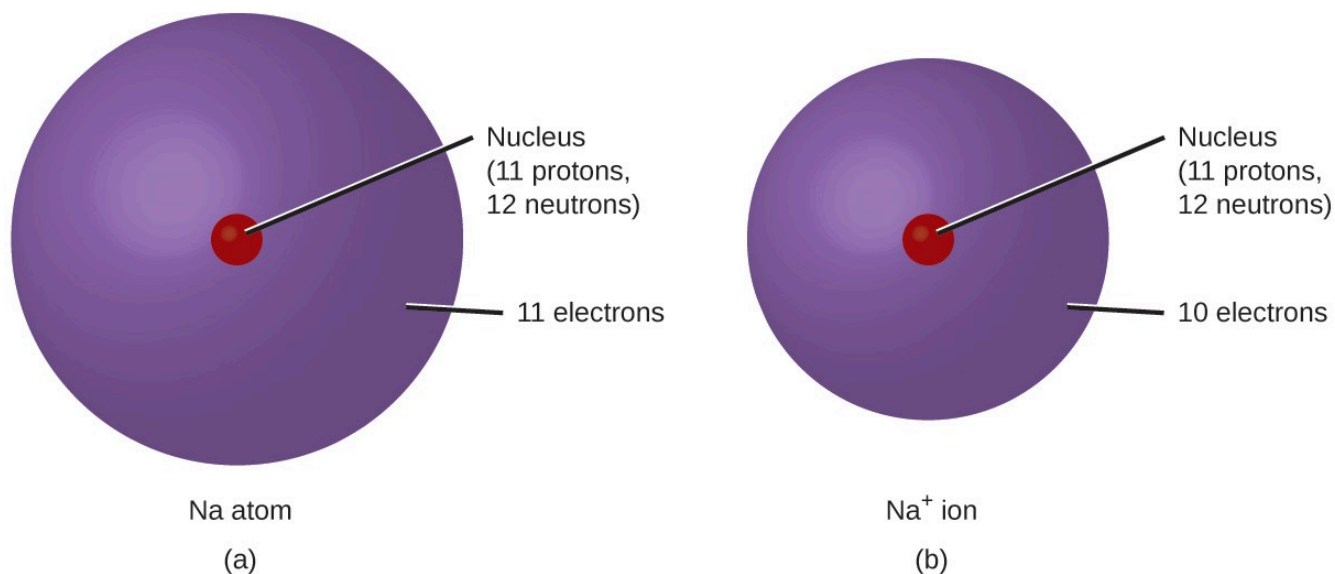
# MOLECULAR AND IONIC COMPOUNDS (3.7)

OpenStax

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

- 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 3.48**).



**Figure 3.48** (a) A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. (b) A sodium cation (Na<sup>+</sup>) 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. By: Rice University [Openstax CC BY NC SA](#)

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  $\text{Ca}^{2+}$ . The name of a metal ion is the same as the name of the metal atom from which it forms, so  $\text{Ca}^{2+}$  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  $\text{Br}^-$ . (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 3.49**). 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.

**Periodic Table of the Elements**

Period	Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18																																								
1																			He																																								
2		Li <sup>+</sup>	Be <sup>2+</sup>												C <sup>4-</sup>	N <sup>3-</sup>	O <sup>2-</sup>	F <sup>-</sup>	Ne																																								
3		Na <sup>+</sup>	Mg <sup>2+</sup>											Al <sup>3+</sup>		P <sup>3-</sup>	S <sup>2-</sup>	Cl <sup>-</sup>	Ar																																								
4		K <sup>+</sup>	Ca <sup>2+</sup>				Cr <sup>3+</sup> Cr <sup>6+</sup>	Mn <sup>2+</sup>	Fe <sup>2+</sup> Fe <sup>3+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>	Cu <sup>+</sup> Cu <sup>2+</sup>	Zn <sup>2+</sup>			As <sup>3-</sup>	Se <sup>2-</sup>	Br <sup>-</sup>	Kr																																								
5		Rb <sup>+</sup>	Sr <sup>2+</sup>									Ag <sup>+</sup>	Cd <sup>2+</sup>				Te <sup>2-</sup>	I <sup>-</sup>	Xe																																								
6		Cs <sup>+</sup>	Ba <sup>2+</sup>								Pt <sup>2+</sup>	Au <sup>+</sup> Au <sup>3+</sup>	Hg <sub>2</sub> <sup>2+</sup> Hg <sup>2+</sup>					At <sup>-</sup>	Rn																																								
7		Fr <sup>+</sup>	Ra <sup>2+</sup>																																																								
<div style="display: flex; align-items: center;"> <div style="margin-right: 10px;"> <p style="font-size: 2em; color: red;">*</p> <p style="font-size: 2em; color: red;">**</p> </div> <table border="1" style="border-collapse: collapse;"> <tr><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr> <tr><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr> </table> </div>																																																											

**Figure 3.49** Some elements exhibit a regular pattern of ionic charge when they form ions. By: Rice University [Openstax CC BY NC SA](https://openstax.org/r/chemistry-rice)

## EXAMPLE 3.15

### 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<sup>3+</sup>.

### Check Your Learning

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

**Answer:**  $\text{Se}^{2-}$ , the selenide ion

### EXAMPLE 3.16

#### 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 of 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  $\text{Mg}^{2+}$ , 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  $\text{N}^{3-}$ , and it is called a nitride ion.

### Check Your Learning

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+:  $\text{Al}^{3+}$ , an aluminum ion. Carbon will form an anion with a charge of 4-:  $\text{C}^{4-}$ , 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](#). 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.

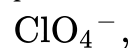
**Table 3.6 Common Polyatomic Ions By: Rice University [OpenStax CC BY-NC-SA 4.0](#)**

Name	Formula	Related Acid	Formula
ammonium	$\text{NH}_4^+$		
hydronium	$\text{H}_3\text{O}^+$		
peroxide	$\text{O}_2^{2-}$		
hydroxide	$\text{OH}^-$		
acetate	$\text{CH}_3\text{COO}^-$	acetic acid	$\text{CH}_3\text{COOH}$
cyanide	$\text{CN}^-$	hydrocyanic acid	$\text{HCN}$
azide	$\text{N}_3^-$	hydrazoic acid	$\text{HN}_3$
carbonate	$\text{CO}_3^{2-}$	carbonic acid	$\text{H}_2\text{CO}_3$
bicarbonate	$\text{HCO}_3^-$		
nitrate	$\text{NO}_3^-$	nitric acid	$\text{HNO}_3$
nitrite	$\text{NO}_2^-$	nitrous acid	$\text{HNO}_2$
sulfate	$\text{SO}_4^{2-}$	sulfuric acid	$\text{H}_2\text{SO}_4$
hydrogen sulfate	$\text{HSO}_4^-$		
sulfite	$\text{SO}_3^{2-}$	sulfurous acid	$\text{H}_2\text{SO}_3$
hydrogen sulfite	$\text{HSO}_3^-$		
phosphate	$\text{PO}_4^{3-}$	phosphoric acid	$\text{H}_3\text{PO}_4$
hydrogen phosphate	$\text{HPO}_4^{2-}$		
dihydrogen phosphate	$\text{H}_2\text{PO}_4^-$		
perchlorate	$\text{ClO}_4^-$	perchloric acid	$\text{HClO}_4$
chlorate	$\text{ClO}_3^-$	chloric acid	$\text{HClO}_3$
chlorite	$\text{ClO}_2^-$	chlorous acid	$\text{HClO}_2$
hypochlorite	$\text{ClO}^-$	hypochlorous acid	$\text{HClO}$
chromate	$\text{CrO}_4^{2-}$	chromic acid	$\text{H}_2\text{Cr}_2\text{O}_4$
dichromate	$\text{Cr}_2\text{O}_7^{2-}$	dichromic acid	$\text{H}_2\text{Cr}_2\text{O}_7$
permanganate	$\text{MnO}_4^-$	permanganic acid	$\text{HMnO}_4$

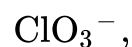


Note that there is a system for naming some polyatomic ions; *-ate* and *-ite* are suffixes designating polyatomic ions containing more or fewer oxygen atoms. *Per-* (short for “hyper”) and *hypo-* (meaning “under”) are prefixes meaning more oxygen atoms than *-ate* and fewer oxygen atoms than *-ite*, respectively. For example,

perchlorate is



chlorate is

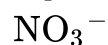


chlorite is

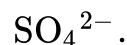


and hypochlorite is  $\text{ClO}^-$ .

Unfortunately, the number of oxygen atoms corresponding to a given suffix or prefix is not consistent; for example, nitrate is



while sulfate is



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.

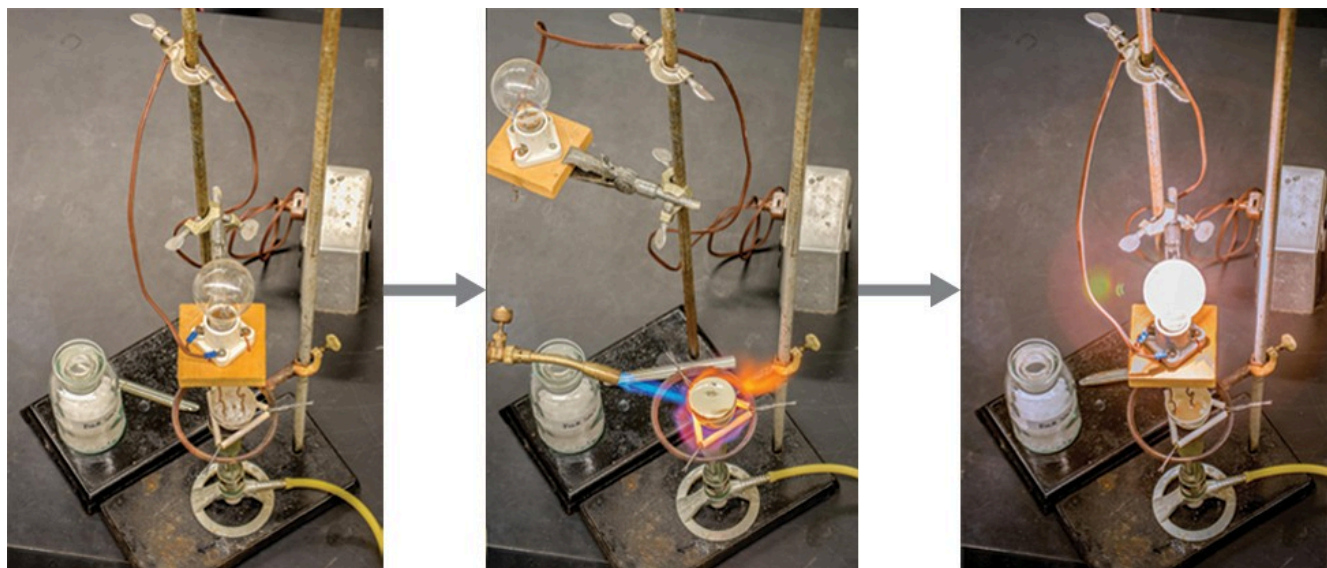
## Ionic Compounds

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,  $\text{Na}^+$ , and each chlorine atom in a sample of chlorine gas (group 17) accepts one electron to form a chloride anion,  $\text{Cl}^-$ , the resulting compound,  $\text{NaCl}$ , is composed of sodium ions and chloride ions in the ratio of one  $\text{Na}^+$  ion for each  $\text{Cl}^-$  ion. Similarly, each calcium atom (group 2) can give up two electrons and transfer one to each of two chlorine atoms to form  $\text{CaCl}_2$ , which is composed of  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  ions in the ratio of one  $\text{Ca}^{2+}$  ion to two  $\text{Cl}^-$  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,  $\text{AlCl}_3$ , 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  $801^\circ\text{C}$  and boils at  $1413^\circ\text{C}$ . (As a comparison, the molecular compound water melts at  $0^\circ\text{C}$  and boils at  $100^\circ\text{C}$ .) 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 3.50**).



**Figure 3.50** Sodium chloride melts at  $801^\circ\text{C}$  and conducts electricity when molten. By: Rice University Openstax CC BY NC SA

### Link to Learning

[Watch this video](#) to see a mixture of salts melt and conduct electricity.

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 3.17

#### Predicting the Formula of an Ionic Compound

The gemstone sapphire (**Figure 3.51**) is mostly a compound of aluminum and oxygen that contains aluminum cations,  $\text{Al}^{3+}$ , and oxygen anions,  $\text{O}^{2-}$ . What is the formula of this compound?



**Figure 3.51**  
Although pure aluminum oxide is colorless, trace amounts of iron and titanium give blue sapphire its characteristic color. By: Rice University  
[Openstax CC BY NC SA](#)

#### 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  $\text{Al}_2\text{O}_3$ .

#### Check Your Learning

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

**Answer:**  $\text{Na}_2\text{S}$

Many ionic compounds contain polyatomic ions ([Table 3.6](#)) 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  $\text{Ca}_3(\text{PO}_4)_2$ . This formula indicates that there are three calcium ions ( $\text{Ca}^{2+}$ ) for every two phosphate ( $\text{PO}_4^{3-}$ ) groups. The

$\text{PO}_4^{3-}$  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 3.18

#### Predicting the Formula of a Compound with a Polyatomic Anion

Baking powder contains calcium dihydrogen phosphate, an ionic compound composed of the ions  $\text{Ca}^{2+}$  and

$\text{H}_2\text{PO}_4^-$ . 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  $\text{Ca}^{2+}$  ion to two

$\text{H}_2\text{PO}_4^-$  ions. We designate this by enclosing the formula for the dihydrogen phosphate ion in parentheses and adding a subscript 2. The formula is  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ .

#### Check Your Learning

Predict the formula of the ionic compound formed between the lithium ion and the peroxide ion,

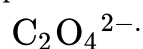
$\text{O}_2^{2-}$  (Hint: Use the periodic table to predict the sign and the charge on the lithium ion.)

**Answer:**  $\text{Li}_2\text{O}_2$

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 their constituent ions. For compounds containing only monatomic ions (such as NaCl) and for many compounds containing polyatomic ions (such as CaSO<sub>4</sub>), these formulas are just the empirical formulas introduced earlier. 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<sup>+</sup> and

C<sub>2</sub>O<sub>4</sub><sup>2-</sup> ions combined in a 2:1 ratio, and its formula is written as Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. 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<sub>2</sub>. This is not the accepted formula for sodium oxalate, however, as it does not accurately represent the compound's polyatomic anion,



## 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 3.19

#### 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<sub>2</sub>O<sub>2</sub>, the bleach and disinfectant hydrogen peroxide

- (c)  $\text{CHCl}_3$ , the anesthetic chloroform
- (d)  $\text{Li}_2\text{CO}_3$ , 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;  $\text{H}_2\text{O}_2$  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;  $\text{CHCl}_3$  is predicted to be molecular.
- (d) Lithium (group 1) is a metal, and carbonate is a polyatomic ion;  $\text{Li}_2\text{CO}_3$  is predicted to be ionic.

### Check Your Learning

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

- (a)  $\text{SO}_2$
- (b)  $\text{CaF}_2$
- (c)  $\text{N}_2\text{H}_4$
- (d)  $\text{Al}_2(\text{SO}_4)_3$

**Answer:** (a) molecular; (b) ionic; (c) molecular; (d) ionic

# CHAPTER 4: CHEMICAL BONDING AND MOLECULAR GEOMETRY



**Figure 4.1**  
Nicknamed “buckyballs,” buckminsterfullerene molecules ( $C_{60}$ ) contain only carbon atoms (left) arranged to form a geometric framework of hexagons and pentagons, similar to the pattern on a soccer ball (center). This molecular structure is named after architect R. Buckminster Fuller, whose innovative designs combined simple geometric shapes to create large, strong structures such as this weather radar dome near Tucson, Arizona (right). By: Rice University [Openstax](#) [CC BY](#) [NC SA](#)

## Chapter Outline

- Ionic Bonding
- Covalent Bonding
- Chemical Nomenclature
- Lewis Symbols and Structures
- Formal Charges and Resonance

- Molecular Structure and Polarity

## Introduction

It has long been known that pure carbon occurs in different forms (allotropes) including graphite and diamonds. But it was not until 1985 that a new form of carbon was recognized: buckminsterfullerene. This molecule was named after the architect and inventor R. Buckminster Fuller (1895–1983), whose signature architectural design was the geodesic dome, characterized by a lattice shell structure supporting a spherical surface. Experimental evidence revealed the formula,  $C_{60}$ , and then scientists determined how 60 carbon atoms could form one symmetric, stable molecule. They were guided by bonding theory—the topic of this chapter—which explains how individual atoms connect to form more complex structures.



# IONIC BONDING (4.1)

OpenStax

---

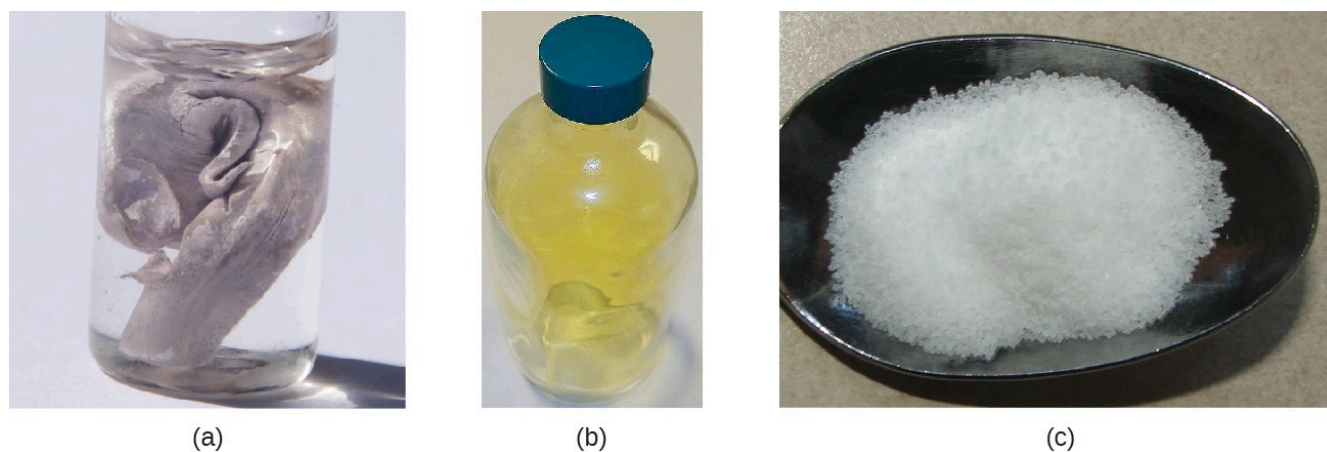
By the end of this section, you will be able to:

- 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,  $\text{Cl}_2$ , a yellow-green gas that is extremely corrosive to most metals and very poisonous to animals and plants. The vigorous reaction between the elements sodium and chlorine forms the white, crystalline compound sodium chloride, common table salt, which contains sodium *cations* and chloride *anions* (**Figure 4.2**). 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.



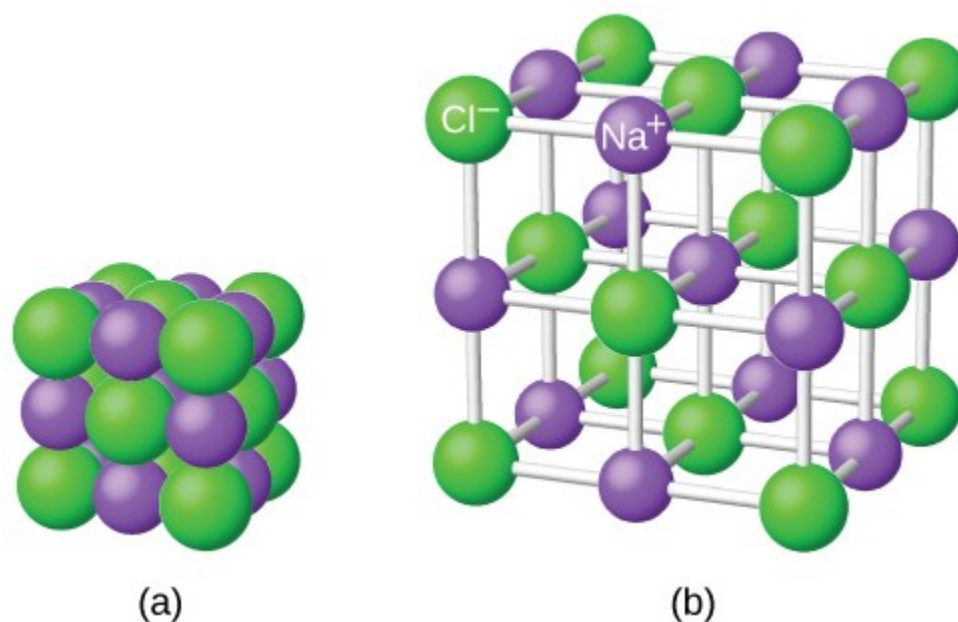
**Figure 4.2** (a) Sodium is a soft metal that must be stored in mineral oil to prevent reaction with air or water. (b) Chlorine is a pale yellow-green gas. (c) When combined, they form white crystals of sodium chloride (table salt). By: Rice University [Openstax CC BY NC SA](#)

## 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,  $\text{NaCl}$  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,  $\text{Al}_2\text{O}_3$ , indicates that this ionic compound contains two aluminum cations,  $\text{Al}^{3+}$ , for every three oxide anions,  $\text{O}^{2-}$  [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 ( $\text{NaCl}$ ) “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  $\text{Na}^+$  cations and  $\text{Cl}^-$  anions (**Figure 4.3**).



**Figure 4.3** The atoms in sodium chloride (common table salt) are arranged to (a) maximize opposite charges interacting. The smaller spheres represent sodium ions; the larger ones represent chloride ions. In the expanded view (b), the geometry can be seen more clearly. Note that each ion is “bonded” to all of the surrounding ions—six in this case. By: Rice University [Openstax CC BY NC SA](#)

The strong electrostatic attraction between  $\text{Na}^+$  and  $\text{Cl}^-$  ions holds them tightly together in solid  $\text{NaCl}$ . It requires 769 kJ of energy to dissociate one mole of solid  $\text{NaCl}$  into separate gaseous  $\text{Na}^+$  and  $\text{Cl}^-$  ions:



## Electronic Structures of Cations

When forming a cation, an atom of a main group element tends to lose all of its valence electrons, thus assuming the electronic structure of the noble gas that precedes it in the periodic table. For groups 1 (the alkali metals) and 2 (the alkaline earth metals), the group numbers are equal to the numbers of valence shell electrons and, consequently, to the charges of the cations formed from atoms of these elements when all valence shell electrons are removed. For example, calcium is a group 2 element whose neutral atoms have 20 electrons and a ground state electron configuration of  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ . When a Ca atom loses both of its valence electrons, the result is a cation with 18 electrons, a 2+ charge, and an electron configuration of  $1s^2 2s^2 2p^6 3s^2 3p^6$ . The  $\text{Ca}^{2+}$  ion is therefore isoelectronic with the noble gas Ar.

For groups 13–17, 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 ( $\text{Al}^{3+}$ ).

Exceptions to the expected behavior involve elements toward the bottom of the groups. In addition to the expected ions  $\text{Tl}^{3+}$ ,  $\text{Sn}^{4+}$ ,  $\text{Pb}^{4+}$ , and  $\text{Bi}^{5+}$ , a partial loss of these atoms' valence shell electrons can also lead to the formation of  $\text{Tl}^{+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Bi}^{3+}$  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,

$\text{Hg}_2^{2+}$  (an ion formed from two mercury atoms, with an Hg-Hg bond), in addition to the expected monatomic ion  $\text{Hg}^{2+}$  (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 ( $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$ ) forms the ion  $\text{Fe}^{2+}$  ( $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ ) by the loss of the  $4s$  electrons and the ion  $\text{Fe}^{3+}$  ( $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ ) by the loss of the  $4s$  electron and one of the  $3d$  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.

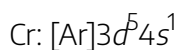
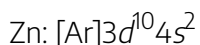
## EXAMPLE 4.1

### 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  $\text{Cr}^{3+}$  and  $\text{Zn}^{2+}$ . Write the electron configurations of these cations.

### Solution

First, write the electron configuration for the neutral atoms:



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:



### Check Your Learning

Potassium and magnesium are required in our diet. Write the electron configurations of the ions expected from these elements.

**Answer:**  $\text{K}^+: [\text{Ar}]$ ,  $\text{Mg}^{2+}: [\text{Ne}]$

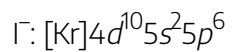
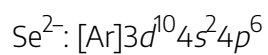
## Electronic Structures of Anions

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  $2-$  ( $\text{O}^{2-}$ ).

### EXAMPLE 4.2

#### 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****Check Your Learning**

Write the electron configurations of a phosphorus atom and its negative ion. Give the charge on the anion.

**Answer:** P:  $[\text{Ne}]3s^23p^3$ ;  $\text{P}^{3-}$ :  $[\text{Ne}]3s^23p^6$

# COVALENT BONDING (4.2)

OpenStax

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

- Describe the formation of covalent bonds
- Define electronegativity and assess the polarity of covalent bonds

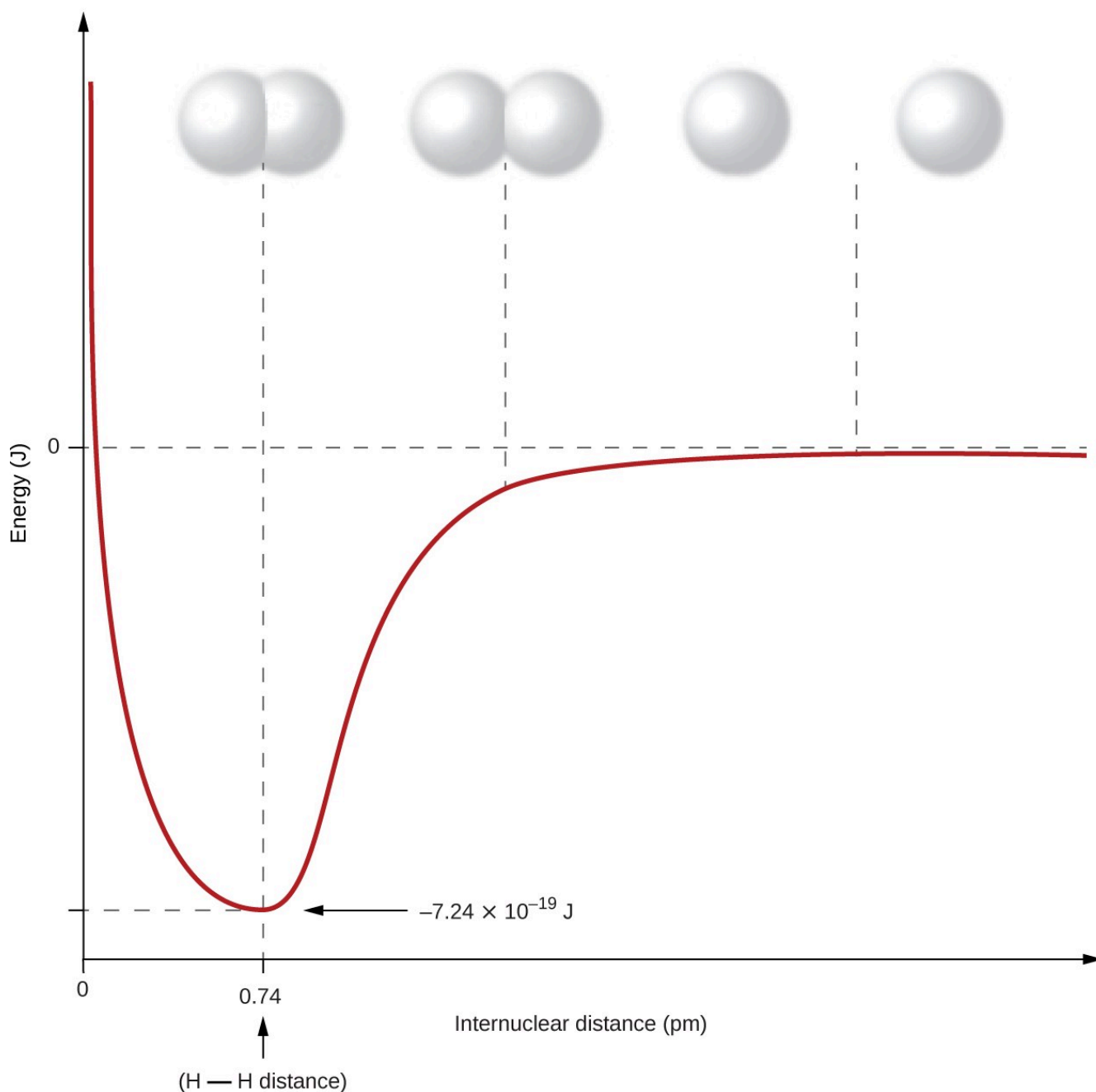
Ionic bonding results from the electrostatic attraction of oppositely charged ions that are typically produced by the transfer of electrons between metallic and nonmetallic atoms. A different type of bonding results from the mutual attraction of atoms for a “shared” pair of electrons. Such bonds are 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  $\text{H}_2$  molecule; each hydrogen atom in the  $\text{H}_2$  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 are insoluble in water; since they are electrically neutral, they 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,  $\text{H}_2$ , contains a covalent bond between its two hydrogen atoms. **Figure 4.4** illustrates why this bond is formed. Starting on the far right, we have two separate hydrogen atoms with a particular potential energy, indicated by the red line. Along the  $x$ -axis is the distance between the two atoms. As the two atoms approach each other (moving left along the  $x$ -axis), their valence orbitals ( $1s$ ) 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 4.4** The potential energy of two separate hydrogen atoms (right) decreases as they approach each other, and the single electrons on each atom are shared to form a covalent bond. The bond length is the internuclear distance at which the lowest potential energy is achieved. By: Rice University [Openstax CC BY NC SA](#)



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  $\text{H}_2$ , 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:



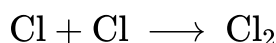
Conversely, the same amount of energy is released when one mole of  $\text{H}_2$  molecules forms from two moles of H atoms:



## Pure vs. Polar Covalent Bonds

If the atoms that form a covalent bond are identical, as in  $\text{H}_2$ ,  $\text{Cl}_2$ , 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.

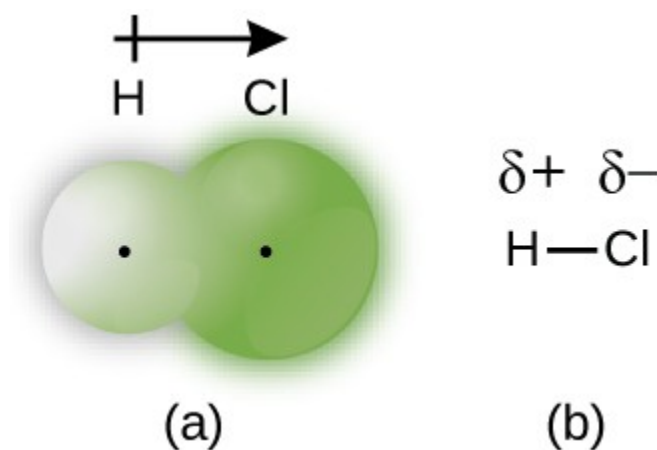
In the case of  $\text{Cl}_2$ , each atom starts off with seven valence electrons, and each Cl shares one electron with the other, forming one covalent bond:



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,  $\text{Cl}_2$  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 4.5** shows the distribution of electrons in the H–Cl bond. Note that the shaded area around Cl is much larger than it is around H. Compare this to **Figure 4.4**, which shows the even distribution of electrons in the  $\text{H}_2$  nonpolar bond.

We sometimes designate the positive and negative atoms in a polar covalent bond using a lowercase Greek letter “delta,”  $\delta$ , with a plus sign or minus sign to indicate whether the atom has a partial positive charge ( $\delta+$ ) or a partial negative charge ( $\delta-$ ). This symbolism is shown for the H–Cl molecule in **Figure 4.5**.

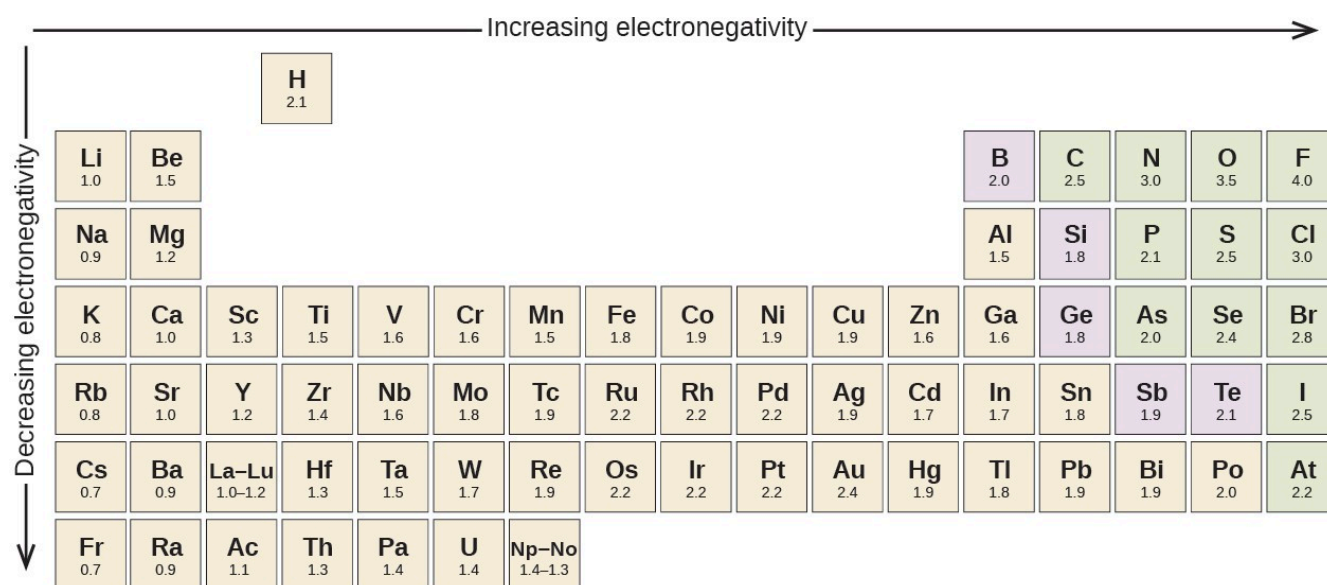


**Figure 4.5** (a) The distribution of electron density in the HCl molecule is uneven. The electron density is greater around the chlorine nucleus. The small black dots indicate the location of the hydrogen and chlorine nuclei in the molecule. (b) Symbols  $\delta+$  and  $\delta-$  indicate the polarity of the H—Cl bond. By: Rice University [Openstax CC BY NC SA](#)

## 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) toward 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 4.6** shows the electronegativity values of the elements as proposed by one of the most famous chemists of the twentieth century: Linus Pauling (**Figure 4.7**). 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 other atoms, since they have a full valence shell. (While noble gas compounds such as XeO<sub>2</sub> do exist, they can only be formed under extreme conditions, and thus they do not fit neatly into the general model of electronegativity.)



**Figure 4.6** The electronegativity values derived by Pauling follow predictable periodic trends, with the higher electronegativities toward the upper right of the periodic table. By Rice University [Openstax CC BY NC SA](#)

## 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.

### PORTRAIT OF A CHEMIST

#### Linus Pauling

Linus Pauling, shown in **Figure 4.7**, 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.

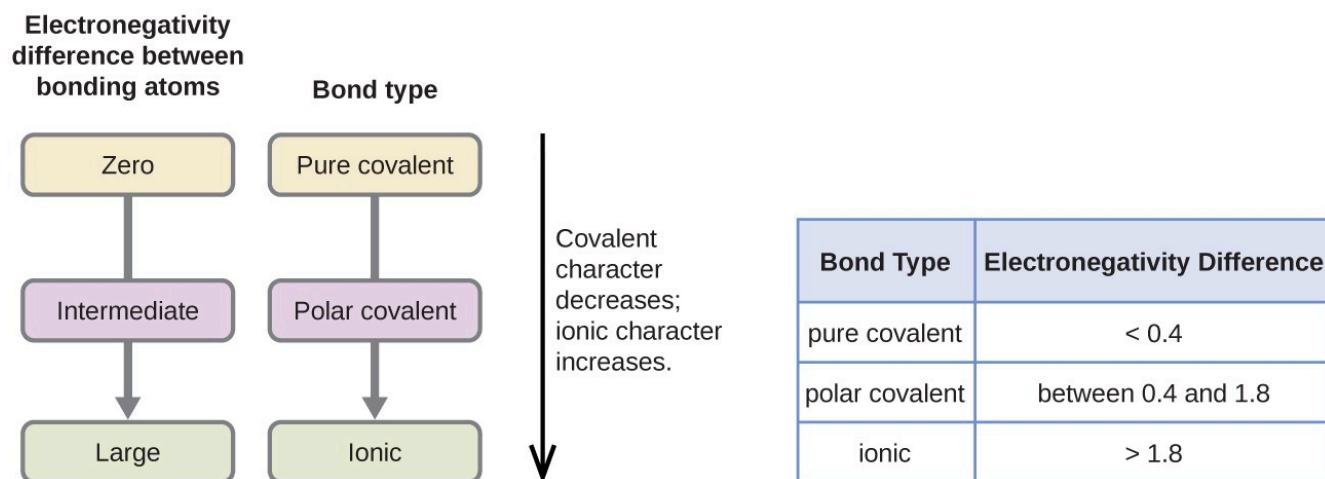


**Figure 4.7** Linus Pauling (1901–1994) made many important contributions to the field of chemistry. He was also a prominent activist, publicizing issues related to health and nuclear weapons. Pauling also contributed to many other fields besides chemistry. His research on sickle cell anemia revealed 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. By: Rice University [Openstax CC BY NC SA](#)

## Electronegativity and Bond Type

The absolute value of the difference in electronegativity ( $\Delta EN$ ) 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 4.8** shows the relationship between electronegativity difference and bond type.



**Figure 4.8** As the electronegativity difference increases between two atoms, the bond becomes more ionic. By: Rice University [Openstax CC BY NC SA](#)

A rough approximation of the electronegativity differences associated with covalent, polar covalent, and ionic bonds is shown in **Figure 4.8**. 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  $\text{NH}_3$  have 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  $\text{MnI}_2$  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  $\text{OH}^-$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$ , 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,  $\text{KNO}_3$ , contains the  $\text{K}^+$  cation and the polyatomic  $\text{NO}_3^-$  anion. Thus, bonding in potassium nitrate is ionic, resulting from the electrostatic attraction between the ions  $\text{K}^+$  and  $\text{NO}_3^-$ , as well as covalent between the nitrogen and oxygen atoms in  $\text{NO}_3^-$ .

### Example 4.3

#### Electronegativity and Bond Polarity

Bond polarities play an important role in determining the structure of proteins. Using the electronegativity values in **Figure 4.6**, 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  $\delta^+$  and  $\delta^-$ :

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  $\delta^-$  designation is the more electronegative of the two. Table 4.1 shows these bonds in order of increasing polarity.

Table 4.1 By: Rice University [OpenStax CC BY-NC-SA 4.0](#)

Bond	$\Delta EN$	Polarity
C-H	0.4	$\delta - \delta+$ <b>C – H</b>
S-H	0.4	$\delta - \delta+$ <b>S – H</b>
C-N	0.5	$\delta + \delta-$ <b>C – N</b>
N-H	0.9	$\delta - \delta+$ <b>N – H</b>
C-O	1.0	$\delta + \delta-$ <b>C – O</b>
O-H	1.4	$\delta - \delta+$ <b>O – H</b>

### Check Your Learning

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 4.6**, arrange the bonds in order of increasing polarity and designate the positive and negative atoms using the symbols  $\delta+$  and  $\delta-$ .

**Answer:**

Table 4.2 By: Rice University [OpenStax CC BY-NC-SA 4.0](#)

Bond	Electronegativity Difference	Polarity
C–C	0.0	nonpolar
C–H	0.4	$\delta - \delta +$ <b>C – H</b>
Si–C	0.7	$\delta + \delta -$ <b>Si – C</b>
Si–O	1.7	$\delta + \delta -$ <b>Si – O</b>



# CHEMICAL NOMENCLATURE (4.3)

OpenStax

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

- Derive names for common types of inorganic compounds using a systematic approach

**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  $\text{NaCl}$ ,  $\text{CaCO}_3$ , and  $\text{N}_2\text{O}_4$ . 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.

## 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 4.3**.

**Table 4.3 Names of Some Ionic Compounds By: Rice University** [OpenStax CC BY-NC-SA 4.0](#)

NaCl, sodium chloride	Na <sub>2</sub> O, sodium oxide
KBr, potassium bromide	CdS, cadmium sulfide
CaI <sub>2</sub> , calcium iodide	Mg <sub>3</sub> N <sub>2</sub> , magnesium nitride
CsF, cesium fluoride	Ca <sub>3</sub> P <sub>2</sub> , calcium phosphide
LiCl, lithium chloride	Al <sub>4</sub> C <sub>3</sub> , aluminum carbide

## Compounds Containing Polyatomic Ions

Compounds containing polyatomic ions are named similarly to those containing only monatomic ions—that is, by naming first the cation and then the anion. Examples are shown in [Table 4.4](#).

**Table 4.4 Names of Some Polyatomic Ionic Compounds By: Rice University** [OpenStax CC BY-NC-SA 4.0](#)

KC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> , potassium acetate	NH <sub>4</sub> Cl, ammonium chloride
NaHCO <sub>3</sub> , sodium bicarbonate	CaSO <sub>4</sub> , calcium sulfate
Al <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> , aluminum carbonate	Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> , magnesium phosphate

## CHEMISTRY IN EVERYDAY LIFE

### 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 4.5](#). 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 4.5 By: Rice University [OpenStax CC BY-NC-SA 4.0](#)

<b>Ionic Compound</b>	<b>Use</b>
NaCl, sodium chloride	ordinary table salt
KI, potassium iodide	added to “iodized” salt for thyroid health
NaF, sodium fluoride	ingredient in toothpaste
NaHCO <sub>3</sub> , sodium bicarbonate	baking soda; used in cooking (and as an antacid)
Na <sub>2</sub> CO <sub>3</sub> , sodium carbonate	washing soda; used in cleaning agents
NaOCl, sodium hypochlorite	active ingredient in household bleach
CaCO <sub>3</sub> calcium carbonate	ingredient in antacids
Mg(OH) <sub>2</sub> , magnesium hydroxide	ingredient in antacids
NaOH, sodium hydroxide	lye; used as drain cleaner
K <sub>3</sub> PO <sub>4</sub> , potassium phosphate	food additive (many purposes)
MgSO <sub>4</sub> , magnesium sulfate	added to purified water
Na <sub>2</sub> HPO <sub>4</sub> , sodium hydrogen phosphate	anti-caking agent; used in powdered products
Na <sub>2</sub> SO <sub>3</sub> , sodium sulfite	preservative

## Compounds Containing a Metal Ion with a Variable Charge

Most of the transition metals and some main group 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+ (see **Figure 3.40**), and the two corresponding compound formulas are  $\text{FeCl}_2$  and  $\text{FeCl}_3$ . 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 4.6](#).

**Table 4.6 Some Ionic Compounds with Variably Charged Metal Ions** By: Rice University [OpenStax CC BY-NC-SA 4.0](#)

Compound	Name
$\text{FeCl}_2$	iron(II) chloride
$\text{FeCl}_3$	iron(III) chloride
$\text{Hg}_2\text{O}$	mercury(I) oxide
$\text{HgO}$	mercury(II) oxide
$\text{SnF}_2$	tin(II) fluoride
$\text{SnF}_4$	tin(IV) fluoride

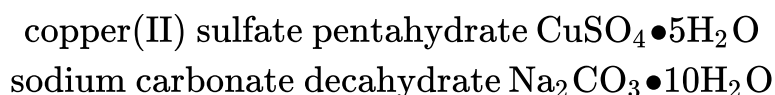
Out-of-date nomenclature used the suffixes *-ic* and *-ous* to designate metals with higher and lower charges, respectively: Iron(III) chloride,  $\text{FeCl}_3$ , was previously called ferric chloride, and iron(II) chloride,  $\text{FeCl}_2$ , was known as ferrous chloride. Though this naming convention 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  $\text{SnF}_2$ , which is more properly named tin(II) fluoride. The other fluoride of tin is  $\text{SnF}_4$ , which was previously called stannic fluoride but is now named tin(IV) fluoride.

## Ionic Hydrates

Ionic compounds that contain water molecules as integral components of their crystals are called **hydrates**. The name for an ionic hydrate is derived by adding a term to the name for the *anhydrous* (meaning “not

hydrated”) compound that indicates the number of water molecules associated with each formula unit of the compound. The added word begins with a Greek prefix denoting the number of water molecules (see [Table 4.7](#)) and ends with “hydrate.” For example, the anhydrous compound copper(II) sulfate also exists as a hydrate containing five water molecules and is named copper(II) sulfate pentahydrate. Washing soda is the common name for a hydrate of sodium carbonate containing 10 water molecules; the systematic name is sodium carbonate decahydrate.

Formulas for ionic hydrates are written by appending a vertically centered dot, a coefficient representing the number of water molecules, and the formula for water. The two examples mentioned in the previous paragraph are represented by the formulas



**Table 4.7 Nomenclature Prefixes** By: Rice University [OpenStax CC BY-NC-SA 4.0](#)

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-

## EXAMPLE 4.4

### Naming Ionic Compounds

Name the following ionic compounds:

- (a)  $\text{Fe}_2\text{S}_3$
- (b)  $\text{CuSe}$
- (c)  $\text{GaN}$

(d)  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

(e)  $\text{Ti}_2(\text{SO}_4)_3$

### Solution

The anions in these compounds have a fixed negative charge ( $\text{S}^{2-}$ ,  $\text{Se}^{2-}$ ,  $\text{N}^{3-}$ , and  $\text{SO}_4^{2-}$ ), 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  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Ti}^{3+}$ . These charges are used in the names of the metal ions:

(a) iron(III) sulfide

(b) copper(II) selenide

(c) gallium(III) nitride

(d) magnesium sulfate heptahydrate

(e) titanium(III) sulfate

### Check Your Learning

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) iron(III) chloride dihydrate

**Answer:** (a)  $\text{CrP}$ ; (b)  $\text{HgS}$ ; (c)  $\text{Mn}_3(\text{PO}_4)_2$ ; (d)  $\text{Cu}_2\text{O}$ ; (e)  $\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$

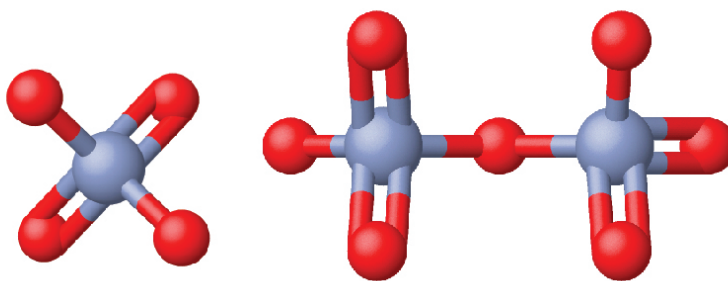
## Chemistry in Everyday Life

### Erin Brockovich and Chromium Contamination

In the early 1990s, legal file clerk Erin Brockovich (**Figure 4.9**) 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 Brockovich* (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 4.9** (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,  $\text{CrO}_4^{2-}$  (left), and dichromate,  $\text{Cr}_2\text{O}_7^{2-}$  (right). By: Rice University [Openstax CC BY NC SA](#)

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. But Cr(VI) 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<sub>2</sub>. 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 number 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 4.6](#).

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<sub>2</sub> 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 4.8](#).



**Table 4.8 Names of Some Molecular Compounds Composed of Two Elements By: Rice University [OpenStax](#) [CC BY-NC-SA 4.0](#)**

Compound	Name	Compound	Name
SO <sub>2</sub>	sulfur dioxide	BCl <sub>3</sub>	boron trichloride
SO <sub>3</sub>	sulfur trioxide	SF <sub>6</sub>	sulfur hexafluoride
NO <sub>2</sub>	nitrogen dioxide	PF <sub>5</sub>	phosphorus pentafluoride
N <sub>2</sub> O <sub>4</sub>	dinitrogen tetroxide	P <sub>4</sub> O <sub>10</sub>	tetraphosphorus decaoxide
N <sub>2</sub> O <sub>5</sub>	dinitrogen pentoxide	IF <sub>7</sub>	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<sub>2</sub>O is known as nitrous oxide even though our rules would specify the name dinitrogen monoxide. (And H<sub>2</sub>O is usually called water, not dihydrogen monoxide.) You should commit to memory the common names of compounds as you encounter them.

### EXAMPLE 4.5

#### Naming Covalent Compounds

Name the following covalent compounds:

- (a) SF<sub>6</sub>
- (b) N<sub>2</sub>O<sub>3</sub>
- (c) Cl<sub>2</sub>O<sub>7</sub>
- (d) P<sub>4</sub>O<sub>6</sub>

### 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

### Check Your Learning

Write the formulas for the following compounds:

- (a) phosphorus pentachloride
- (b) dinitrogen monoxide
- (c) iodine heptafluoride
- (d) carbon tetrachloride

**Answer:** (a)  $\text{PCl}_5$ ; (b)  $\text{N}_2\text{O}$ ; (c)  $\text{IF}_7$ ; (d)  $\text{CCl}_4$

### LINK TO LEARNING

The following [website](#) provides practice with naming chemical compounds and writing chemical formulas. You can choose binary, polyatomic, and variable charge ionic compounds, as well as molecular compounds.

## 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,  $\text{H}^+$ , 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  $\text{HCl}$  (hydrogen chloride) is dissolved in water, the solution is called *hydrochloric acid*. Several other examples of this nomenclature are shown in [Table 4.9](#).

**Table 4.9 Names of Some Simple Acids By: Rice University [OpenStax CC BY-NC-SA 4.0](#)**

Name of Gas	Name of Acid
$\text{HF}(g)$ , hydrogen fluoride	$\text{HF}(aq)$ , hydrofluoric acid
$\text{HCl}(g)$ , hydrogen chloride	$\text{HCl}(aq)$ , hydrochloric acid
$\text{HBr}(g)$ , hydrogen bromide	$\text{HBr}(aq)$ , hydrobromic acid
$\text{HI}(g)$ , hydrogen iodide	$\text{HI}(aq)$ , hydroiodic acid
$\text{H}_2\text{S}(g)$ , hydrogen sulfide	$\text{H}_2\text{S}(aq)$ , 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:

- Omit “hydrogen”
- Start with the root name of the anion
- Replace *-ate* with *-ic*, or *-ite* with *-ous*
- Add “acid”

For example, consider  $\text{H}_2\text{CO}_3$  (which you might be tempted to call “hydrogen carbonate”). To name this correctly, “hydrogen” is omitted; the *-ate* of carbonate is replaced with *-ic*; and acid is added—so its name is carbonic acid. Other examples are given in [Table 4.10](#). There are some exceptions to the general naming method (e.g.,  $\text{H}_2\text{SO}_4$  is called sulfuric acid, not sulfic acid, and  $\text{H}_2\text{SO}_3$  is sulfurous, not sulfous, acid).

**Table 4.10 Names of Common Oxyacids By: Rice University [OpenStax CC BY-NC-SA 4.0](#)**

Formula	Anion Name	Acid Name
$\text{HC}_2\text{H}_3\text{O}_2$	acetate	acetic acid
$\text{HNO}_3$	nitrate	nitric acid
$\text{HNO}_2$	nitrite	nitrous acid
$\text{HClO}_4$	perchlorate	perchloric acid
$\text{H}_2\text{CO}_3$	carbonate	carbonic acid
$\text{H}_2\text{SO}_4$	sulfate	sulfuric acid
$\text{H}_2\text{SO}_3$	sulfite	sulfurous acid
$\text{H}_3\text{PO}_4$	phosphate	phosphoric acid

# LEWIS SYMBOLS AND STRUCTURES (4.4)

OpenStax

---

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

- Write Lewis symbols for neutral atoms and ions
- Draw Lewis structures depicting the bonding in simple molecules

Thus far in this chapter, 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 4.9** shows the Lewis symbols for the elements of the third period of the periodic table.

Atoms	Electronic Configuration	Lewis Symbol
sodium	$[\text{Ne}]3s^1$	$\text{Na} \cdot$
magnesium	$[\text{Ne}]3s^2$	$\cdot \text{Mg} \cdot$
aluminum	$[\text{Ne}]3s^2 3p^1$	$\cdot \overset{\cdot}{\underset{\cdot}{\text{Al}}} \cdot$
silicon	$[\text{Ne}]3s^2 3p^2$	$\cdot \overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{Si}}}} \cdot$
phosphorus	$[\text{Ne}]3s^2 3p^3$	$\cdot \overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{P}}}}} \cdot$
sulfur	$[\text{Ne}]3s^2 3p^4$	$\cdot \overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{S}}}}} \cdot$
chlorine	$[\text{Ne}]3s^2 3p^5$	$\cdot \overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{Cl}}}}} \cdot$
argon	$[\text{Ne}]3s^2 3p^6$	$\cdot \overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{Ar}}}}} \cdot$

**Figure 4.9** Lewis symbols illustrate the number of valence electrons for each element in the third period of the periodic table.

Lewis symbols can also be used to illustrate the formation of cations from atoms, as shown here for sodium and calcium:



**Figure 4.10** By: Rice University [Openstax CC BY NC SA](#)

Likewise, they can be used to show the formation of anions from atoms, as shown here for chlorine and sulfur:



**Figure 4.11** By: Rice University [Openstax CC BY NC SA](#)

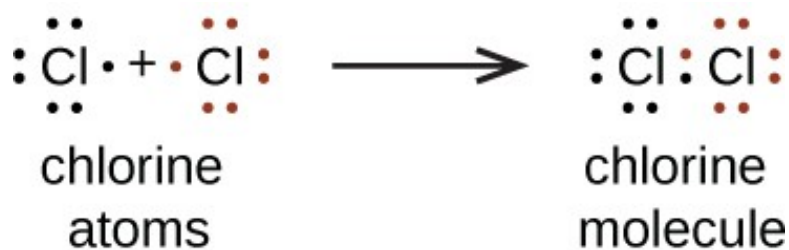
**Figure 4.12** demonstrates the use of Lewis symbols to show the transfer of electrons during the formation of ionic compounds.

Metal		Nonmetal		Ionic Compound
$\text{Na} \cdot$ sodium atom	+	$:\ddot{\text{Cl}} \cdot$ chlorine atom	$\longrightarrow$	$\text{Na}^+ \left[ :\ddot{\text{Cl}}: \right]^-$ sodium chloride (sodium ion and chloride ion)
$\cdot \text{Mg} \cdot$ magnesium atom	+	$:\ddot{\text{O}} \cdot$ oxygen atom	$\longrightarrow$	$\text{Mg}^{2+} \left[ :\ddot{\text{O}}: \right]^{2-}$ magnesium oxide (magnesium ion and oxide ion)
$\cdot \text{Ca} \cdot$ calcium atom	+	$2 :\ddot{\text{F}} \cdot$ fluorine atoms	$\longrightarrow$	$\text{Ca}^{2+} \left[ :\ddot{\text{F}}: \right]_2^-$ calcium fluoride (calcium ion and two fluoride ions)

**Figure 4.12** 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:



**Figure 4.13** By: Rice University [Openstax](#) CC BY NC SA

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 sometimes used to indicate a shared pair of electrons:



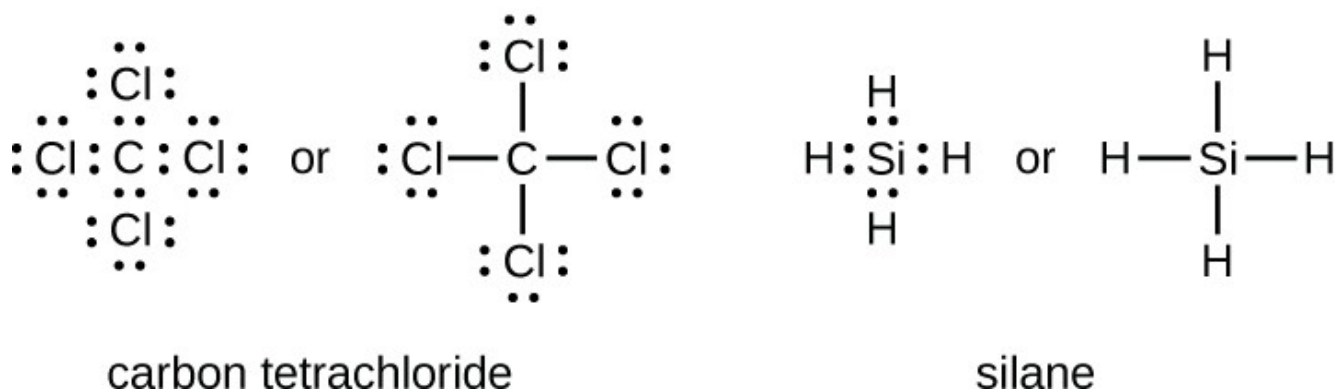
**Figure 4.14** By: Rice University [Openstax](#)  
CC BY NC SA

A single shared pair of electrons is called a **single bond**. Each Cl atom interacts with eight valence electrons: 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**.

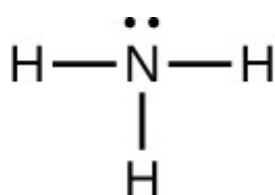
The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons); this is especially true of the nonmetals of the second period of the periodic table (C, N, O, and F). For example, each atom of a group 14 element has four 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. The transition elements and inner transition elements also do not follow the octet rule:



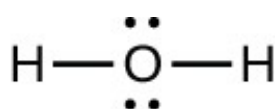
**Figure 4.15** By: Rice University [Openstax](#) CC BY NC SA

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:

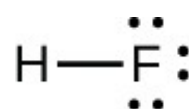




ammonia

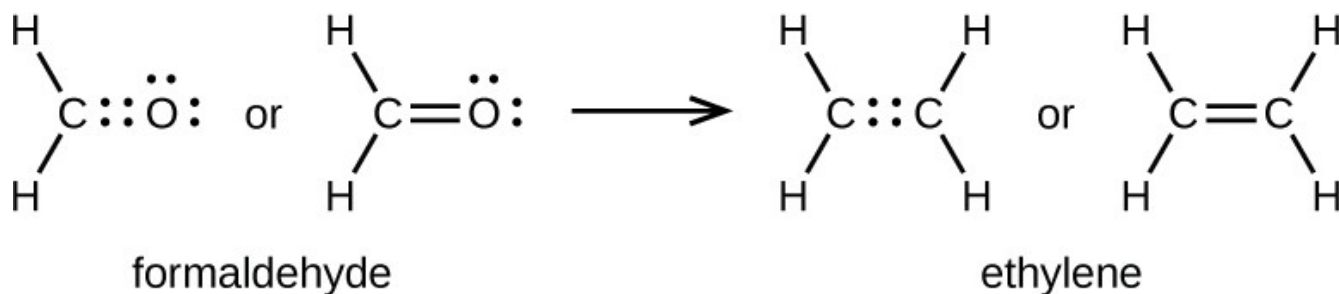


Water

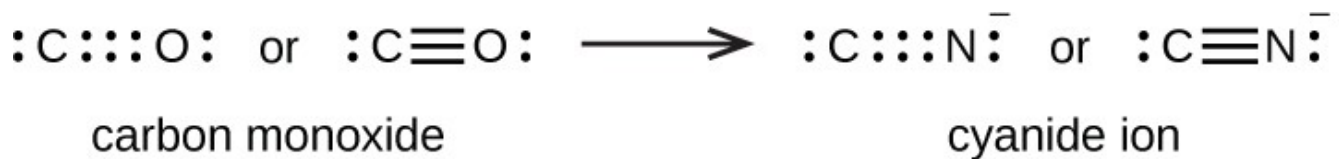
hydrogen  
fluoride**Figure 4.16** By: Rice University [Openstax CC BY NC SA](#)

## 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  $\text{CH}_2\text{O}$  (formaldehyde) and between the two carbon atoms in  $\text{C}_2\text{H}_4$  (ethylene):

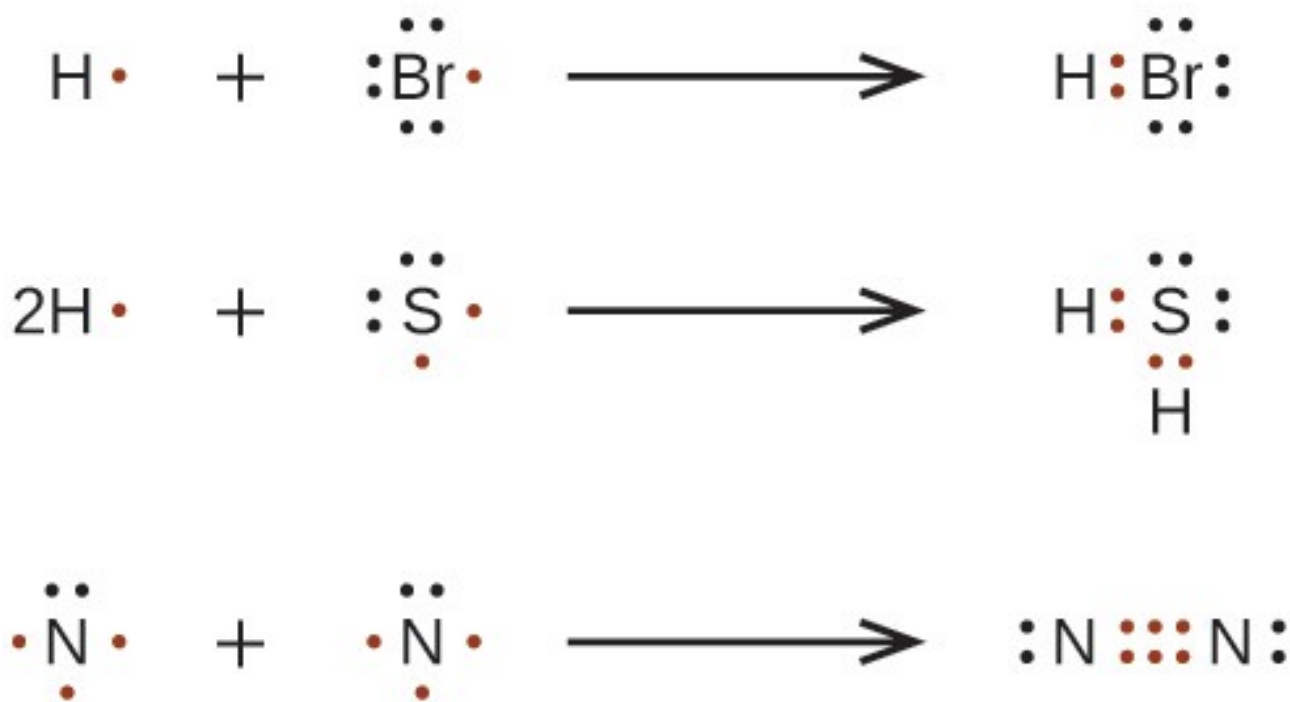
**Figure 4.17** By: Rice University [Openstax CC BY NC SA](#)

A **triple bond** forms when three electron pairs are shared by a pair of atoms, as in carbon monoxide ( $\text{CO}$ ) and the cyanide ion ( $\text{CN}^-$ ):

**Figure 4.18** By: Rice University [Openstax CC BY NC SA](#)

## 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:



**Figure 4.19** By: Rice University [Openstax CC BY NC SA](#)

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. 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<sub>4</sub>, CHO<sub>2</sub><sup>-</sup>, NO<sup>+</sup>, and OF<sub>2</sub> 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:



$$\text{Si: } 4 \text{ valence electrons/atom} \times 1 \text{ atom} = 4$$

$$+ \text{H: } 1 \text{ valence electron/atom} \times 4 \text{ atoms} = 4$$


---

$$= 8 \text{ valence electrons}$$

- For a *negative ion*, such as  $\text{CHO}_2^-$ , 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):



$$\text{C: } 4 \text{ valence electrons/atom} \times 1 \text{ atom} = 4$$

$$\text{H: } 1 \text{ valence electron/atom} \times 1 \text{ atom} = 1$$

$$\text{O: } 6 \text{ valence electrons/atom} \times 2 \text{ atoms} = 12$$

$$+ \quad \quad \quad 1 \text{ additional electron} = 1$$


---

$$= 18 \text{ valence electrons}$$

- For a *positive ion*, such as  $\text{NO}^+$ , 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:



$$\text{N: } 5 \text{ valence electrons/atom} \times 1 \text{ atom} = 5$$

$$\text{O: } 6 \text{ valence electron/atom} \times 1 \text{ atom} = 6$$

$$+ \text{ } -1 \text{ electron (positive charge)} \quad = -1$$


---

$$= 10 \text{ valence electrons}$$

- Since  $\text{OF}_2$  is a neutral molecule, we simply add the number of valence electrons:

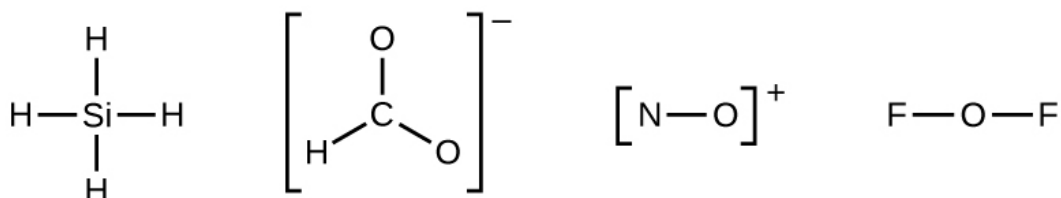


$$\text{O: } 6 \text{ valence electrons/atom} \times 1 \text{ atom} = 6$$

$$+ \text{F: } 7 \text{ valence electrons/atom} \times 2 \text{ atoms} = 14$$

$$= 20 \text{ valence electrons}$$

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):

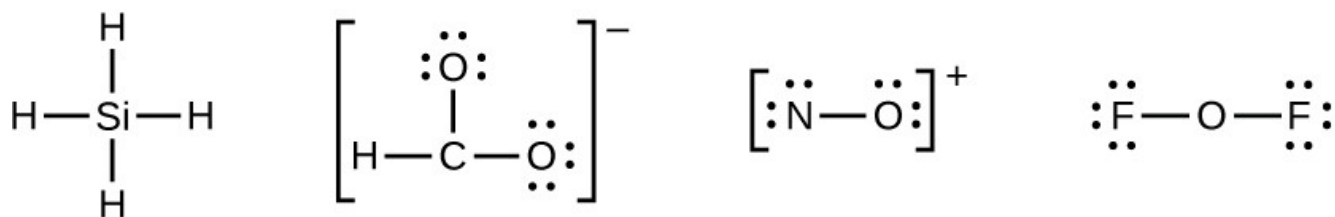


**Figure 4.20** By: Rice University [Openstax CC BY NC SA](#)

When several arrangements of atoms are possible, as for CHO<sub>2</sub><sup>-</sup>, 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<sub>2</sub><sup>-</sup>, the less electronegative carbon atom occupies the central position with the oxygen and hydrogen atoms surrounding it. Other examples include P in POCl<sub>3</sub>, S in SO<sub>2</sub>, and Cl in ClO<sub>4</sub><sup>-</sup>. An exception is that hydrogen is almost never a central atom. As the most electronegative element, fluorine also cannot be a central atom.

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

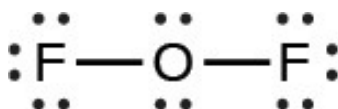
- There are no remaining electrons on SiH<sub>4</sub>, so it is unchanged:



**Figure 4.21** By: Rice University [Openstax CC BY NC SA](#)

4. Place all remaining electrons on the central atom.

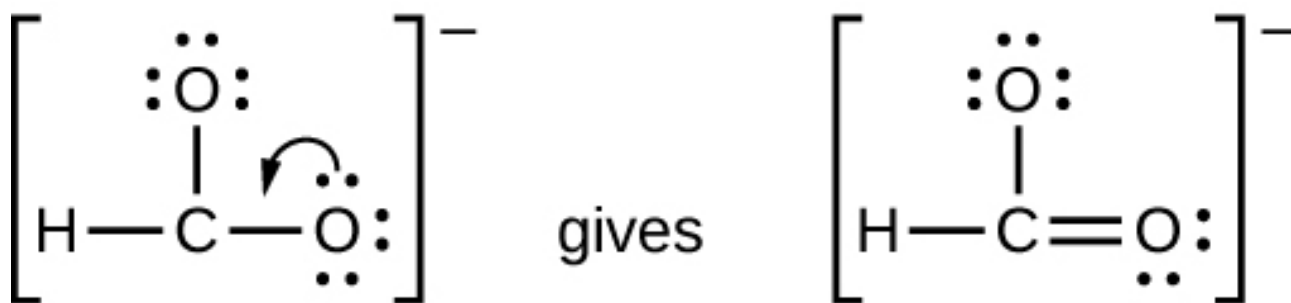
- For  $\text{SiH}_4$ ,  $\text{CHO}_2^-$ , and  $\text{NO}^+$ , there are no remaining electrons; we already placed all of the electrons determined in Step 1.
- For  $\text{OF}_2$ , we had 16 electrons remaining in Step 3, and we placed 12, leaving 4 to be placed on the central atom:



**Figure 4.22** By: Rice University [Openstax CC BY NC SA](#)

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

- $\text{SiH}_4$ : Si already has an octet, so nothing needs to be done.
- $\text{CHO}_2^-$ : We have distributed the valence electrons as lone pairs on the oxygen atoms, but the carbon atom lacks an octet:



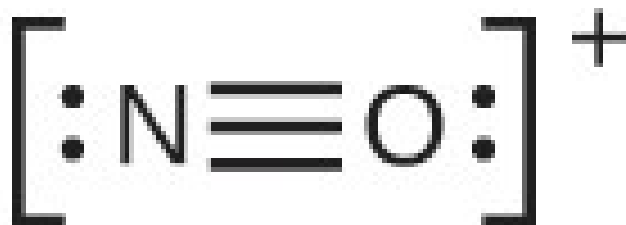
**Figure 4.23** By: Rice University [Openstax CC BY NC SA](#)

- $\text{NO}^+$ : For this ion, we added eight valence 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:



**Figure 4.24** By: Rice University [Openstax](#) [CC BY NC SA](#)

This still does not produce an octet, so we must move another pair, forming a triple bond:



**Figure 4.25** By: Rice University [Openstax](#) [CC BY NC SA](#)

- In  $\text{OF}_2$ , each atom has an octet as drawn, so nothing changes.

## EXAMPLE 4.6

### 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 ( $\text{H}_3\text{CCH}_3$ ), acetylene ( $\text{HCCH}$ ), and ammonia ( $\text{NH}_3$ ). What are the Lewis structures of these molecules?

### Solution

Step 1. *Calculate the number of valence electrons.*

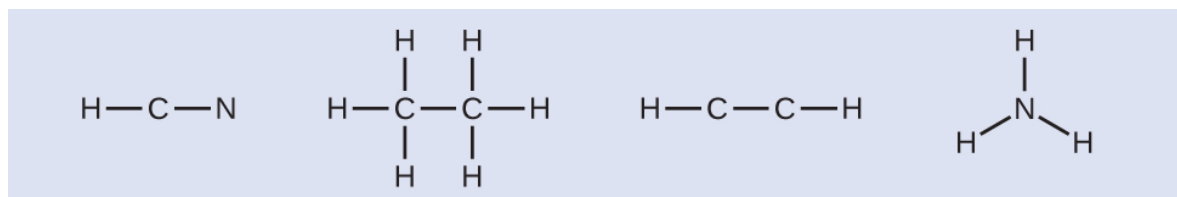
$$\text{HCN: } (1 \times 1) + (4 \times 1) + (5 \times 1) = 10$$

$$\text{H}_3\text{CCH}_3: (1 \times 3) + (2 \times 4) + (1 \times 3) = 14$$

$$\text{HCCH: } (1 \times 1) + (2 \times 4) + (1 \times 1) = 10$$

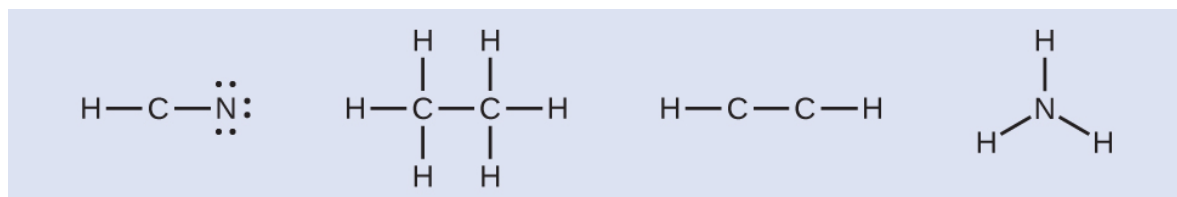
$$\text{NH}_3: (5 \times 1) + (3 \times 1) = 8$$

Step 2. *Draw a skeleton and connect the atoms with single bonds.* Remember that H is never a central atom:



**Figure 4.26** By: Rice University [Openstax CC BY NC SA](#)

Step 3. *Where needed, distribute electrons to the terminal atoms:*



**Figure 4.27** By: Rice University [Openstax CC BY NC SA](#)

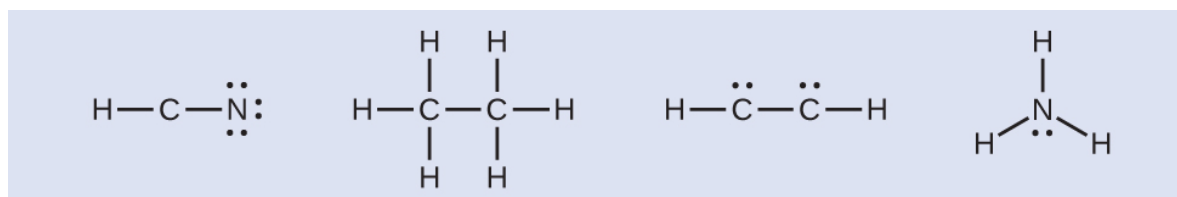
HCN: six electrons placed on N

H<sub>3</sub>CCH<sub>3</sub>: no electrons remain

HCCH: no terminal atoms capable of accepting electrons

NH<sub>3</sub>: no terminal atoms capable of accepting electrons

Step 4. *Where needed, place remaining electrons on the central atom:*



**Figure 4.28** By: Rice University [Openstax CC BY NC SA](#)

HCN: no electrons remain

H<sub>3</sub>CCH<sub>3</sub>: no electrons remain

HCCH: four electrons placed on carbon

NH<sub>3</sub>: two electrons placed on nitrogen

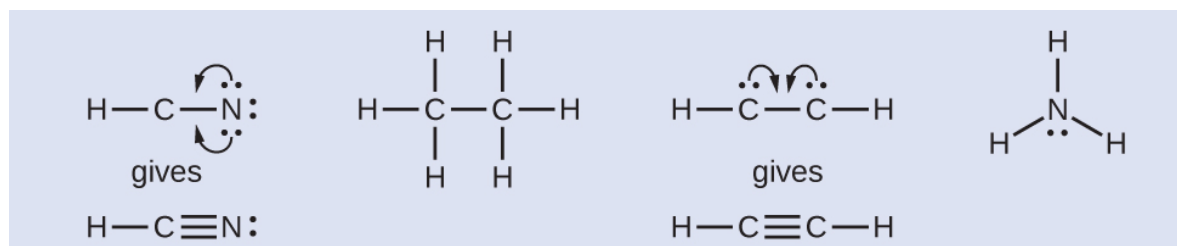
Step 5. *Where needed, rearrange electrons to form multiple bonds in order to obtain an octet on each atom:*

HCN: form two more C–N bonds

H<sub>3</sub>CCH<sub>3</sub>: all atoms have the correct number of electrons

HCCH: form a triple bond between the two carbon atoms

NH<sub>3</sub>: all atoms have the correct number of electrons



**Figure 4.29** By: Rice University [Openstax CC BY NC SA](#)

## Check Your Learning

Both carbon monoxide, CO, and carbon dioxide, CO<sub>2</sub>, are products of the combustion of fossil fuels. Both of these gases also cause problems: CO is toxic, and CO<sub>2</sub> has been implicated in global climate change. What are the Lewis structures of these two molecules?

**Answer:**



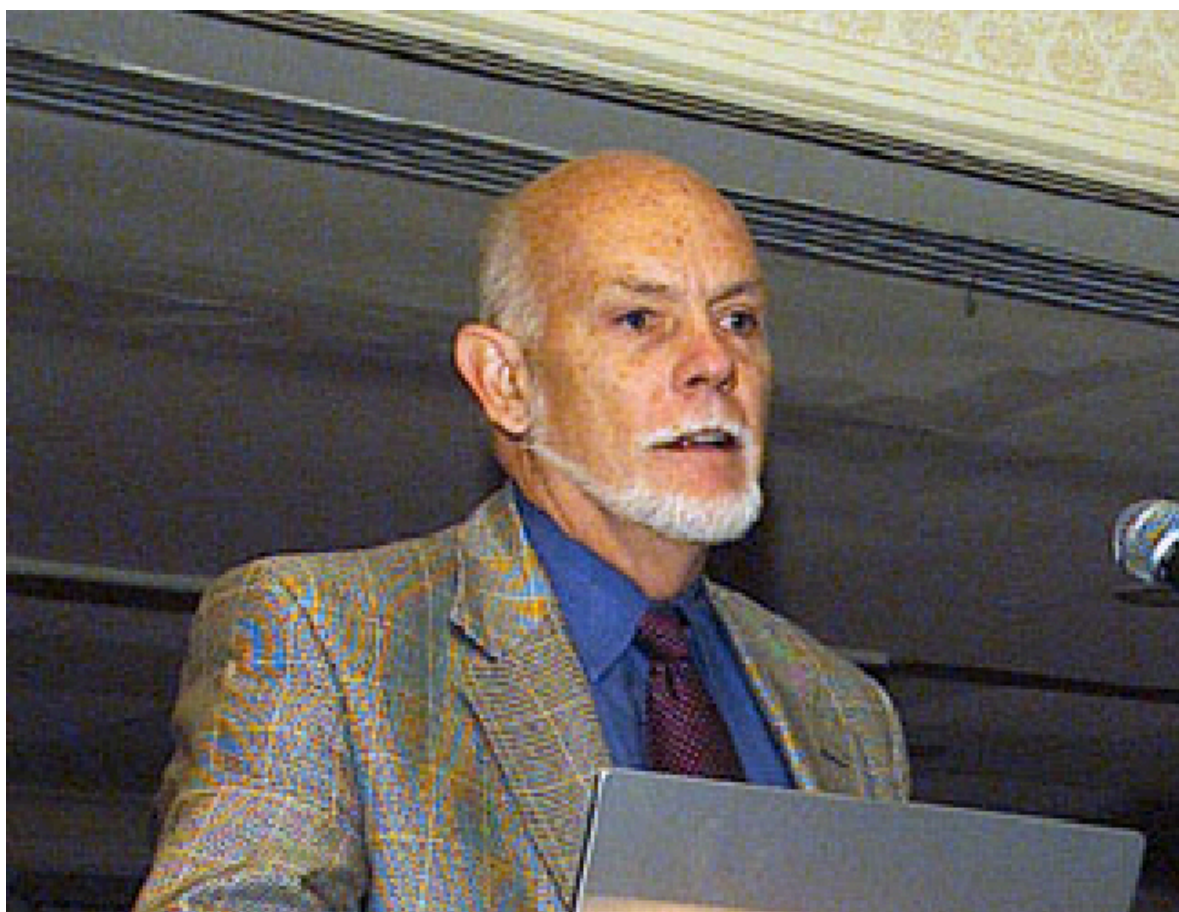
**Figure 4.30** By: Rice University [Openstax CC BY NC SA](#)



## HOW SCIENCES INTERCONNECT

### 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 (**Figure 4.31**), Robert Curl, and Harold Kroto for their work in discovering a new form of carbon, the  $C_{60}$  buckminsterfullerene molecule (**Figure 4.1**). 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, shows promise in a variety of applications. 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.



**Figure 4.31** Richard Smalley (1943–2005), a professor of physics, chemistry, and astronomy at Rice University, was one of the leading advocates for fullerene chemistry. Upon his death in 2005, the US Senate honored him as the “Father of Nanotechnology.” (credit: United States Department of Energy) By: Rice University [Openstax CC BY NC SA](#)

## Exceptions to the Octet Rule

Many covalent molecules have central atoms that do not have eight electrons in their Lewis structures. These molecules fall into three categories:

- Odd-electron molecules have an odd number of valence electrons and therefore have an unpaired electron.
- Electron-deficient molecules have a central atom that has fewer electrons than needed for a noble gas configuration.

- Hypervalent molecules have a central atom that has more electrons than needed for a noble gas configuration.

## Odd-Electron Molecules

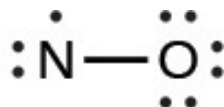
We call molecules that contain an odd number of electrons free radicals. Nitric oxide, NO, is an example of an odd-electron molecule; it is produced in internal combustion engines when oxygen and nitrogen react at high temperatures.

To draw the Lewis structure for an odd-electron molecule like NO, we follow the same five steps we would for other molecules but with a few minor changes:

*Determine the total number of valence (outer shell) electrons.* The sum of the valence electrons is 5 (from N) + 6 (from O) = 11. The odd number immediately tells us that we have a free radical, so we know that not every atom can have eight electrons in its valence shell.

*Draw a skeleton structure of the molecule.* We can easily draw a skeleton with an N–O single bond:  
N–O

*Distribute the remaining electrons as lone pairs on the terminal atoms.* In this case, there is no central atom, so we distribute the electrons around both atoms. We give eight electrons to the more electronegative atom in these situations; thus, oxygen has the filled valence shell:



**Figure 4.32** By:  
Rice University  
[Openstax CC BY](#)  
[NCSA](#)

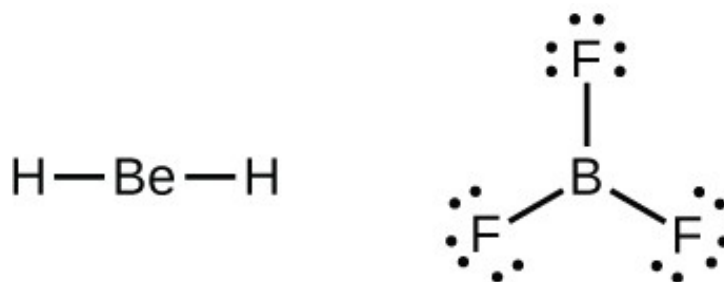
*Place all remaining electrons on the central atom.* Since there are no remaining electrons, this step does not apply. *Rearrange the electrons to make multiple bonds with the central atom in order to obtain octets wherever possible.* We know that an odd-electron molecule cannot have an octet for every atom, but we want to get each atom as close to an octet as possible. In this case, nitrogen has only five electrons around it. To move closer to an octet for nitrogen, we take one of the lone pairs from oxygen and use it to form a NO double bond (we cannot take another lone pair of electrons on oxygen and form a triple bond because nitrogen would then have nine electrons):



**Figure 4.33** By:  
Rice University  
[Openstax CC BY](#)  
[NC SA](#)

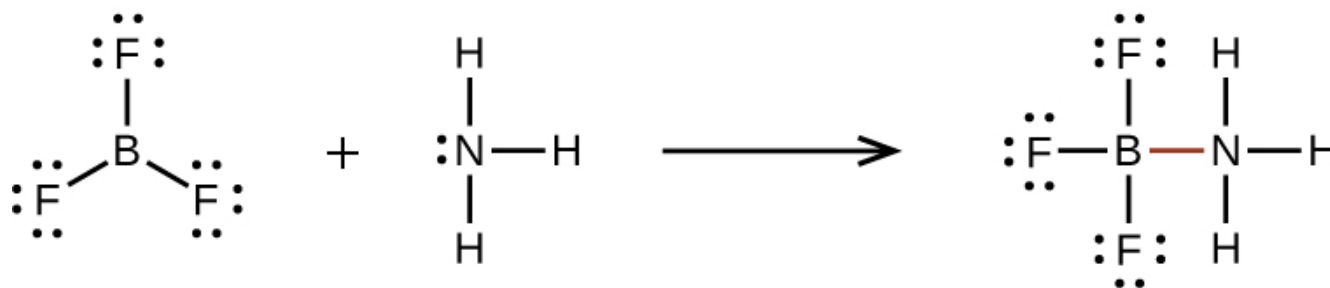
## Electron-Deficient Molecules

We will also encounter a few molecules that contain central atoms that do not have a filled valence shell. Generally, these are molecules with central atoms from groups 2 and 13, outer atoms that are hydrogen, or other atoms that do not form multiple bonds. For example, in the Lewis structures of beryllium dihydride,  $\text{BeH}_2$ , and boron trifluoride,  $\text{BF}_3$ , the beryllium and boron atoms each have only four and six electrons, respectively. It is possible to draw a structure with a double bond between a boron atom and a fluorine atom in  $\text{BF}_3$ , satisfying the octet rule, but experimental evidence indicates the bond lengths are closer to that expected for B–F single bonds. This suggests the best Lewis structure has three B–F single bonds and an electron-deficient boron. The reactivity of the compound is also consistent with an electron-deficient boron. However, the B–F bonds are slightly shorter than what is actually expected for B–F single bonds, indicating that some double bond character is found in the actual molecule.



**Figure 4.34** By: Rice University [Openstax CC BY NC SA](#)

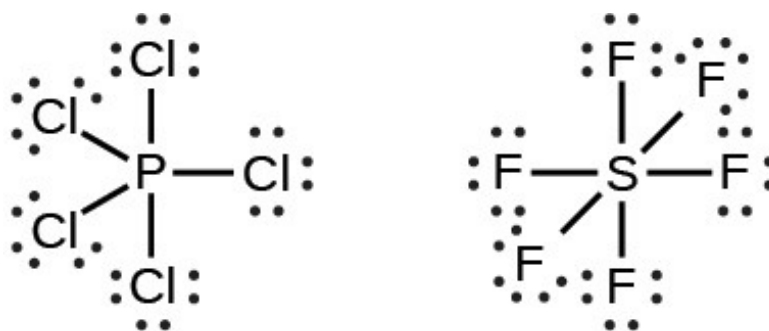
An atom like the boron atom in  $\text{BF}_3$ , which does not have eight electrons, is very reactive. It readily combines with a molecule containing an atom with a lone pair of electrons. For example,  $\text{NH}_3$  reacts with  $\text{BF}_3$  because the lone pair on nitrogen can be shared with the boron atom:



**Figure 4.35** By: Rice University [Openstax CC BY NC SA](#)

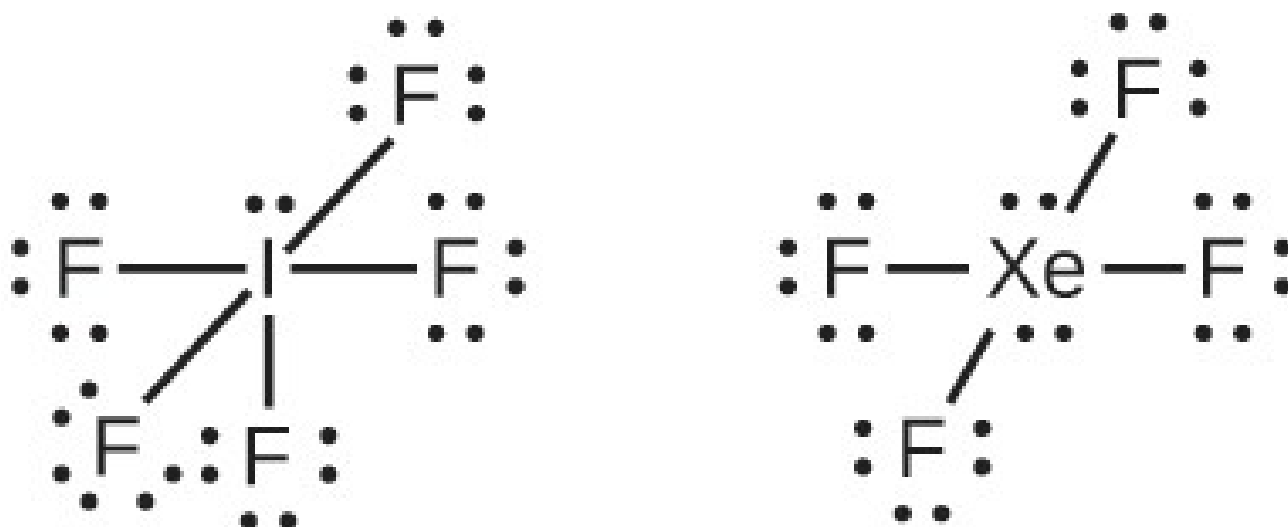
## Hypervalent Molecules

Elements in the second period of the periodic table ( $n = 2$ ) can accommodate only eight electrons in their valence shell orbitals because they have only four valence orbitals (one  $2s$  and three  $2p$  orbitals). Elements in the third and higher periods ( $n \geq 3$ ) have more than four valence orbitals and can share more than four pairs of electrons with other atoms because they have empty  $d$  orbitals in the same shell. Molecules formed from these elements are sometimes called hypervalent molecules. **Figure 4.36** shows the Lewis structures for two hypervalent molecules,  $\text{PCl}_5$  and  $\text{SF}_6$ .



**Figure 4.36** In  $\text{PCl}_5$ , the central atom phosphorus shares five pairs of electrons. In  $\text{SF}_6$ , sulfur shares six pairs of electrons. By: Rice University [Openstax CC BY NC SA](#)

In some hypervalent molecules, such as  $\text{IF}_5$  and  $\text{XeF}_4$ , some of the electrons in the outer shell of the central atom are lone pairs:



**Figure 4.37** By: Rice University [Openstax CC BY NC SA](#)

When we write the Lewis structures for these molecules, we find that we have electrons left over after filling the valence shells of the outer atoms with eight electrons. These additional electrons must be assigned to the central atom.

## EXAMPLE 4.7

### Writing Lewis Structures: Octet Rule Violations

Xenon is a noble gas, but it forms a number of stable compounds. We examined XeF<sub>4</sub> earlier. What are the Lewis structures of XeF<sub>2</sub> and XeF<sub>6</sub>?

### Solution

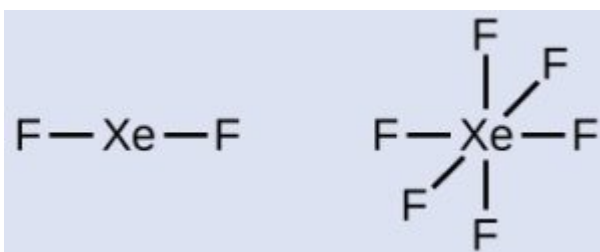
We can draw the Lewis structure of any covalent molecule by following the six steps discussed earlier. In this case, we can condense the last few steps, since not all of them apply.

Step 1. *Calculate the number of valence electrons:*

$$\text{XeF}_2: 8 + (2 \times 7) = 22$$

$$\text{XeF}_6: 8 + (6 \times 7) = 50$$

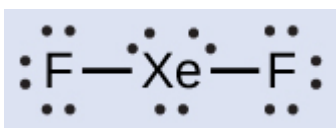
Step 2. *Draw a skeleton joining the atoms by single bonds.* Xenon will be the central atom because fluorine cannot be a central atom:



**Figure 4.38** By:  
Rice University  
[Openstax CC BY](#)  
[NC SA](#)

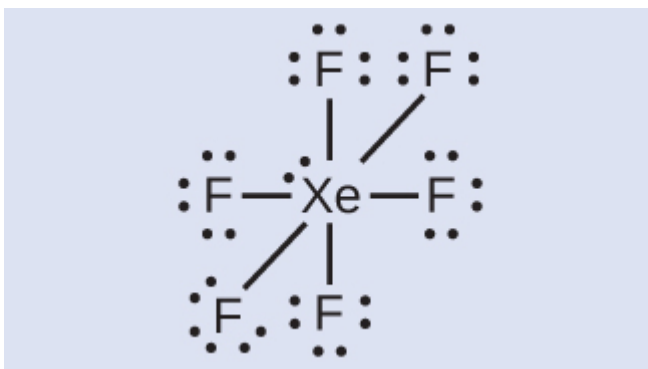
Step 3. *Distribute the remaining electrons.*

$\text{XeF}_2$ : We place three lone pairs of electrons around each F atom, accounting for 12 electrons and giving each F atom 8 electrons. Thus, six electrons (three lone pairs) remain. These lone pairs must be placed on the Xe atom. This is acceptable because Xe atoms have empty valence shell  $d$  orbitals and can accommodate more than eight electrons. The Lewis structure of  $\text{XeF}_2$  shows two bonding pairs and three lone pairs of electrons around the Xe atom:



**Figure 4.38** By:  
Rice University  
[Openstax CC BY](#)  
[NC SA](#)

$\text{XeF}_6$ : We place three lone pairs of electrons around each F atom, accounting for 36 electrons. Two electrons remain, and this lone pair is placed on the Xe atom:

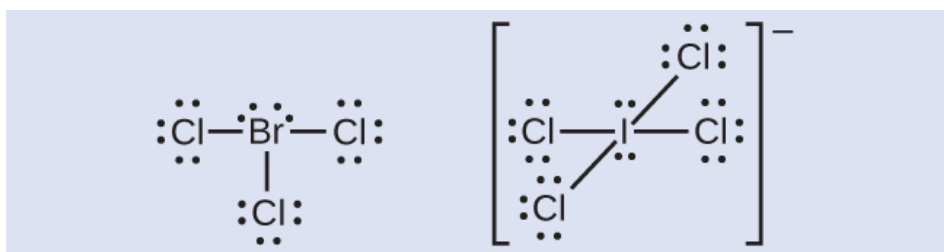


**Figure 4.40** By:  
Rice University  
[Openstax CC BY](#)  
[NC SA](#)

### Check Your Learning

The halogens form a class of compounds called the interhalogens, in which halogen atoms covalently bond to each other. Write the Lewis structures for the interhalogens  $\text{BrCl}_3$  and  $\text{ICl}_4^-$ .

**Answer:**



**Figure 4.41** By:  
Rice University  
[Openstax CC BY](#)  
[NC SA](#)



# FORMAL CHARGES AND RESONANCE (4.5)

OpenStax

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

- Compute formal charges for atoms in any Lewis structure
- Use formal charges to identify the most reasonable Lewis structure for a given molecule
- Explain the concept of resonance and draw Lewis structures representing resonance forms for a given molecule

In the previous section, we discussed how to write Lewis structures for molecules and polyatomic ions. As we have seen, however, in some cases, there is seemingly more than one valid structure for a molecule. We can use the concept of formal charges to help us predict the most appropriate Lewis structure when more than one is reasonable.

## Calculating Formal Charge

The **formal charge** of an atom in a molecule is the *hypothetical* charge the atom would have if we could redistribute the electrons in the bonds evenly between the atoms. Another way of saying this is that formal charge results when we take the number of valence electrons of a neutral atom, subtract the nonbonding electrons, and then subtract the number of bonds connected to that atom in the Lewis structure.

Thus, we calculate the formal charge as follows:

$$\text{formal charge} = \# \text{ valence shell electrons (free atom)} - \# \text{ lone pair electrons} - \frac{1}{2} \# \text{ bonding electrons}$$

We can double-check formal charge calculations by determining the sum of the formal charges for the whole structure. The sum of the formal charges of all atoms in a molecule must be zero; the sum of the formal charges in an ion should equal the charge of the ion.

We must remember that the formal charge calculated for an atom is not the *actual* charge of the atom in the molecule. The formal charge is only a useful bookkeeping procedure; it does not indicate the presence of actual charges.

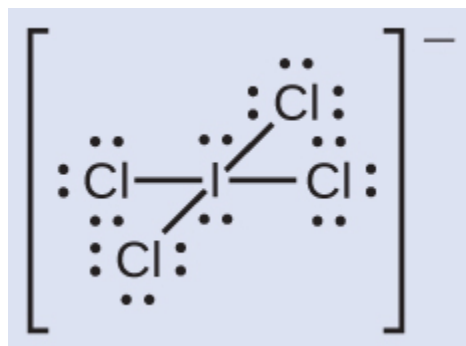
## EXAMPLE 4.8

## Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen ion  $\text{ICl}_4^-$ .

## Solution

Step 1. We divide the bonding electron pairs equally for all I–Cl bonds:



**Figure 4.42** By: Rice University  
Openstax CC BY NC SA

Step 2. We assign lone pairs of electrons to their atoms. Each Cl atom now has seven electrons assigned to it, and the I atom has eight.

Step 3. Subtract this number from the number of valence electrons for the neutral atom:

$$\text{I: } 7 - 8 = -1$$

$$\text{Cl: } 7 - 7 = 0$$

The sum of the formal charges of all the atoms equals  $-1$ , which is identical to the charge of the ion ( $-1$ ).

## Check Your Learning

Calculate the formal charge for each atom in the carbon monoxide molecule:



**Figure 4.43** By:  
Rice University  
[Openstax CC BY NC](#)  
[SA](#)

**Answer:** C -1, O +1

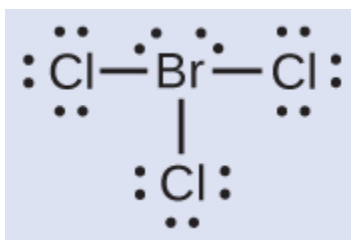
## EXAMPLE 4.9

### Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen molecule  $\text{BrCl}_3$ .

#### Solution

Step 1. *Assign one of the electrons in each Br–Cl bond to the Br atom and one to the Cl atom in that bond:*



**Figure 4.44** By: Rice  
University [Openstax CC BY NC](#)  
[SA](#)

Step 2. *Assign the lone pairs to their atom.* Now each Cl atom has seven electrons, and the Br atom has seven electrons.

Step 3. Subtract this number from the number of valence electrons for the neutral atom. This gives the formal charge:

$$\text{Br: } 7 - 7 = 0$$

$$\text{Cl: } 7 - 7 = 0$$

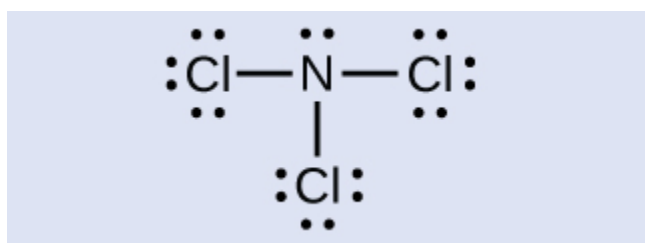
All atoms in  $\text{BrCl}_3$  have a formal charge of zero, and the sum of the formal charges totals zero, as it must in a neutral molecule.

### Check Your Learning

Determine the formal charge for each atom in  $\text{NCl}_3$ .

**Answer:**

N: 0; all three Cl atoms: 0



**Figure 4.45** By: Rice University [Openstax CC BY NC SA](#)

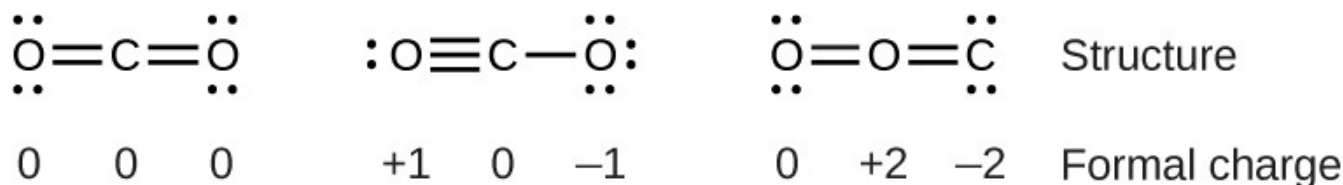
## Using Formal Charge to Predict Molecular Structure

The arrangement of atoms in a molecule or ion is called its molecular structure. In many cases, following the steps for writing Lewis structures may lead to more than one possible molecular structure—different multiple-bond and lone-pair electron placements or different arrangements of atoms, for instance. A few guidelines involving formal charge can be helpful in deciding which of the possible structures is most likely for a particular molecule or ion:

1. A molecular structure in which all formal charges are zero is preferable to one in which some formal charges are not zero.
2. If the Lewis structure must have nonzero formal charges, the arrangement with the smallest nonzero formal charges is preferable.
3. Lewis structures are preferable when adjacent formal charges are zero or of the opposite sign.

4. When we must choose among several Lewis structures with similar distributions of formal charges, the structure with the negative formal charges on the more electronegative atoms is preferable.

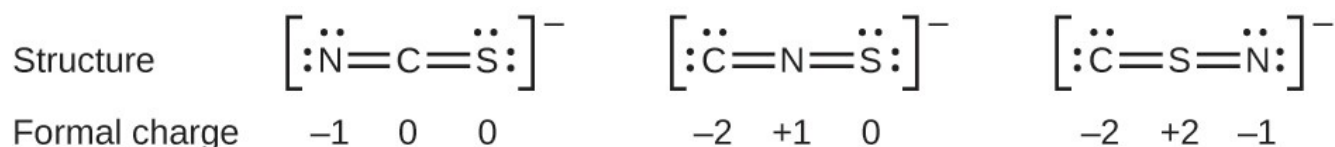
To see how these guidelines apply, let us consider some possible structures for carbon dioxide,  $\text{CO}_2$ . We know from our previous discussion that the less electronegative atom typically occupies the central position, but formal charges allow us to understand *why* this occurs. We can draw three possibilities for the structure: carbon in the center and double bonds, carbon in the center with a single and triple bond, and oxygen in the center with double bonds:



**Figure 4.46** By: Rice University [Openstax CC BY NC SA](#)

Comparing the three formal charges, we can definitively identify the structure on the left as preferable because it has only formal charges of zero (Guideline 1).

As another example, the thiocyanate ion, an ion formed from a carbon atom, a nitrogen atom, and a sulfur atom, could have three different molecular structures:  $\text{NCS}^-$ ,  $\text{CNS}^-$ , or  $\text{CSN}^-$ . The formal charges present in each of these molecular structures can help us pick the most likely arrangement of atoms. Possible Lewis structures and the formal charges for each of the three possible structures for the thiocyanate ion are shown here:



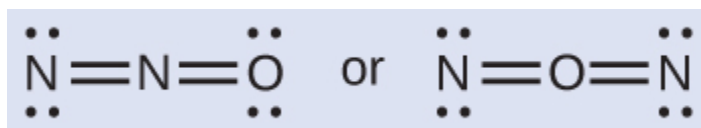
**Figure 4.47** By: Rice University [Openstax CC BY NC SA](#)

Note that the sum of the formal charges in each case is equal to the charge of the ion ( $-1$ ). However, the first arrangement of atoms is preferred because it has the lowest number of atoms with nonzero formal charges (Guideline 2). Also, it places the least electronegative atom in the center and the negative charge on the more electronegative element (Guideline 4).

## EXAMPLE 4.10

## Using Formal Charge to Determine Molecular Structure

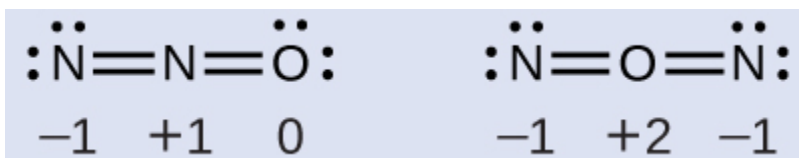
Nitrous oxide,  $\text{N}_2\text{O}$ , commonly known as laughing gas, is used as an anesthetic in minor surgeries, such as the routine extraction of wisdom teeth. Which is the likely structure for nitrous oxide?



**Figure 4.48** By: Rice University [Openstax CC BY NC SA](#)

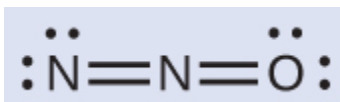
## Solution

Determining formal charge yields the following:



**Figure 4.49** By: Rice University [Openstax CC BY NC SA](#)

The structure with a terminal oxygen atom best satisfies the criteria for the most stable distribution of formal charge:

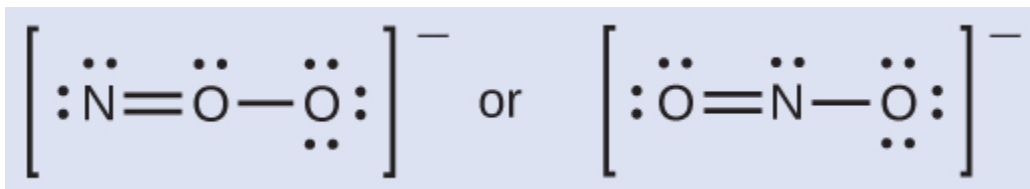


**Figure 4.50** By: Rice University [Openstax CC BY NC SA](#)

The number of atoms with formal charges is minimized (Guideline 2), and there is no formal charge larger than one (Guideline 2). This is again consistent with the preference for having the less electronegative atom in the central position.

### Check Your Learning

Which is the most likely molecular structure for the nitrite  $\text{NO}_2^-$  ion?



**Figure 4.51** By: Rice University [Openstax CC BY NC SA](#)

**Answer:**  $\text{ONO}^-$

## Resonance

Notice that the more likely structure for the nitrite anion in Example 4.10 may actually be drawn in two different ways, distinguished by the locations of the N-O and N=O bonds:

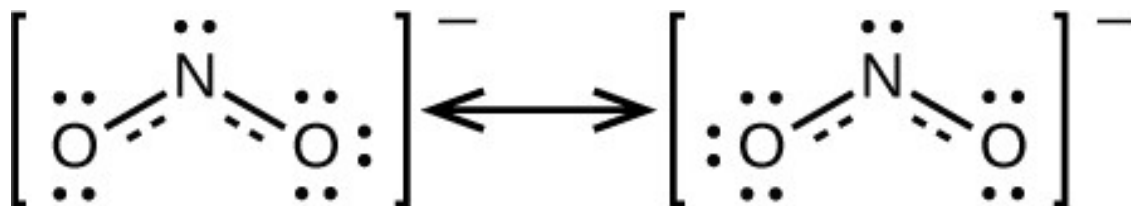


**Figure 4.52** By: Rice University [Openstax CC BY NC SA](#)

If nitrite ions do indeed contain a single and a double bond, we would expect the two bond lengths to be different. A double bond between two atoms is shorter (and stronger) than a single bond between the same two atoms. Experiments show, however, that both N-O bonds in  $\text{NO}_2^-$  have the same strength and length and are identical in all other properties.

It is not possible to write a single Lewis structure for  $\text{NO}_2^-$  in which nitrogen has an octet and both bonds are equivalent. Instead, we use the concept of resonance: If two or more Lewis structures with the same arrangement of atoms can be written for a molecule or ion, the actual distribution of electrons is an *average* of that shown by the various Lewis structures. The actual distribution of electrons in each of the nitrogen-oxygen bonds in  $\text{NO}_2^-$  is the average of a double bond and a single bond. We call the individual

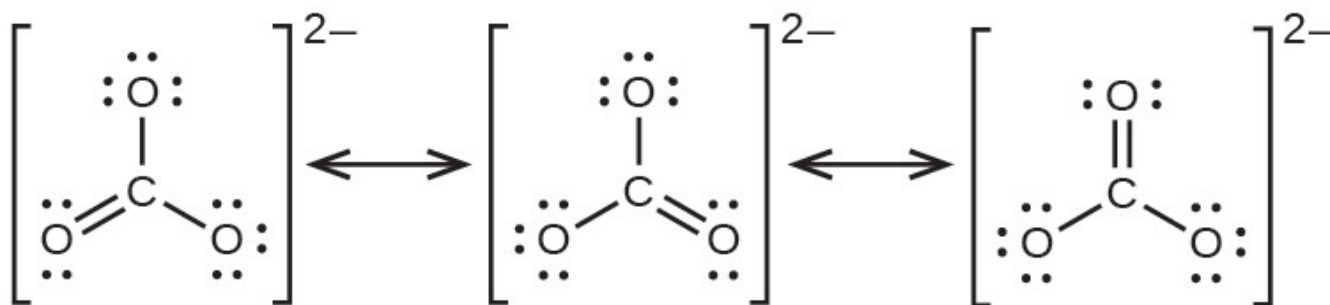
Lewis structures resonance forms. The actual electronic structure of the molecule (the average of the resonance forms) is called a resonance hybrid of the individual resonance forms. A double-headed arrow between Lewis structures indicates that they are resonance forms.



**Figure 4.53** By: Rice University [Openstax CC BY NC SA](#)

We should remember that a molecule described as a resonance hybrid *never* possesses an electronic structure described by either resonance form. It does not fluctuate between resonance forms; rather, the actual electronic structure is *always* the average of that shown by all resonance forms. George Wheland, one of the pioneers of resonance theory, used a historical analogy to describe the relationship between resonance forms and resonance hybrids. A medieval traveler, having never before seen a rhinoceros, described it as a hybrid of a dragon and a unicorn because it had many properties in common with both. Just as a rhinoceros is neither a dragon sometimes nor a unicorn at other times, a resonance hybrid is neither of its resonance forms at any given time. Like a rhinoceros, it is a real entity that experimental evidence has shown to exist. It has some characteristics in common with its resonance forms, but the resonance forms themselves are convenient, imaginary images (like the unicorn and the dragon).

The carbonate anion,  $\text{CO}_3^{2-}$ , provides a second example of resonance:



**Figure 4.54** By: Rice University [Openstax CC BY NC SA](#)

One oxygen atom must have a double bond to carbon to complete the octet on the central atom. All oxygen atoms, however, are equivalent, and the double bond could form from any one of the three atoms. This gives rise to three resonance forms of the carbonate ion. Because we can write three identical resonance structures, we know that the actual arrangement of electrons in the carbonate ion is the average of the three structures. Again, experiments show that all three C–O bonds are exactly the same.



## LINK TO LEARNING

Use this [online quiz](#) to practice your skills in drawing resonance structures and estimating formal charges.

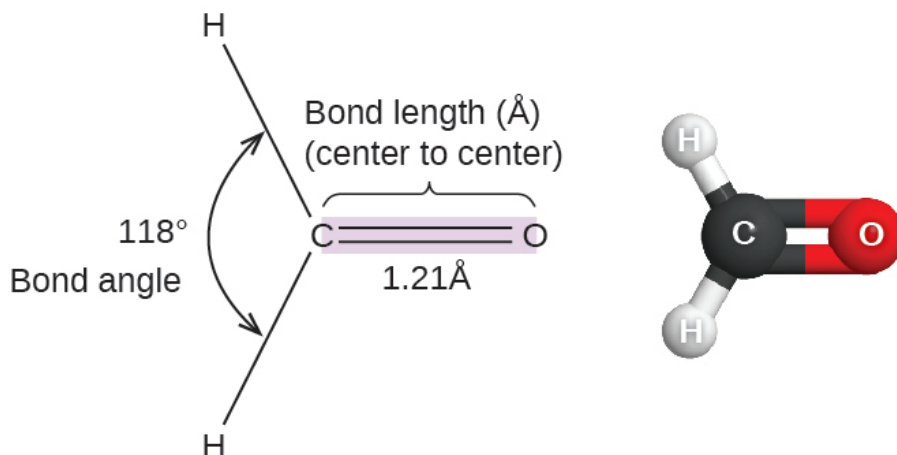
# MOLECULAR STRUCTURE AND POLARITY (4.6)

OpenStax

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

- 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, the 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 4.55**). 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 ( $1 \text{ Å} = 10^{-10} \text{ m}$ ) or picometers ( $1 \text{ pm} = 10^{-12} \text{ m}$ ,  $100 \text{ pm} = 1 \text{ Å}$ ).



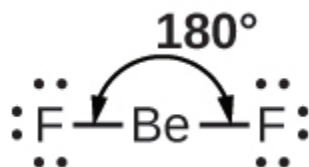
**Figure 4.55** Bond distances (lengths) and angles are shown for the formaldehyde molecule, H<sub>2</sub>CO. By: Rice University [Openstax CC BY NC SA](#)

## 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.

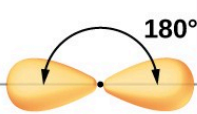
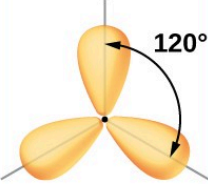
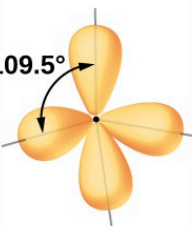
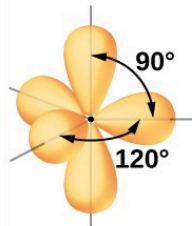
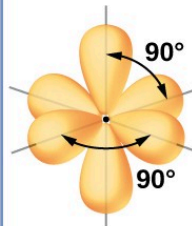
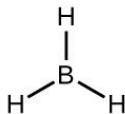
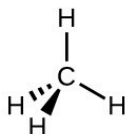
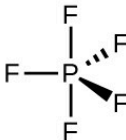

VSEPR theory predicts the arrangement of electron pairs around each central atom and, usually, the correct arrangement of atoms in a molecule. We should understand, however, that the theory only considers electron-pair repulsions. Other interactions, such as nuclear-nuclear repulsions and nuclear-electron 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  $\text{BeF}_2$  molecule. The Lewis structure of  $\text{BeF}_2$  (**Figure 4.56**) 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  $180^\circ$  (**Figure 4.56**).



**Figure 4.56** The  $\text{BeF}_2$  molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the Be atom. By: Rice University [Openstax CC BY NC SA](#)

**Figure 4.57** 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	$\text{H}-\text{Be}-\text{H}$				
Electron pair geometry	Linear; $180^\circ$ angle	Trigonal planar; all angles $120^\circ$	Tetrahedral; all angles $109.5^\circ$	Trigonal bipyramidal; angles of $90^\circ$ or $120^\circ$ 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 $90^\circ$ or $180^\circ$

**Figure 4.57** The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs). By: Rice University [Openstax CC BY NC SA](#)

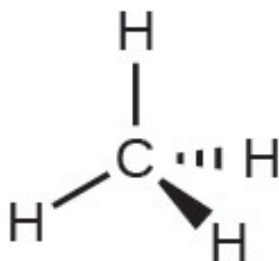
## Electron-Pair Geometry versus Molecular Structure

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 4.57** describe all regions where electrons are located, bonds as well as lone pairs. Molecular structure describes the location of the *atoms*, not the electrons.

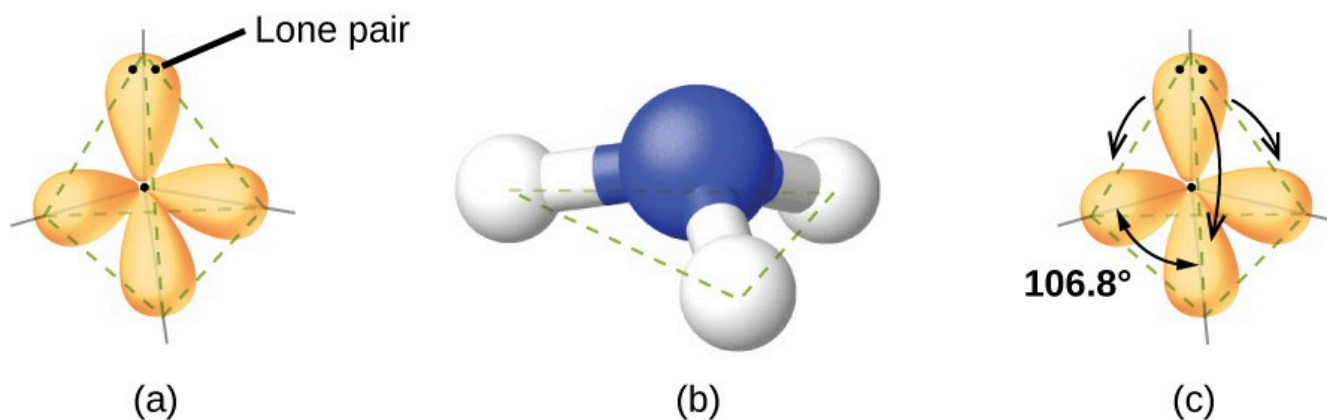
We differentiate between these two situations by naming the geometry that includes *all* electron pairs the **electron-pair geometry**. The structure that includes only the placement of the atoms in the molecule is called the **molecular structure**. The electron-pair geometries will be the same as the 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.

For example, the methane molecule,  $\text{CH}_4$ , 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 4.58**). On the other hand, the ammonia molecule,  $\text{NH}_3$ , 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 4.59**).



**Figure 4.58** The molecular structure of the methane molecule,  $\text{CH}_4$ , 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. By: Rice University [Openstax](#) [CC BY NC SA](#)



**Figure 4.59** (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  $109.5^\circ$ . By: Rice University [Openstax CC BY NC SA](#)

As seen in **Figure 4.59**, small distortions from the ideal angles in **Figure 4.57** 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:

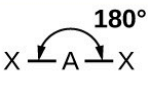
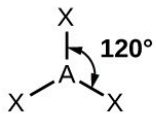

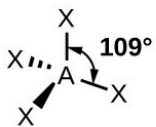
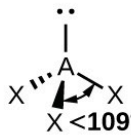

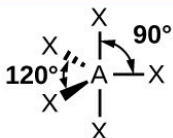
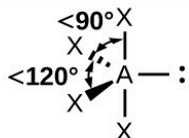
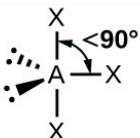
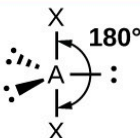

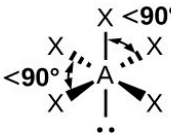
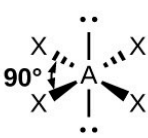
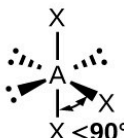
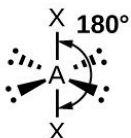
$$\text{lone pair-lone pair} > \text{lone pair-bonding pair} > \text{bonding pair-bonding pair}$$

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:

$$\text{lone pair} > \text{triple bond} > \text{double bond} > \text{single bond}$$

Consider formaldehyde,  $\text{H}_2\text{CO}$ , which is used as a preservative for biological and anatomical specimens (**Figure 4.55**). 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  $120^\circ$  bond angles, but we see that the double bond causes slightly larger angles ( $121^\circ$ ), and the angle between the single bonds is slightly smaller ( $118^\circ$ ).

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 4.59**) with the nitrogen atom at the apex and the three hydrogen atoms forming the base. The ideal bond angles in a trigonal pyramid are based on the tetrahedral electron pair geometry. Again, there are slight deviations from the ideal because lone pairs occupy larger regions of space than bonding electrons. The H–N–H bond angles in  $\text{NH}_3$  are slightly smaller than the  $109.5^\circ$  angle in a regular tetrahedron (**Figure 4.55**) because the lone pair-bonding pair repulsion is greater than the bonding pair-bonding pair repulsion (**Figure 4.59**). **Figure 4.60** illustrates the ideal molecular structures, which are predicted based on the electron-pair geometries for various combinations of lone pairs and bonding pairs.

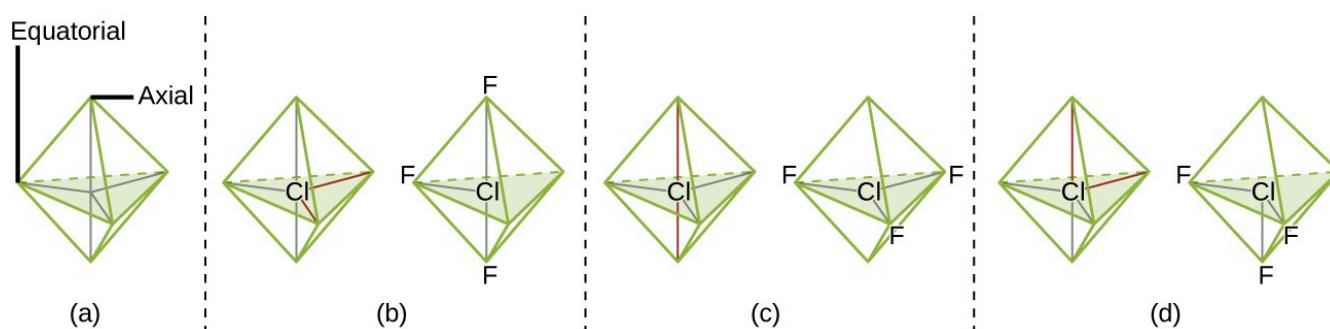
Number of electron pairs	Electron pair geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal planar	 Bent or angular			
4	 Tetrahedral	 Trigonal pyramid	 Bent or angular		
5	 Trigonal bipyramid	 Sawhorse or seesaw	 T-shape	 Linear	
6	 Octahedral	 Square pyramid	 Square planar	 T-shape	 Linear

**Figure 4.60** 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. By: Rice University [Openstax CC BY NC SA](#)

According to VSEPR theory, the terminal atom locations (Xs in **Figure 4.60**) are equivalent within the linear, trigonal planar, and tetrahedral electron-pair geometries (the first three rows of the table). It does not matter which X is replaced with a lone pair because the molecules can be rotated to convert positions. For trigonal bipyramidal electron-pair geometries, however, there are two distinct X positions, as shown in **Figure 4.61**: an **axial position** (if we hold a model of a trigonal bipyramid by the two axial positions, we have an axis around which we can rotate the model) and an **equatorial position** (three positions form an equator around the middle of the molecule). As shown in **Figure 4.60**, the axial position is surrounded by bond angles of  $90^\circ$ , whereas the equatorial position has more space available because of the  $120^\circ$  bond angles. In a trigonal

bipyramidal electron-pair geometry, lone pairs always occupy equatorial positions because these more spacious positions can more easily accommodate the larger lone pairs.

Theoretically, we can come up with three possible arrangements for the three bonds and two lone pairs for the  $\text{ClF}_3$  molecule (**Figure 4.61**). The stable structure is the one that puts the lone pairs in equatorial locations, giving a T-shaped molecular structure.



**Figure 4.61** (a) In a trigonal bipyramid, the two axial positions are located directly across from one another, whereas the three equatorial positions are located in a triangular arrangement. (b–d) The two lone pairs (red lines) in  $\text{ClF}_3$  have several possible arrangements, but the T-shaped molecular structure (b) is the one actually observed, consistent with the larger lone pairs both occupying equatorial positions. By: Rice University [Openstax CC BY NC SA](#)

When a central atom has two lone electron pairs and four bonding regions, we have an octahedral electron-pair geometry. The two lone pairs are on opposite sides of the octahedron ( $180^\circ$  apart), giving a square planar molecular structure that minimizes lone pair-lone pair repulsions (**Figure 4.60**).

## 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 4.60**, first column).
4. Use the number of lone pairs to determine the molecular structure (**Figure 4.60**). 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.



## EXAMPLE 4.11

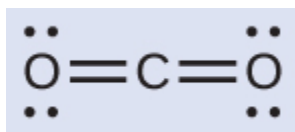
**Predicting Electron-Pair Geometry and Molecular Structure:  $\text{CO}_2$  and  $\text{BCl}_3$** 

Predict the electron-pair geometry and molecular structure for each of the following:

- (a) carbon dioxide,  $\text{CO}_2$ , a molecule produced by the combustion of fossil fuels
- (b) boron trichloride,  $\text{BCl}_3$ , an important industrial chemical

**Solution**

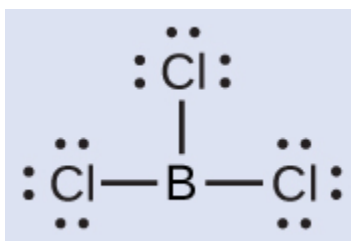
(a) We write the Lewis structure of  $\text{CO}_2$  as:



**Figure 4.62** By: Rice University  
Openstax CC BY NC SA

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  $180^\circ$ . The electron-pair geometry and molecular structure are identical, and  $\text{CO}_2$  molecules are linear.

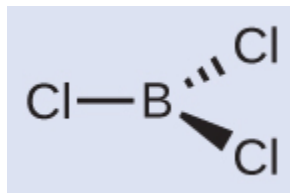
(b) We write the Lewis structure of  $\text{BCl}_3$  as:



**Figure 4.63** By: Rice University  
Openstax CC BY NC SA

Thus we see that  $\text{BCl}_3$  contains three bonds, and there are no lone pairs of electrons on boron.

The arrangement of three regions of high electron density gives a trigonal planar electron-pair geometry. The B–Cl bonds lie in a plane with  $120^\circ$  angles between them.  $\text{BCl}_3$  also has a trigonal planar molecular structure (**Figure 4.64**).



**Figure 4.64** By: Rice University [Openstax CC BY NC SA](#)

The electron-pair geometry and molecular structure of  $\text{BCl}_3$  are both trigonal planar. Note that the VSEPR geometry indicates the correct bond angles ( $120^\circ$ ), unlike the Lewis structure shown above.

### Check Your Learning

Carbonate,  $\text{CO}_3^{2-}$ , 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.

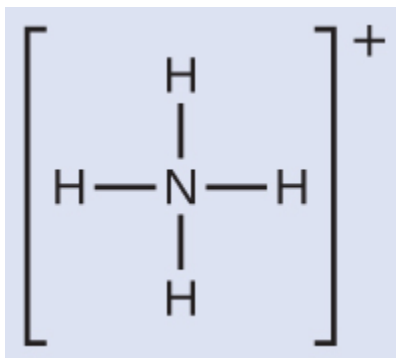
## EXAMPLE 4.12

### Predicting Electron-Pair Geometry and Molecular Structure: Ammonium

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  $\text{NH}_4^+$  cation.

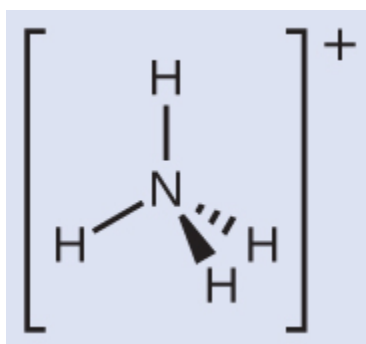
## Solution

We write the Lewis structure of  $\text{NH}_4^+$  as:



**Figure 4.65** By: Rice University  
[Openstax CC BY NC SA](#)

We can see that  $\text{NH}_4^+$  contains four bonds from the nitrogen atom to hydrogen atoms and no lone pairs. We expect the four regions of high electron density to arrange themselves so that they point to the corners of a tetrahedron with the central nitrogen atom in the middle (**Figure 4.60**). Therefore, the electron pair geometry of  $\text{NH}_4^+$  is tetrahedral, and the molecular structure is also tetrahedral (**Figure 4.66**).



**Figure 4.66** The ammonium ion displays a tetrahedral electron-pair geometry as well as a tetrahedral molecular structure. By: Rice University  
[Openstax CC BY NC SA](#)

### Check Your Learning

Identify a molecule with a trigonal bipyramidal molecular structure.

**Answer:** Any molecule with five electron pairs around the central atoms including no lone pairs will be trigonal bipyramidal.  $\text{PF}_5$  is a common example.

The next several examples illustrate the effect of lone pairs of electrons on molecular structure.

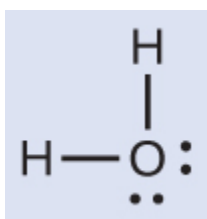
### EXAMPLE 4.13

#### Predicting Electron-Pair Geometry and Molecular Structure: Lone Pairs on the Central Atom

Predict the electron-pair geometry and molecular structure of a water molecule.

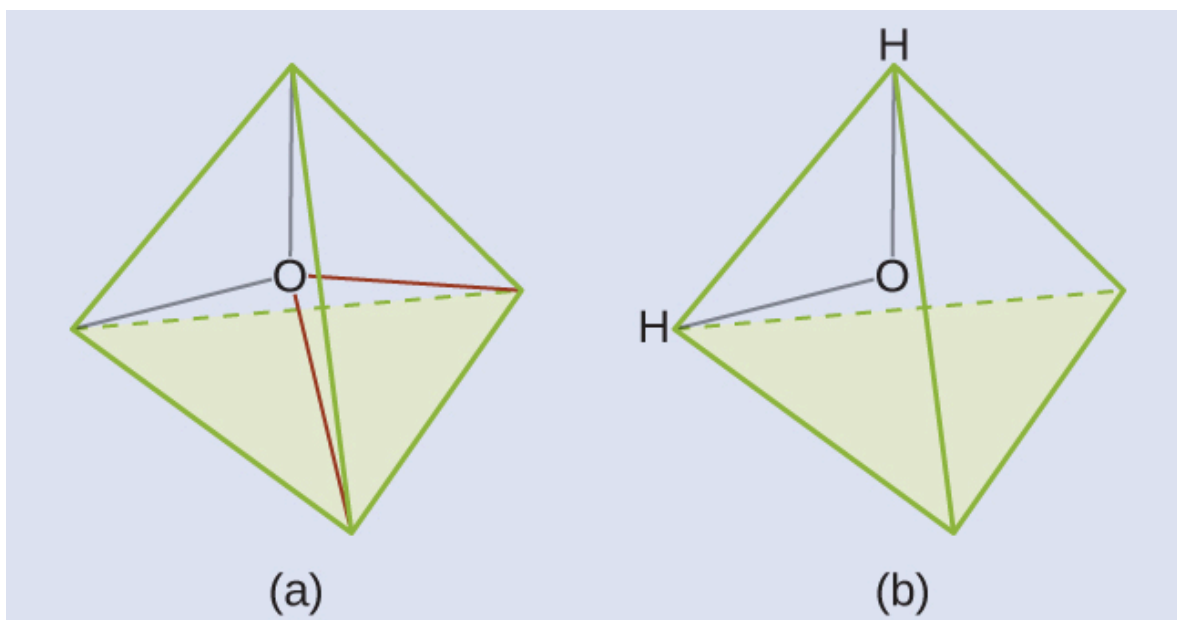
#### Solution

The Lewis structure of  $\text{H}_2\text{O}$  indicates that there are four regions of high electron density around the oxygen atom: two lone pairs and two chemical bonds:



**Figure 4.67** By:  
Rice University  
[Openstax CC BY](#)  
[NC SA](#)

We predict that these four regions are arranged in a tetrahedral fashion, as indicated in **Figure 4.68**. Thus, the electron-pair geometry is tetrahedral, and the molecular structure is bent with an angle slightly less than  $109.5^\circ$ . In fact, the bond angle is  $104.5^\circ$ .



**Figure 4.68** (a)  $\text{H}_2\text{O}$  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.  
By: Rice University [Openstax CC BY NC SA](#)

### Check Your Learning

The hydronium ion,  $\text{H}_3\text{O}^+$ , forms when acids are dissolved in water. Predict the electron-pair geometry and molecular structure of this cation.

**Answer:** Electron pair geometry: tetrahedral; molecular structure: trigonal pyramidal

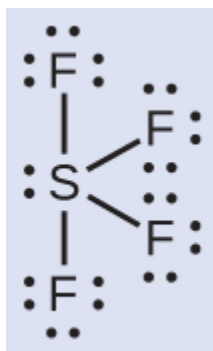
## EXAMPLE 4.14

Predicting Electron-Pair Geometry and Molecular Structure:  $\text{SF}_4$ 

Sulfur tetrafluoride,  $\text{SF}_4$ , is extremely valuable for the preparation of fluorine-containing compounds used as herbicides (i.e.,  $\text{SF}_4$  is used as a fluorinating agent). Predict the electron-pair geometry and molecular structure of an  $\text{SF}_4$  molecule.

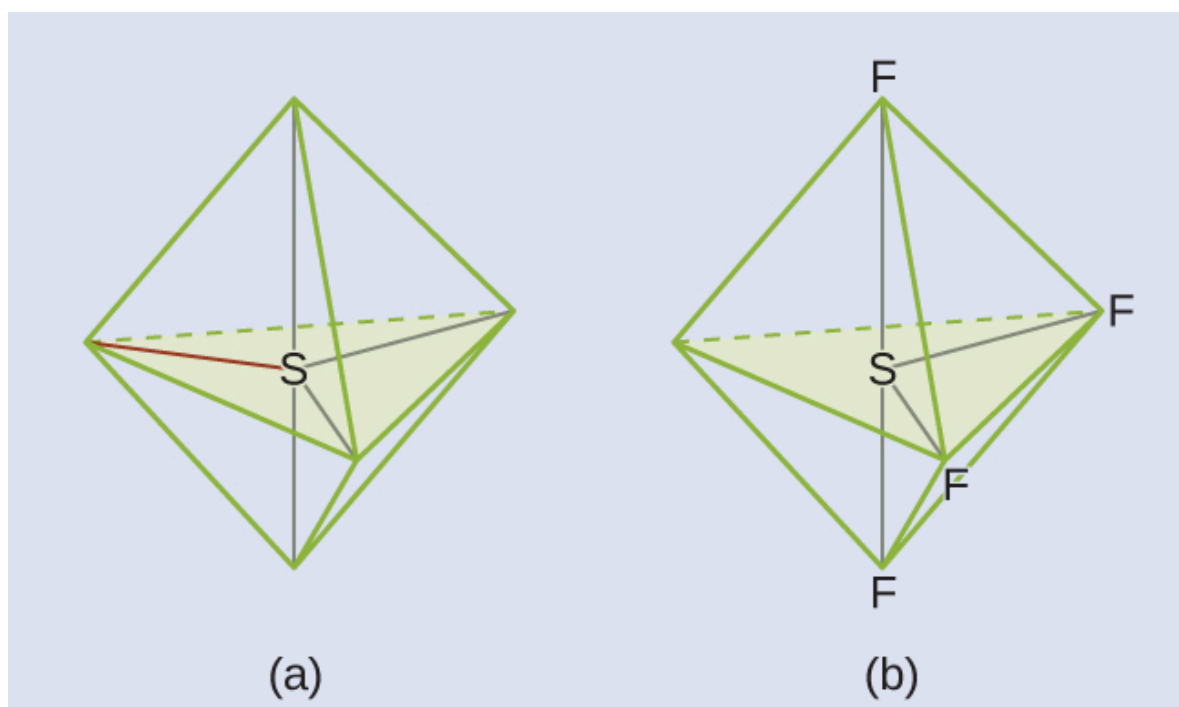
## Solution

The Lewis structure of  $\text{SF}_4$  indicates five regions of electron density around the sulfur atom: one lone pair and four bonding pairs:



**Figure 4.69** By:  
Rice University  
[Openstax CC BY](#)  
[NC SA](#)

We expect these five regions to adopt a trigonal bipyramidal electron-pair geometry. To minimize lone pair repulsions, the lone pair occupies one of the equatorial positions. The molecular structure (**Figure 4.65**) is that of a seesaw (**Figure 4.60**).



**Figure 4.70** (a)  $\text{SF}_4$  has a trigonal bipyramidal arrangement of the five regions of electron density. (b) One of the regions is a lone pair, which results in a seesaw-shaped molecular structure. By: Rice University Openstax CC BY NC SA

### Check Your Learning

Predict the electron pair geometry and molecular structure for molecules of  $\text{XeF}_2$ .

**Answer:** The electron-pair geometry is trigonal bipyramidal. The molecular structure is linear.

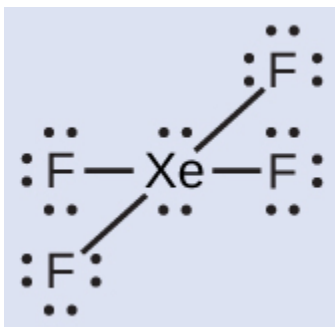
## EXAMPLE 4.15

### Predicting Electron-Pair Geometry and Molecular Structure: $\text{XeF}_4$

Of all the noble gases, xenon is the most reactive, frequently reacting with elements such as oxygen and fluorine. Predict the electron-pair geometry and molecular structure of the  $\text{XeF}_4$  molecule.

## Solution

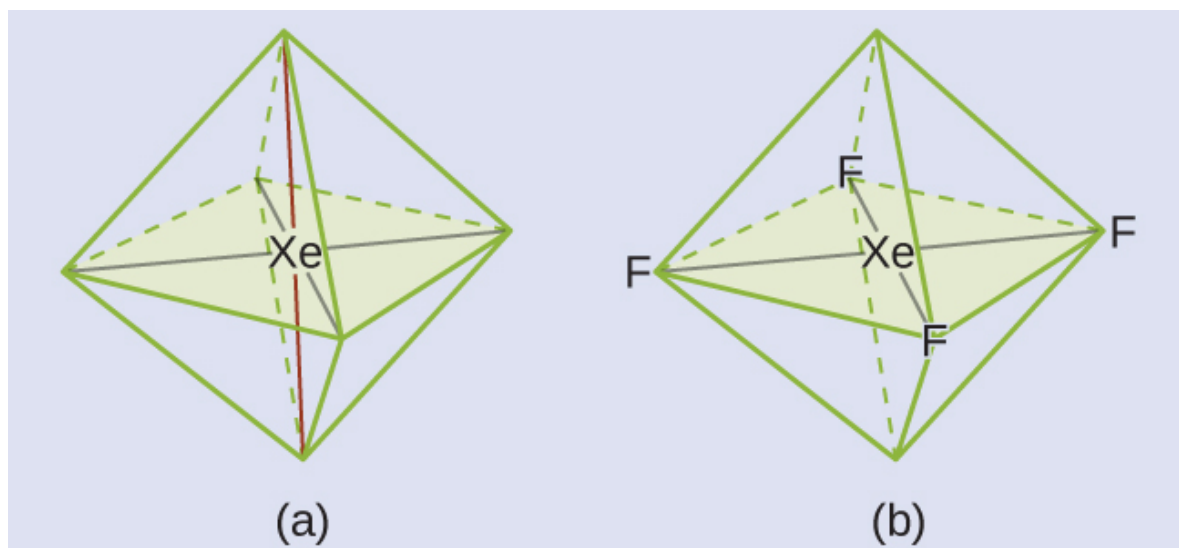
The Lewis structure of  $\text{XeF}_4$  indicates six regions of high electron density around the xenon atom: two lone pairs and four bonds:



**Figure 4.71** By: Rice University [Openstax CC BY NC SA](#)

These six regions adopt an octahedral arrangement (**Figure 4.60**), which is the electron-pair geometry. To minimize repulsions, the lone pairs should be on opposite sides of the central atom (**Figure 4.72**). The five atoms are all in the same plane and have a square planar molecular structure.





**Figure 4.72** (a) XeF<sub>4</sub> adopts an octahedral arrangement with two lone pairs (red lines) and four bonds in the electron-pair geometry. (b) The molecular structure is square planar with the lone pairs directly across from one another. By: Rice University [Openstax CC BY NC SA](#)

### Check Your Learning

In a certain molecule, the central atom has three lone pairs and two bonds. What will the electron pair geometry and molecular structure be?

**Answer:** Electron pair geometry: trigonal bipyramidal; molecular structure: linear

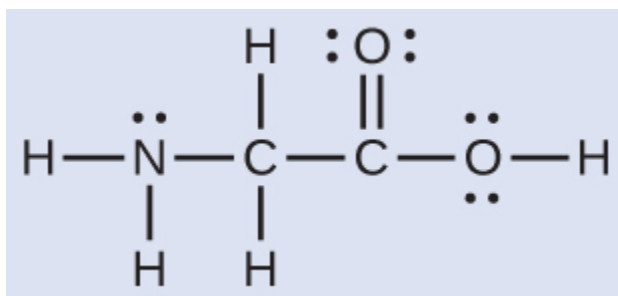
## Molecular Structure for Multicenter Molecules

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 4.16

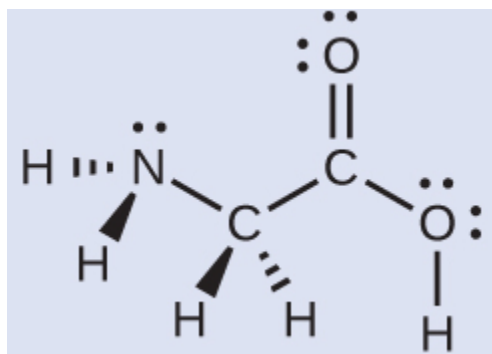
## Predicting Structure in Multicenter Molecules

The Lewis structure for the simplest amino acid, glycine,  $\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$ , is shown here. Predict the local geometry for the nitrogen atom, the two carbon atoms, and the oxygen atom with a hydrogen atom attached:



**Figure 4.73** By: Rice University [Openstax CC BY NC SA](#)

## Solution



**Figure 4.74** By: Rice University [Openstax CC BY NC SA](#)

Consider each central atom independently. The electron-pair geometries:

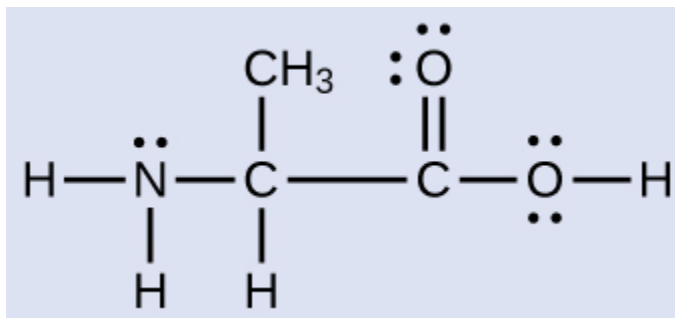
- nitrogen—four regions of electron density; tetrahedral
- carbon ( $\text{CH}_2$ )—four regions of electron density; tetrahedral
- carbon ( $\text{CO}_2$ )—three regions of electron density; trigonal planar
- oxygen ( $\text{OH}$ )—four regions of electron density; tetrahedral

The local structures:

- nitrogen—three bonds, one lone pair; trigonal pyramidal
- carbon ( $\text{CH}_2$ )—four bonds, no lone pairs; tetrahedral
- carbon ( $\text{CO}_2$ )—three bonds (double bond counts as one bond), no lone pairs; trigonal planar
- oxygen ( $\text{OH}$ )—two bonds, two lone pairs; bent ( $109^\circ$ )

### Check Your Learning

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:



**Figure 4.75** By: Rice University [Openstax CC BY NC SA](#)

**Answer:** Electron-pair geometries: nitrogen—tetrahedral; carbon ( $\text{CH}$ )—tetrahedral; carbon ( $\text{CH}_3$ )—tetrahedral; carbon ( $\text{CO}_2$ )—trigonal planar; oxygen ( $\text{OH}$ )—tetrahedral; local structures: nitrogen—trigonal pyramidal; carbon ( $\text{CH}$ )—tetrahedral; carbon ( $\text{CH}_3$ )—tetrahedral; carbon ( $\text{CO}_2$ )—trigonal planar; oxygen ( $\text{OH}$ )—bent ( $109^\circ$ )

### LINK TO LEARNING

The [molecular shape simulator](#) lets you build various molecules and practice naming their electron-pair geometries and molecular structures.

## EXAMPLE 4.17

**Molecular Simulation**

Using a [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 the 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:

**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.

**Check Your Learning**

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<sub>4</sub> is a molecule that adopts this structure.

## Molecular Polarity and Dipole Moment

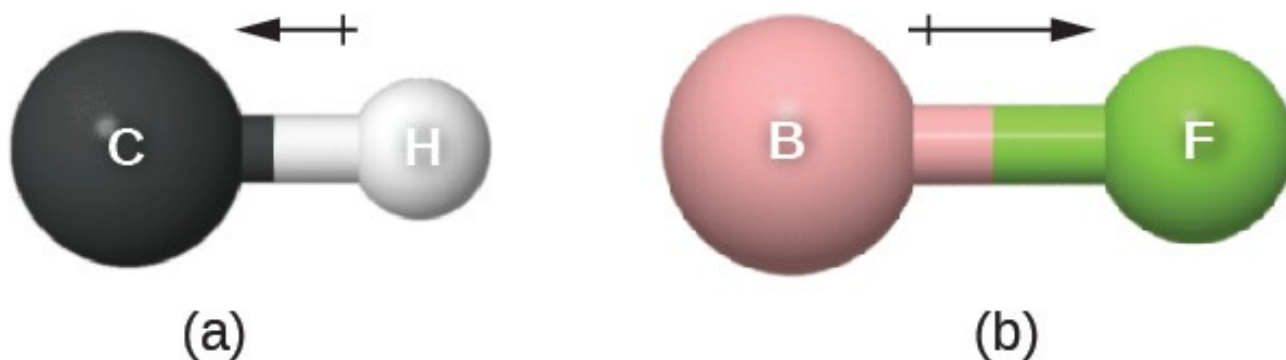
As discussed previously, polar covalent bonds connect two atoms with differing electronegativities, leaving one atom with a partial positive charge ( $\delta^+$ ) and the other atom with a partial negative charge ( $\delta^-$ ), as the electrons are pulled toward the more electronegative atom. This separation of charge gives rise to a bond dipole moment. The magnitude of a bond dipole moment is represented by the Greek letter mu ( $\mu$ ) and is given by the formula

shown here, where  $Q$  is the magnitude of the partial charges (determined by the electronegativity difference), and  $r$  is the distance between the charges:

**Formula does not parse**

$$\mu = Qr$$

This bond moment can be represented as a vector, a quantity having both direction and magnitude (**Figure 4.76**). 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 of the bond 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.



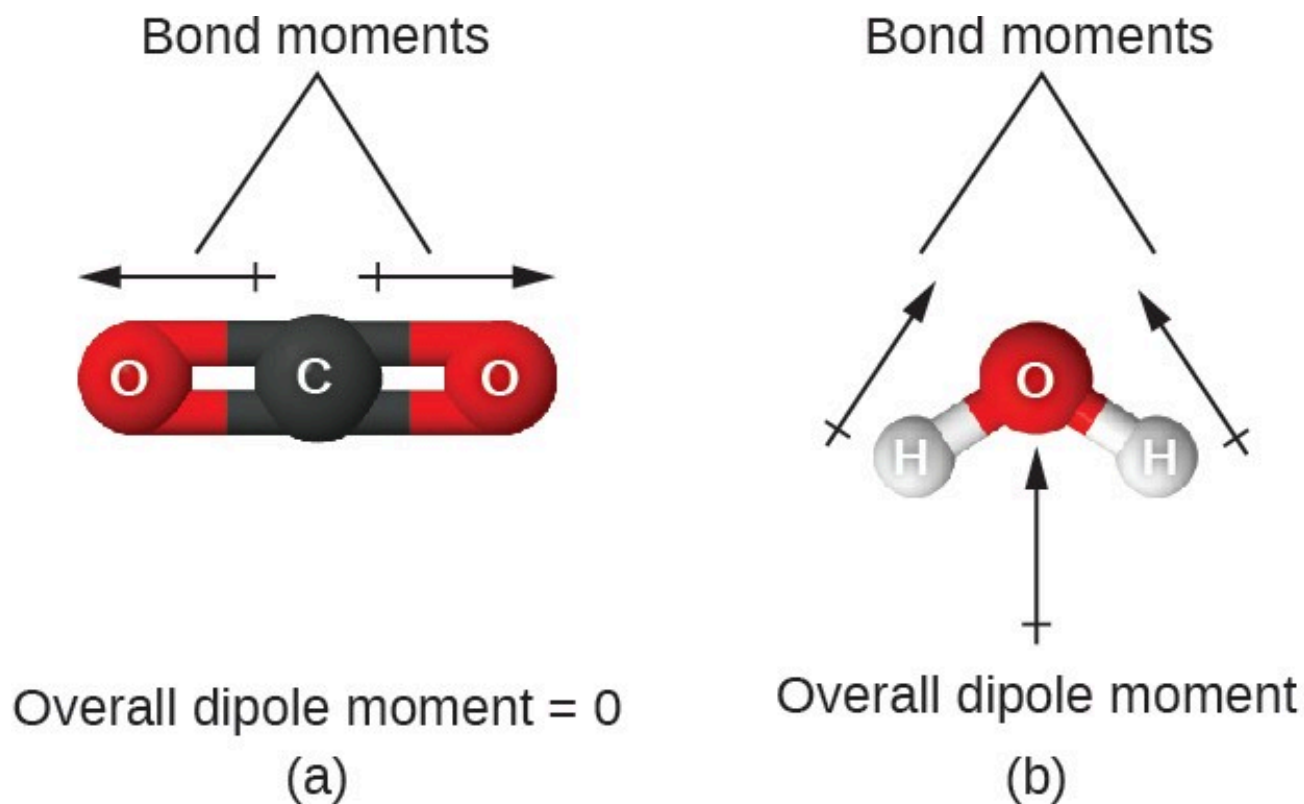
**Figure 4.76** (a) There is a small difference in electronegativity between C and H, represented as a short vector. (b) The electronegativity difference between B and F is much larger, so the vector representing the bond moment is much longer. By: Rice University [Openstax CC BY NC SA](#)

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  $\text{Br}_2$  and  $\text{N}_2$  have no difference in electronegativity, so their dipole moment is zero. For heteronuclear molecules such as  $\text{CO}$ , there is a small dipole moment. For  $\text{HF}$ , there is a larger dipole moment because there is a larger difference in electronegativity.

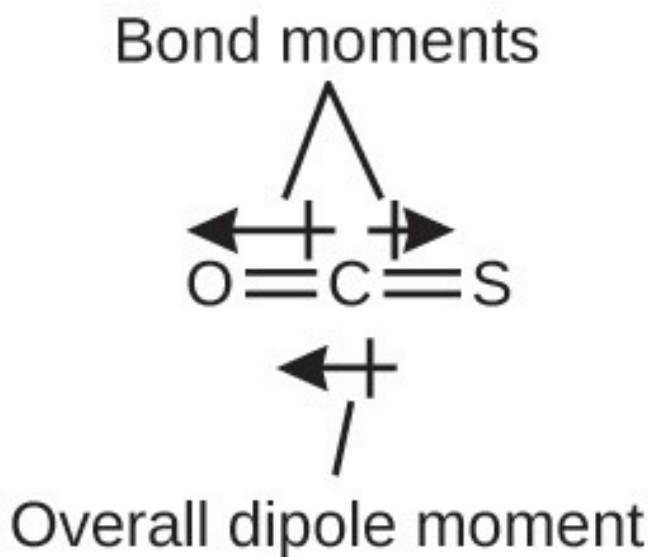
When a molecule contains more than one bond, the geometry must be taken into account. If the bonds in a molecule are arranged such that their bond moments cancel (vector sum equals zero), then the molecule is nonpolar. This is the situation in  $\text{CO}_2$  (**Figure 4.77**). Each of the bonds is polar, but the molecule as a whole is nonpolar. From the Lewis structure, and using VSEPR theory, we determine that the  $\text{CO}_2$  molecule is linear with polar  $\text{C}=\text{O}$  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 4.77**), 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 4.77** 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  $\text{CO}_2$  molecule is nonpolar. (b) In contrast, water is polar because the OH bond moments do not cancel out. By: Rice University [Openstax CC BY NC SA](#)

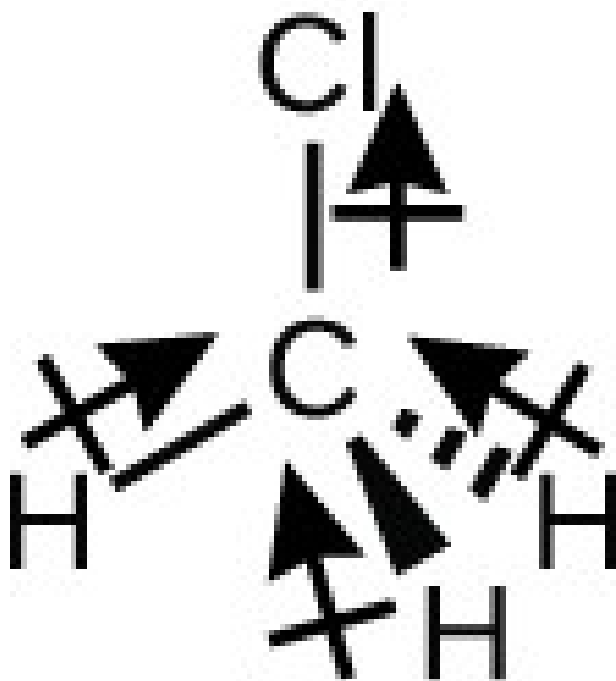
The OCS molecule has a structure similar to  $\text{CO}_2$ , but a sulfur atom has replaced one of the oxygen atoms. To determine if this molecule is polar, we draw the molecular structure. VSEPR theory predicts a linear molecule:



**Figure 4.78** By: Rice University [Openstax](#) [CC BY NC SA](#)

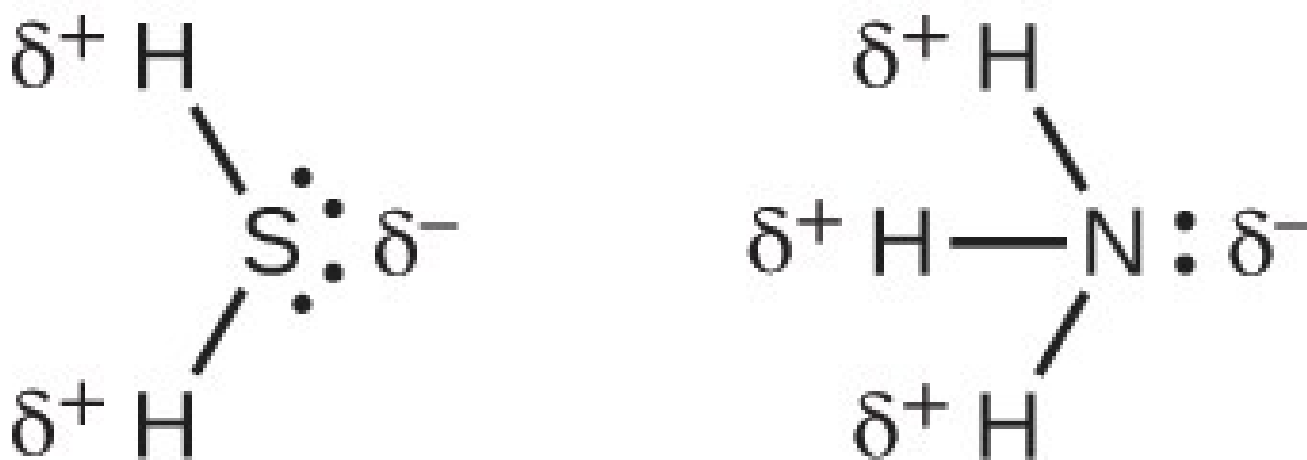
The C-O bond is considerably polar. Although C and S have very similar electronegativity values, S is slightly more electronegative than C, and so the C-S bond is just slightly polar. Because oxygen is more electronegative than sulfur, the oxygen end of the molecule is the negative end.

Chloromethane,  $\text{CH}_3\text{Cl}$ , is a tetrahedral molecule with three slightly polar C-H bonds and a more polar C-Cl bond. The relative electronegativities of the bonded atoms are  $\text{H} < \text{C} < \text{Cl}$ , and so the bond moments all point toward the Cl end of the molecule and sum to yield a considerable dipole moment (the molecules are relatively polar).



**Figure 4.79** By: Rice University [Openstax CC BY NC SA](#)

For molecules of high symmetry such as  $\text{BF}_3$  (trigonal planar),  $\text{CH}_4$  (tetrahedral),  $\text{PF}_5$  (trigonal bipyramidal), and  $\text{SF}_6$  (octahedral), all the bonds are of identical polarity (same bond moment), and they are oriented in geometries that yield nonpolar molecules (dipole moment is zero). Molecules of less geometric symmetry, however, may be polar even when all bond moments are identical. For these molecules, the directions of the equal bond moments are such that they sum to give a nonzero dipole moment and a polar molecule. Examples of such molecules include hydrogen sulfide,  $\text{H}_2\text{S}$  (nonlinear), and ammonia,  $\text{NH}_3$  (trigonal pyramidal).



**Figure 4.80** By: Rice University [Openstax CC BY NC SA](#)

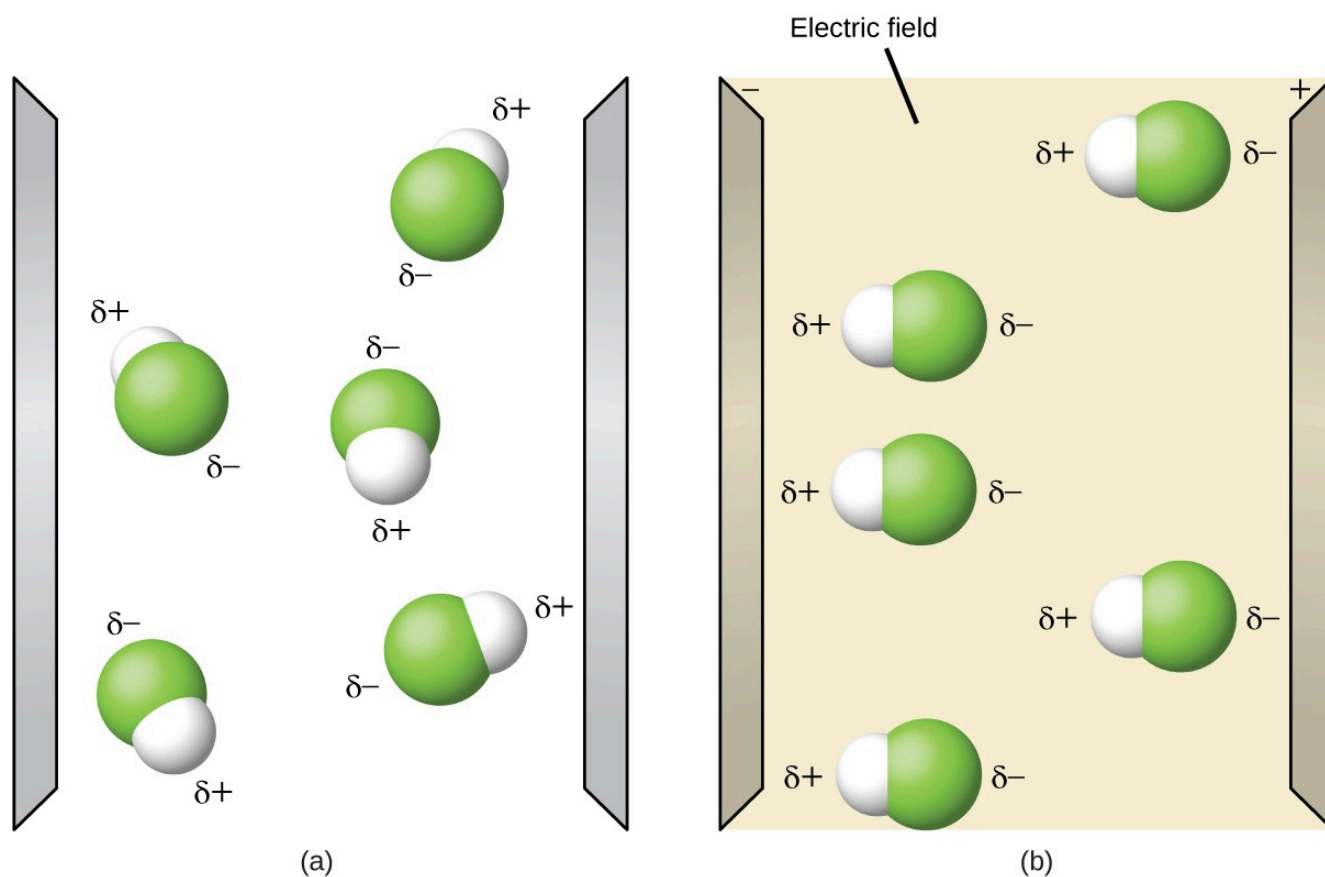


To summarize, to be polar, a molecule must:

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 4.81**). 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 4.81** (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. By: Rice University [Openstax](#) [CC BY NC SA](#)

## LINK TO LEARNING

The [molecule polarity simulation](#) provides many ways to explore dipole moments of bonds and molecules.

## EXAMPLE 4.1

### 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 adjusters. 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 4.81**.

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.

### Check Your Learning

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.



# CHAPTER 5: ADVANCED THEORIES OF BONDING

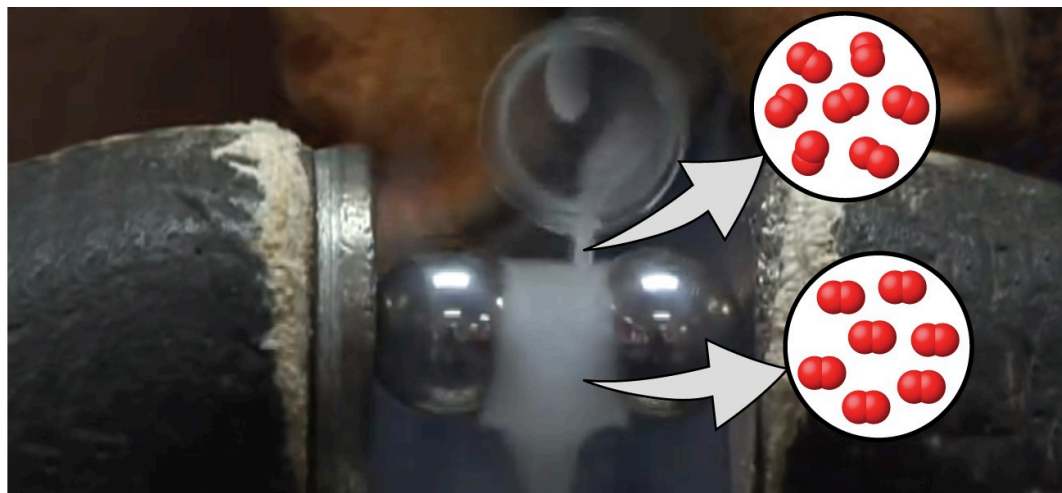


Figure 5.1 Oxygen molecules orient randomly most of the time, as shown in the top magnified view. However, when we pour liquid oxygen through a magnet, the molecules line up with the magnetic field, and the attraction allows them to stay suspended between the poles of the magnet where the magnetic field is strongest. Other diatomic molecules (like  $N_2$ ) flow past the magnet. The detailed explanation of bonding described in this chapter allows us to understand this phenomenon. By: Rice University [Openstax CC BY NC SA](#)

## Chapter Outline

- Valence Bond Theory
- Hybrid Atomic Orbitals
- Multiple Bonds

- Molecular Orbital Theory

## Introduction

We have examined the basic ideas of bonding, showing that atoms share electrons to form molecules with stable Lewis structures and that we can predict the shapes of those molecules by valence shell electron pair repulsion (VSEPR) theory. These ideas provide an important starting point for understanding chemical bonding. But these models sometimes fall short in their abilities to predict the behavior of real substances. How can we reconcile the geometries of *s*, *p*, and *d* atomic orbitals with molecular shapes that show angles like 120° and 109.5°? Furthermore, we know that electrons and magnetic behavior are related through electromagnetic fields. Both N<sub>2</sub> and O<sub>2</sub> have fairly similar Lewis structures that contain lone pairs of electrons.



**Figure 5.2** By: Rice University [Openstax CC BY NC SA](#)

Yet oxygen demonstrates very different magnetic behavior than nitrogen. We can pour liquid nitrogen through a magnetic field with no visible interactions, while liquid oxygen (shown in **Figure 5.1**) is attracted to the magnet and floats in the magnetic field. We need to understand the additional concepts of valence bond theory, orbital hybridization, and molecular orbital theory to understand these observations.

# VALENCE BOND THEORY (5.1)

OpenStax

---

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

- Describe the formation of covalent bonds in terms of atomic orbital overlap
- Define and give examples of  $\sigma$  and  $\pi$  bonds

As we know, a scientific theory is a strongly supported explanation for observed natural laws or large bodies of experimental data. For a theory to be accepted, it must explain experimental data and be able to predict behavior. For example, VSEPR theory has gained widespread acceptance because it predicts three-dimensional molecular shapes that are consistent with experimental data collected for thousands of different molecules. However, VSEPR theory does not provide an explanation of chemical bonding.

## Atomic Orbital Overlap

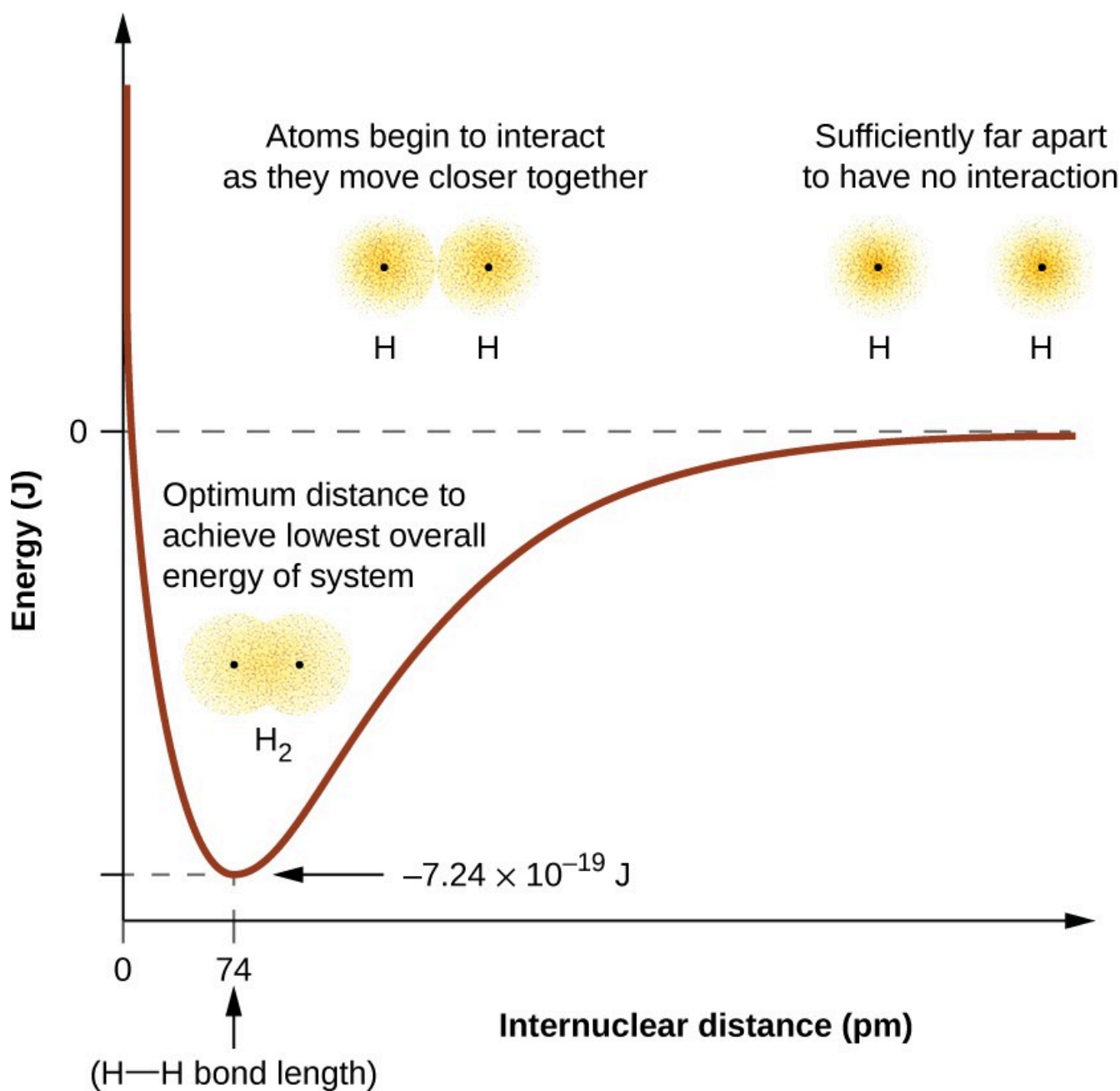
There are successful theories that describe the electronic structure of atoms. We can use quantum mechanics to predict the specific regions around an atom where electrons are likely to be located: A spherical shape for an  $s$  orbital, a dumbbell shape for a  $p$  orbital, and so forth. However, these predictions only describe the orbitals around free atoms. When atoms bond to form molecules, atomic orbitals are not sufficient to describe the regions where electrons will be located in the molecule. A more complete understanding of electron distributions requires a model that can account for the electronic structure of molecules. One popular theory holds that a covalent bond forms when a pair of electrons is shared by two atoms and is simultaneously attracted by the nuclei of both atoms. In the following sections, we will discuss how such bonds are described by valence bond theory and hybridization.

**Valence bond theory** describes a covalent bond as the overlap of half-filled atomic orbitals (each containing a single electron) that yield a pair of electrons shared between the two bonded atoms. We say that orbitals on two different atoms **overlap** when a portion of one orbital and a portion of a second orbital occupy the same region of space. According to valence bond theory, a covalent bond results when two conditions are met: (1) An orbital on one atom overlaps an orbital on a second atom, and (2) the single electrons in each orbital

combine to form an electron pair. The mutual attraction between this negatively charged electron pair and the two atoms' positively charged nuclei serves to physically link the two atoms through a force we define as a covalent bond. The strength of a covalent bond depends on the extent of overlap of the orbitals involved. Orbitals that overlap extensively form bonds that are stronger than those that have less overlap.

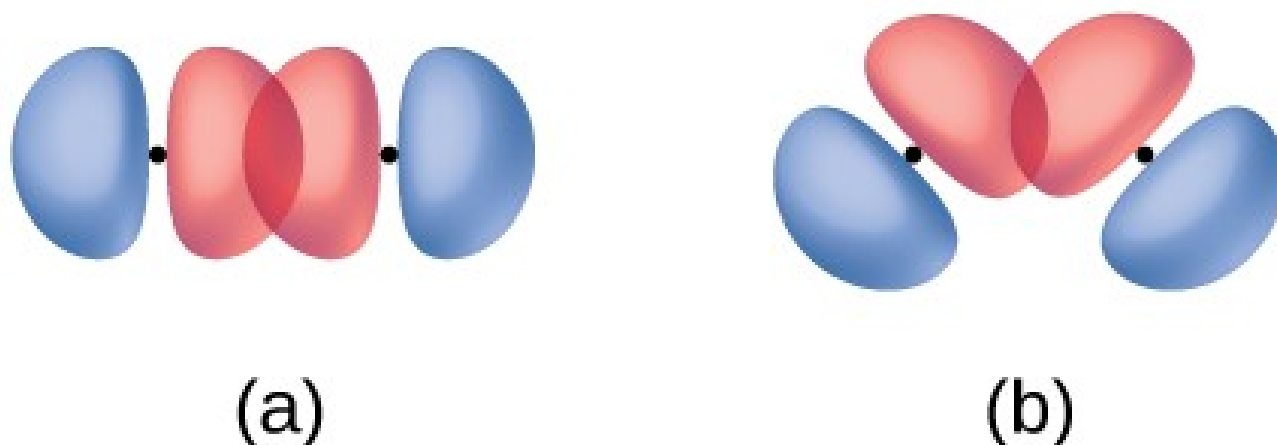
The energy of the system depends on how much the orbitals overlap. **Figure 5.3** illustrates how the sum of the energies of two hydrogen atoms (the colored curve) changes as they approach each other. When the atoms are far apart, there is no overlap, and by convention, we set the sum of the energies at zero. As the atoms move together, their orbitals begin to overlap. Each electron begins to feel the attraction of the nucleus in the other atom. In addition, the electrons begin to repel each other, as do the nuclei. While the atoms are still widely separated, the attractions are slightly stronger than the repulsions, and the energy of the system decreases. (A bond begins to form.) As the atoms move closer together, the overlap increases, so the attraction of the nuclei for the electrons continues to increase (as do the repulsions among electrons and between the nuclei). At some specific distance between the atoms, which varies depending on the atoms involved, the energy reaches its lowest (most stable) value. This optimum distance between the two bonded nuclei is the bond distance between the two atoms. The bond is stable because at this point, the attractive and repulsive forces combine to create the lowest possible energy configuration. If the distance between the nuclei were to decrease further, the repulsions between nuclei and the repulsions as electrons that are confined in closer proximity to each other would become stronger than the attractive forces. The energy of the system would then rise (making the system destabilized), as shown at the far left of **Figure 5.3**.





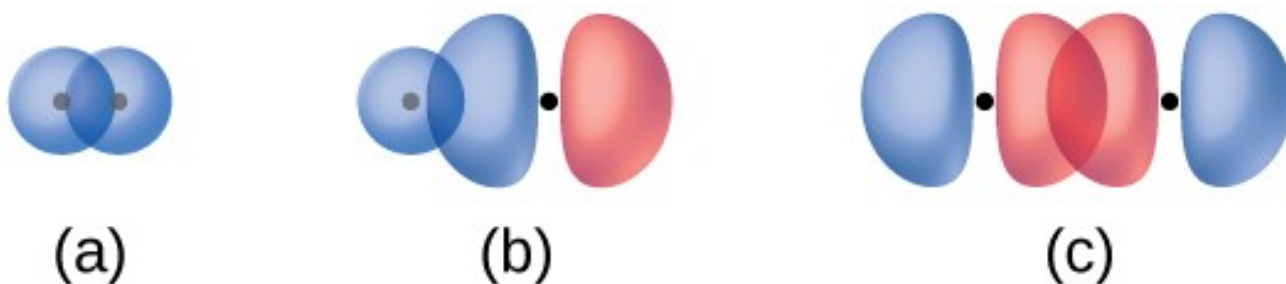
**Figure 5.3** (a) The interaction of two hydrogen atoms changes as a function of distance. (b) The energy of the system changes as the atoms interact. The lowest (most stable) energy occurs at a distance of 74 pm, which is the bond length observed for the  $\text{H}_2$  molecule. By: Rice University [Openstax CC BY NC SA](#)

In addition to the distance between two orbitals, the orientation of orbitals also affects their overlap (other than for two  $s$  orbitals, which are spherically symmetric). Greater overlap is possible when orbitals are oriented such that they overlap on a direct line between the two nuclei. **Figure 5.4** illustrates this for two  $p$  orbitals from different atoms; the overlap is greater when the orbitals overlap end to end rather than at an angle.



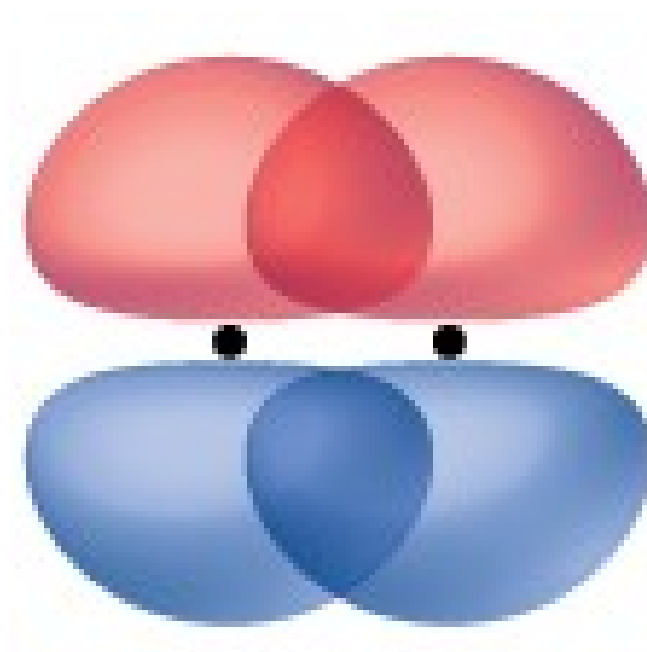
**Figure 5.4** (a) The overlap of two  $p$  orbitals is greatest when the orbitals are directed end to end. (b) Any other arrangement results in less overlap. The dots indicate the locations of the nuclei. By: Rice University Openstax CC BY NC SA

The overlap of two  $s$  orbitals (as in  $\text{H}_2$ ), the overlap of an  $s$  orbital and a  $p$  orbital (as in  $\text{HCl}$ ), and the end-to-end overlap of two  $p$  orbitals (as in  $\text{Cl}_2$ ) all produce **sigma bonds ( $\sigma$  bonds)**, as illustrated in **Figure 5.5**. A  $\sigma$  bond is a covalent bond in which the electron density is concentrated in the region along the internuclear axis; that is, a line between the nuclei would pass through the center of the overlap region. Single bonds in Lewis structures are described as  $\sigma$  bonds in valence bond theory.



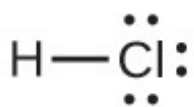
**Figure 5.5** Sigma ( $\sigma$ ) bonds form from the overlap of the following: (a) two  $s$  orbitals, (b) an  $s$  orbital and a  $p$  orbital, and (c) two  $p$  orbitals. The dots indicate the locations of the nuclei. By: Rice University Openstax CC BY NC SA

A **pi bond ( $\pi$  bond)** is a type of covalent bond that results from the side-by-side overlap of two  $p$  orbitals, as illustrated in **Figure 5.6**. In a  $\pi$  bond, the regions of orbital overlap lie on opposite sides of the internuclear axis. Along the axis itself, there is a **node**, that is, a plane with no probability of finding an electron.

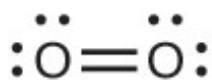


**Figure 5.6** Pi ( $\pi$ ) bonds form from the side-by-side overlap of two p orbitals. The dots indicate the location of the nuclei. By: Rice University [Openstax](#) [CC BY NC SA](#)

While all single bonds are  $\sigma$  bonds, multiple bonds consist of both  $\sigma$  and  $\pi$  bonds. As the Lewis structures below suggest,  $\text{O}_2$  contains a double bond, and  $\text{N}_2$  contains a triple bond. The double bond consists of one  $\sigma$  bond and one  $\pi$  bond, and the triple bond consists of one  $\sigma$  bond and two  $\pi$  bonds. Between any two atoms, the first bond formed will always be a  $\sigma$  bond, but there can only be one  $\sigma$  bond in any one location. In any multiple bond, there will be one  $\sigma$  bond, and the remaining one or two bonds will be  $\pi$  bonds. These bonds are described in more detail later in this chapter.



One  $\sigma$  bond  
No  $\pi$  bonds



One  $\sigma$  bond  
One  $\pi$  bond

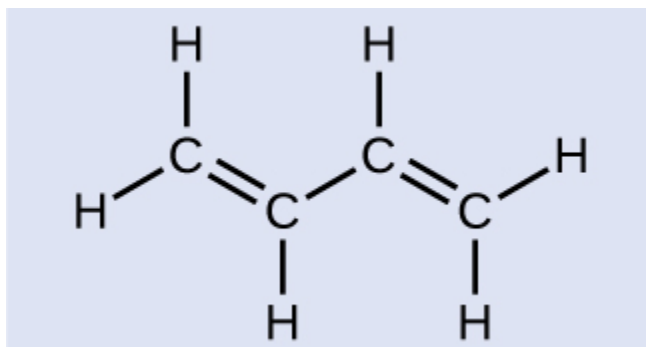


One  $\sigma$  bond  
Two  $\pi$  bonds

**Figure 5.7** By: Rice University [Openstax](#) [CC BY NC SA](#)

## Example 5.1

### Counting $\sigma$ and $\pi$ Bonds



**Figure 5.8** By: Rice University [Openstax CC BY NC SA](#)

Butadiene,  $C_4H_6$ , is used to make synthetic rubber. Identify the number of  $\sigma$  and  $\pi$  bonds contained in this molecule.

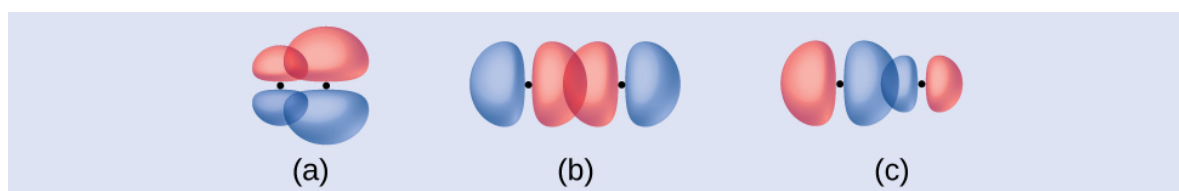
### Solution

There are six  $\sigma$  C–H bonds and one  $\sigma$  C–C bond for a total of seven from the single bonds. There are two double bonds that each have a  $\pi$  bond in addition to the  $\sigma$  bond. This gives a total of nine  $\sigma$  and two  $\pi$  bonds overall.

### Check Your Learning

Identify each illustration as depicting a  $\sigma$  or  $\pi$  bond:

- (a) side-by-side overlap of a  $4p$  and a  $2p$  orbital
- (b) end-to-end overlap of a  $4p$  and  $4p$  orbital
- (c) end-to-end overlap of a  $4p$  and a  $2p$  orbital



**Figure 5.9** By: Rice University [Openstax](#) [CC BY NC SA](#)

**Answer:** (a) is a  $\pi$  bond with a node along the axis connecting the nuclei, while (b) and (c) are  $\sigma$  bonds that overlap along the axis.

## Dipole Moments and Ionic Character

Now that we have seen the importance of understanding the connection between the location of electrons in atoms and the properties of elements, we can expand our understanding of the connection between atoms. This will be an introduction to more advanced aspects of the chemical bond, which is the very heart of chemistry itself. With the sole exception of the noble gases, atoms by themselves do not possess the most stable possible electron configuration. That is where the concept of chemical bonding comes into its own: Atoms can attain a stable configuration by exchanging electrons with another atom, resulting in the formation of ions.

Ions, in turn, can associate by charge—simple Coulombic attraction—resulting in the formation of compounds we call ionic compounds. We will look at the ionic nature of bonds first, from a simple positive-negative attraction standpoint. Just as important is that some atoms bond by sharing rather than exchanging electrons; the sharing of electrons gives rise to the covalent bond. To add just one more dimension, some chemical species are neither completely ionic nor completely covalent; these species possess a permanent dipole and are classified as polar.

In your introductory physics course, you will likely discuss the concept of Coulombic interactions in much more rigorous detail than we will do here. We are interested primarily in the differences in properties between species that arise from their relative covalent, ionic, or polar nature—not in a rigorous model of those properties. We are concerned with the connection between potential energy and force and the relative separation (or lack of separation) between charges. We begin by defining the electric or Coulomb force as the product of the charges divided by the square of the distance between those charges:

$$F = \frac{Q_1 Q_2}{d^2}$$

Here,  $Q$  is taken to be the fundamental constant of electron charge: One electron has a charge of  $1.60218 \times 10^{-19}$  C. (We will work exclusively in the SI system, so distances will be measured in meters (m)).

And as you may recall, energy is force times distance, so

$$E = \frac{Q_1 Q_2}{d}$$

To illustrate the trend in attractive force, we will consider first the attractive force between two ions of single charge separated by a distance of  $2d$ :

$$F = \frac{(1)(-1)}{(2d)^2} = -\frac{1}{4d^2}$$

And then the attractive force between two ions of double charge separated by a distance  $d$ :

$$F = \frac{(2)(-2)}{(d)^2} = -\frac{4}{d^2}$$

The force of attraction increases with the charge and decreases with increased distance. If all matter were composed of ions, that would be the end of the story, but it clearly is not. There are molecules for which the charge—either positive or negative—is permanently concentrated more on one atom than the other. Notice we say atom, because these compounds are not composed of ions but rather of atoms sharing electrons through covalent bonds.

## Bond Dipole Moments

The concept of a bond dipole moment allows us to examine the partial separation of charge between atoms. It is a simple model when applied to diatomic molecules, which will be more than sufficient for our purposes. The dipole moment of a bond is defined as the charge times the distance—charge once again being measured in multiples of the charge on an electron, or coulombs. The distance will always be in meters. Because we are considering very small charges and distances, and because it is the relative separation of charge rather than the actual value for it that we are interested in, we will introduce a new unit called the Debye, named after the physical chemist Peter Debye:

$$1 \text{ Debye (D)} = 3.336 \times 10^{-30} \text{ C}\cdot\text{m} \quad \mu = Q \times d$$

The usefulness of the Debye unit will be shown by example:

For HCl, the bond dipole moment is known to be 1.08 D. For HI, the bond dipole moment is known to be 0.44 D.

Comparing the two, we can see that HI is less polar than HCl, which is what we would expect based on electronegativity values.

We have now made a transition between the concept of an ionic compound and a partially ionic one. Of course, the partially ionic compound must also by definition be partially covalent.

## Partial Ionic Character

The concept of the bond dipole moment helps bridge the concepts of ionic and covalent bonding. Because there is a separation of charge that is less complete than it is in an ionic bond, we can refer to polar bonds

as being partially ionic in nature. In contrast to sodium chloride, hydrogen chloride shows partial charges (indicated with a delta notation) on the hydrogen and chlorine. As you would expect from the electronegativity values, hydrogen carries a partial positive charge, while chlorine carries a partial negative charge. Where do these charges come from?

It is easy to come up with the partial charges by comparing the actual dipole moments (which can be obtained experimentally, using spectroscopy) with the dipole expected in the limiting case (that is, if we were to consider the molecule ionic). The actual dipole moment is 1.03 D.

## EXAMPLE 5.2

### Finding the Partial Ionic Character

What are the partial charges of an HCl molecule, whose bond length is 0.127 nm?

#### Solution

The bond dipole moment is

$$(1.60218 \times 10^{-19} \text{ C}) (0.127 \times 10^{-9} \text{ m}) \text{ or } 2.03 \times 10^{-29} \text{ C} \cdot \text{m}.$$

$$\text{Converted to D, this is } (2.03 \times 10^{-29} \text{ C} \cdot \text{m}) \left( \frac{1 \text{ Debye}}{3.336 \times 10^{-30} \text{ C} \cdot \text{m}} \right) \text{ or } 6.09 \text{ D}.$$

Were HCl completely ionic, this would be its molecular dipole moment. To get the partial ionic character, we divide the experimentally measured bond moment by this limiting value:

$$\% \text{ ionic character} = \frac{\mu_{\text{exp}}}{\mu_{\text{lim}}} \times 100 \% = \frac{(1.03 \text{ D})}{(6.09 \text{ D})} \times 100 \% = 17 \%$$

#### Check Your Learning

Repeat the calculation for HI, which has a dipole moment of 0.42 D and a bond length of 0.161 nm.

**Answer:** Calculated 7.73, percent 5.43

What does the result suggest about the relative polarity of the HI bond vs. that of the HCl bond? Does the calculated dipole and percent ionic character reconcile with the difference in electronegativity between Cl and I?

The electron configuration of an atom or ion is key to understanding the chemical behavior of an element. The atoms that make up the element combine in various ways, ranging from the mostly ionic (NaCl) to the partially ionic (HCl) to what we will call purely covalent. At the most fundamental level, all chemical bonds involve electrons, and a significant percentage of chemical and physical properties can be explained by considering the location and separation of charge in a species. By understanding the structure of matter at the atomic level, we can begin to build an understanding of the behavior of matter at both the microscopic and macroscopic levels.

An understanding of dipoles and partial ionic character is fundamental to understanding the interactions between particles, which we will examine in the chapter on liquids and solids. These intermolecular forces become important in the liquid and solid states of matter.



# HYBRID ATOMIC ORBITALS (5.2)

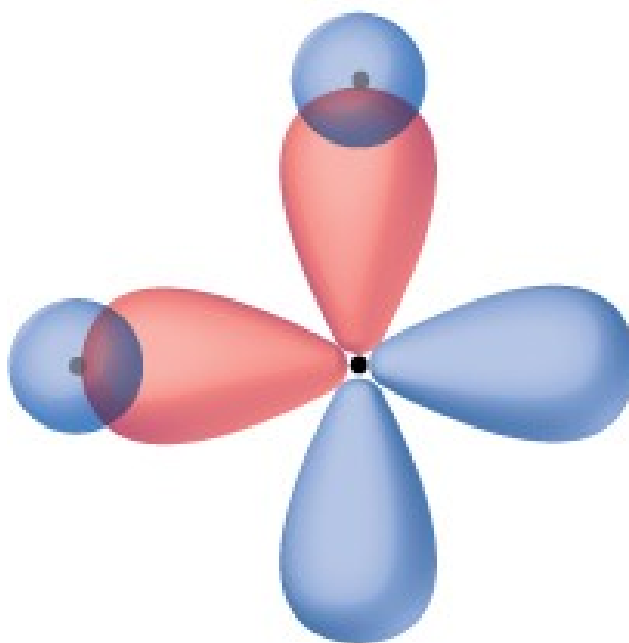
OpenStax

---

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

- Explain the concept of atomic orbital hybridization
- Determine the hybrid orbitals associated with various molecular geometries

Thinking in terms of overlapping atomic orbitals is one way for us to explain how chemical bonds form in diatomic molecules. However, to understand how molecules with more than two atoms form stable bonds, we require a more detailed model. As an example, let us consider the water molecule, in which we have one oxygen atom bonding to two hydrogen atoms. Oxygen has the electron configuration  $1s^2 2s^2 2p^4$ , with two unpaired electrons (one in each of the two  $2p$  orbitals). Valence bond theory would predict that the two O–H bonds form from the overlap of these two  $2p$  orbitals with the  $1s$  orbitals of the hydrogen atoms. If this were the case, the bond angle would be  $90^\circ$ , as shown in **Figure 5.10**, because  $p$  orbitals are perpendicular to each other. Experimental evidence shows that the bond angle is  $104.5^\circ$ , not  $90^\circ$ . The prediction of the valence bond theory model does not match the real-world observations of a water molecule; a different model is needed.



**Figure 5.10** The hypothetical overlap of two of the 2p orbitals on an oxygen atom (red) with the 1s orbitals of two hydrogen atoms (blue) would produce a bond angle of 90°. This is not consistent with experimental evidence. By: Rice University Openstax CC BY NC SA

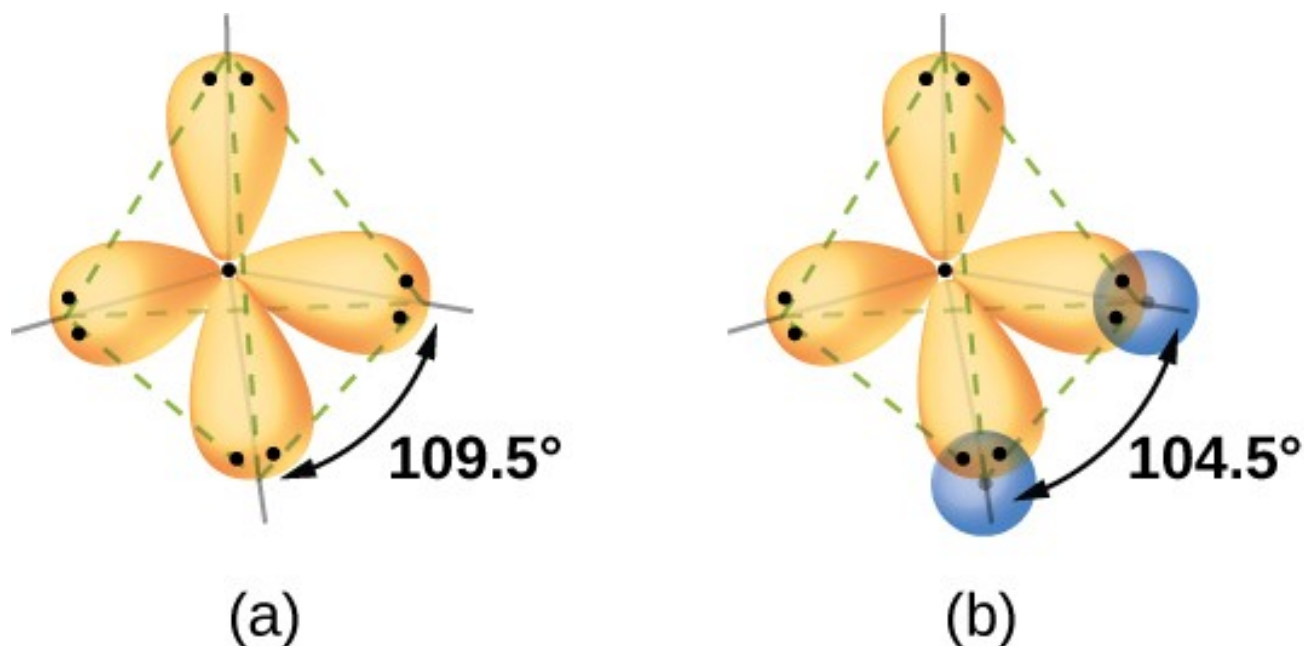
1

Quantum-mechanical calculations suggest why the observed bond angles in  $\text{H}_2\text{O}$  differ from those predicted by the overlap of the 1s orbital of the hydrogen atoms with the 2p orbitals of the oxygen atom. The mathematical expression known as the wave function,  $\psi$ , contains information about each orbital and the wavelike properties of electrons in an isolated atom. When atoms are bound together in a molecule, the wave functions combine to produce new mathematical descriptions that have different shapes. This process of combining the wave functions for atomic orbitals is called **hybridization** and is mathematically accomplished by the *linear combination of atomic orbitals*, LCAO (a technique that we will encounter again later). The new orbitals that result are called **hybrid orbitals**. The valence orbitals in an *isolated* oxygen atom are a 2s orbital and three 2p orbitals. The valence orbitals in an oxygen atom in a water molecule differ; they consist of four equivalent hybrid orbitals that point approximately toward the corners of a tetrahedron (**Figure 5.11**). Consequently, the overlap of the O and H orbitals should result in a tetrahedral bond angle (109.5°). The

---

1. Note that orbitals may sometimes be drawn in an elongated “balloon” shape rather than in a more realistic “plump” shape in order to make the geometry easier to visualize.

observed angle of  $104.5^\circ$  is experimental evidence for which quantum-mechanical calculations give a useful explanation: Valence bond theory must include a hybridization component to give accurate predictions.



**Figure 5.11** (a) A water molecule has four regions of electron density, so VSEPR theory predicts a tetrahedral arrangement of hybrid orbitals. (b) Two of the hybrid orbitals on oxygen contain lone pairs, and the other two overlap with the 1s orbitals of hydrogen atoms to form the O–H bonds in  $\text{H}_2\text{O}$ . This description is more consistent with the experimental structure. By: Rice University [Openstax](#) [CC BY NC SA](#)

The following ideas are important in understanding hybridization:

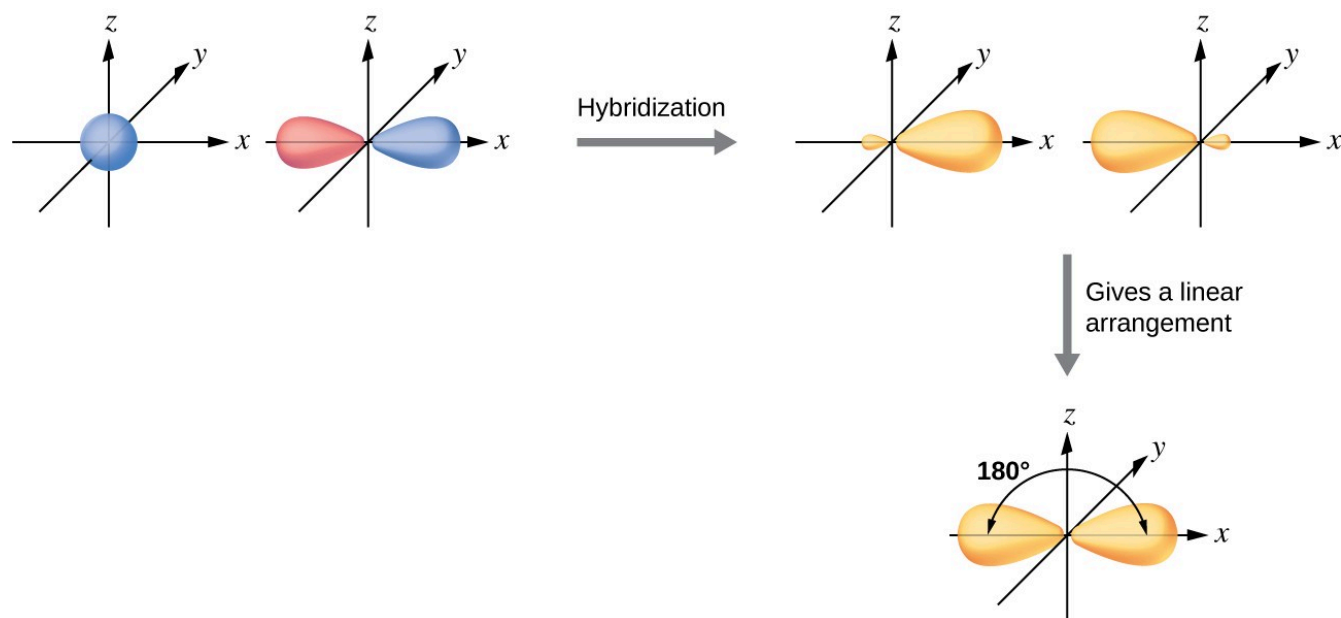
1. Hybrid orbitals do not exist in isolated atoms. They are formed only in covalently bonded atoms.
2. Hybrid orbitals have shapes and orientations that are very different from those of the atomic orbitals in isolated atoms.
3. A set of hybrid orbitals is generated by combining atomic orbitals. The number of hybrid orbitals in a set is equal to the number of atomic orbitals that were combined to produce the set.
4. All orbitals in a set of hybrid orbitals are equivalent in shape and energy.
5. The type of hybrid orbitals formed in a bonded atom depends on its electron-pair geometry as predicted by the VSEPR theory.
6. Hybrid orbitals overlap to form  $\sigma$  bonds. Unhybridized orbitals overlap to form  $\pi$  bonds.

In the following sections, we shall discuss the common types of hybrid orbitals.

## *sp* Hybridization

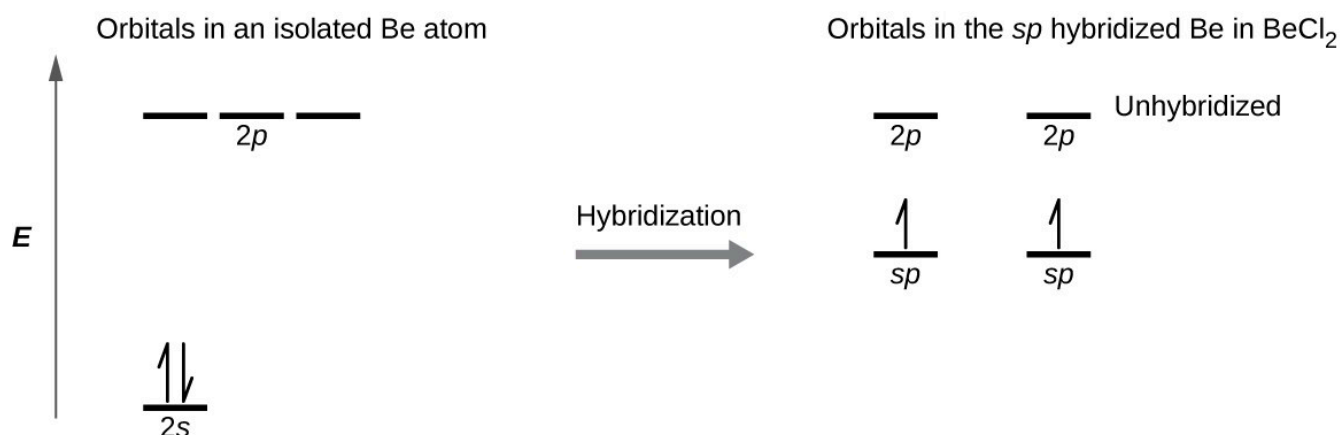
The beryllium atom in a gaseous  $\text{BeCl}_2$  molecule is an example of a central atom with no lone pairs of electrons

in a linear arrangement of three atoms. There are two regions of valence electron density in the  $\text{BeCl}_2$  molecule that correspond to the two covalent Be–Cl bonds. To accommodate these two electron domains, two of the Be atom's four valence orbitals will mix to yield two hybrid orbitals. This hybridization process involves mixing the valence  $s$  orbital with one of the valence  $p$  orbitals to yield two equivalent  **$sp$  hybrid orbitals** that are oriented in a linear geometry (**Figure 5.12**). In this figure, the set of  $sp$  orbitals appears similar in shape to the original  $p$  orbital, but there is an important difference. The number of atomic orbitals combined always equals the number of hybrid orbitals formed. The  $p$  orbital is one orbital that can hold up to two electrons. The  $sp$  set is two equivalent orbitals that point  $180^\circ$  from each other. The two electrons that were originally in the  $s$  orbital are now distributed to the two  $sp$  orbitals, which are half-filled. In gaseous  $\text{BeCl}_2$ , these half-filled hybrid orbitals will overlap with orbitals from the chlorine atoms to form two identical  $\sigma$  bonds.



**Figure 5.12** Hybridization of an  $s$  orbital (blue) and a  $p$  orbital (red) of the same atom produces two  $sp$  hybrid orbitals (yellow). Each hybrid orbital is oriented primarily in just one direction. Note that each  $sp$  orbital contains one lobe that is significantly larger than the other. The set of two  $sp$  orbitals is oriented at  $180^\circ$ , which is consistent with the geometry for two domains. By: Rice University [Openstax CC BY NC SA](#)

We illustrate the electronic differences in an isolated Be atom and in the bonded Be atom in the orbital energy-level diagram in **Figure 5.13**. These diagrams represent each orbital by a horizontal line (indicating its energy) and each electron by an arrow. Energy increases toward the top of the diagram. We use one upward arrow to indicate one electron in an orbital and two arrows (up and down) to indicate two electrons of opposite spin.



**Figure 5.13** This orbital energy-level diagram shows the  $sp$  hybridized orbitals on Be in the linear  $\text{BeCl}_2$  molecule. Each of the two  $sp$  hybrid orbitals holds one electron and is thus half filled and available for bonding via overlap with a Cl  $3p$  orbital. By: Rice University [Openstax CC BY NC SA](#)

When atomic orbitals hybridize, the valence electrons occupy the newly created orbitals. The Be atom had two valence electrons, so each of the  $sp$  orbitals gets one of these electrons. Each of these electrons pairs up with the unpaired electron on a chlorine atom when a hybrid orbital and a chlorine orbital overlap during the formation of the Be–Cl bonds.

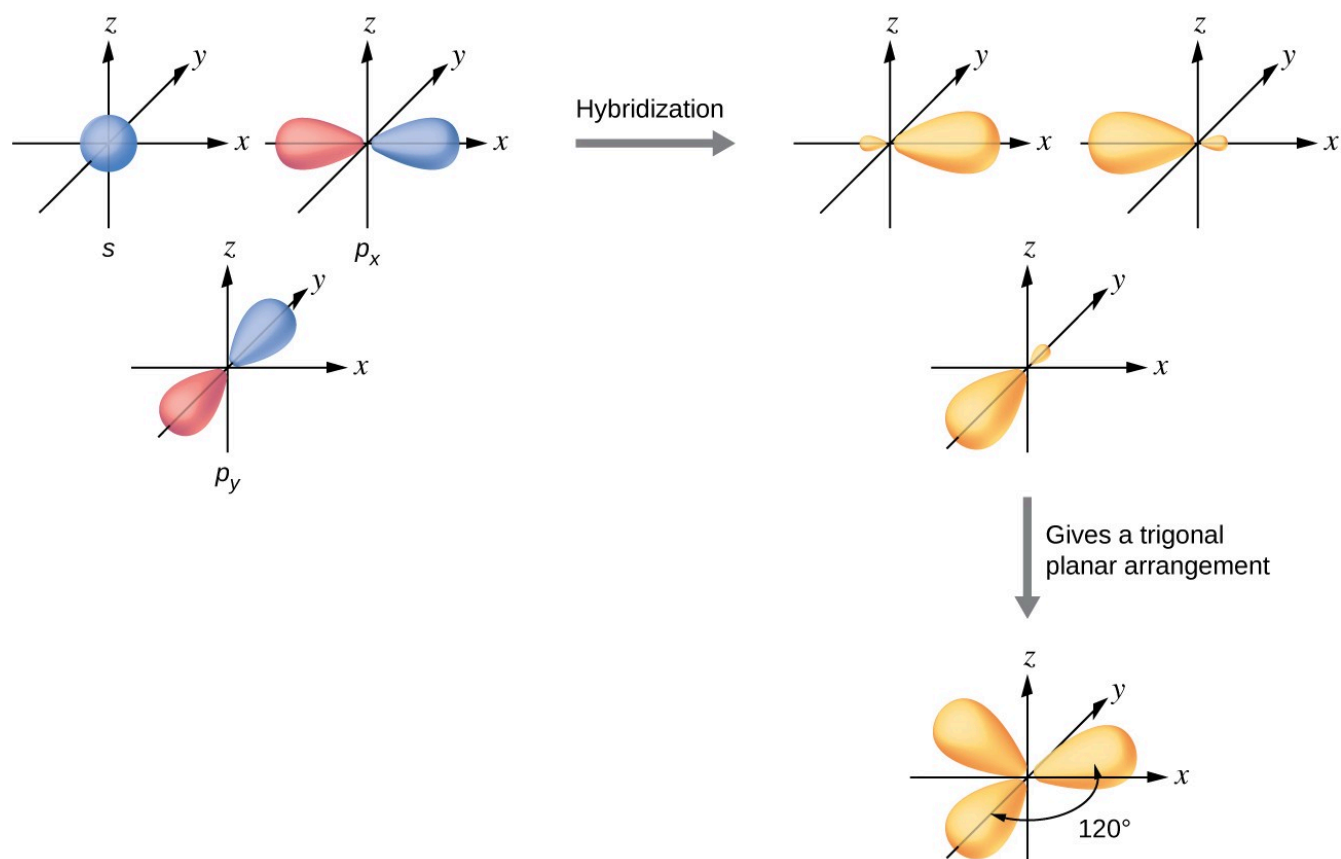
Any central atom surrounded by just two regions of valence electron density in a molecule will exhibit  $sp$  hybridization. Other examples include the mercury atom in the linear  $\text{HgCl}_2$  molecule, the zinc atom in  $\text{Zn}(\text{CH}_3)_2$ , which contains a linear C–Zn–C arrangement, and the carbon atoms in HCCH and  $\text{CO}_2$ .

Link to Learning

[Check out the University of Wisconsin-Oshkosh website](#) to learn about visualizing hybrid orbitals in three dimensions.

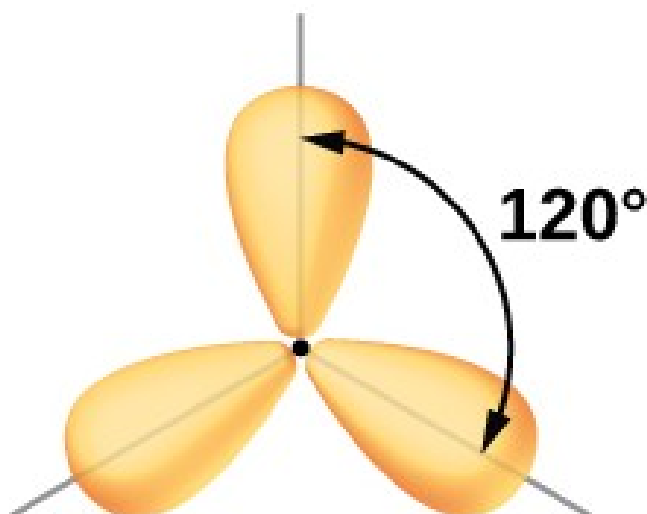
## $sp^2$ Hybridization

The valence orbitals of a central atom surrounded by three regions of electron density consist of a set of three  **$sp^2$  hybrid orbitals** and one unhybridized  $p$  orbital. This arrangement results from  $sp^2$  hybridization, the mixing of one  $s$  orbital and two  $p$  orbitals to produce three identical hybrid orbitals oriented in a trigonal planar geometry (**Figure 5.14**).



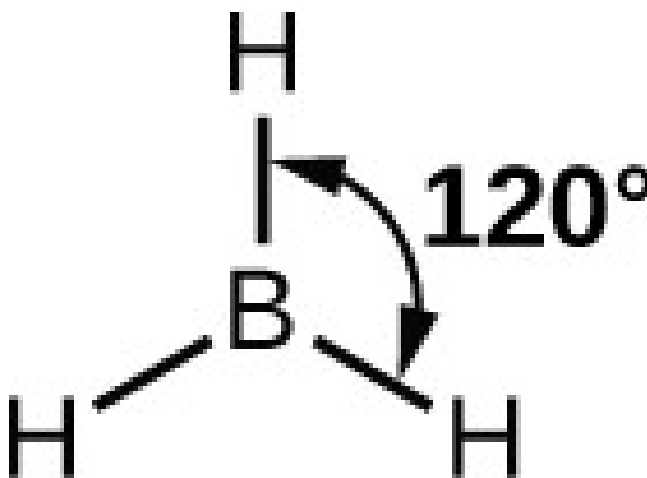
**Figure 5.14** The hybridization of an s orbital (blue) and two p orbitals (red) produces three equivalent  $sp^2$  hybridized orbitals (yellow) oriented at  $120^\circ$  with respect to each other. The remaining unhybridized p orbital is not shown here but is located along the z axis. By: Rice University [Openstax CC BY NC SA](#)

Although quantum mechanics yields the “plump” orbital lobes as depicted in **Figure 5.14**, sometimes for clarity, these orbitals are drawn thinner and without the minor lobes, as in **Figure 5.15**, to avoid obscuring other features of a given illustration. We will use these “thinner” representations whenever the true view is too crowded to easily visualize.

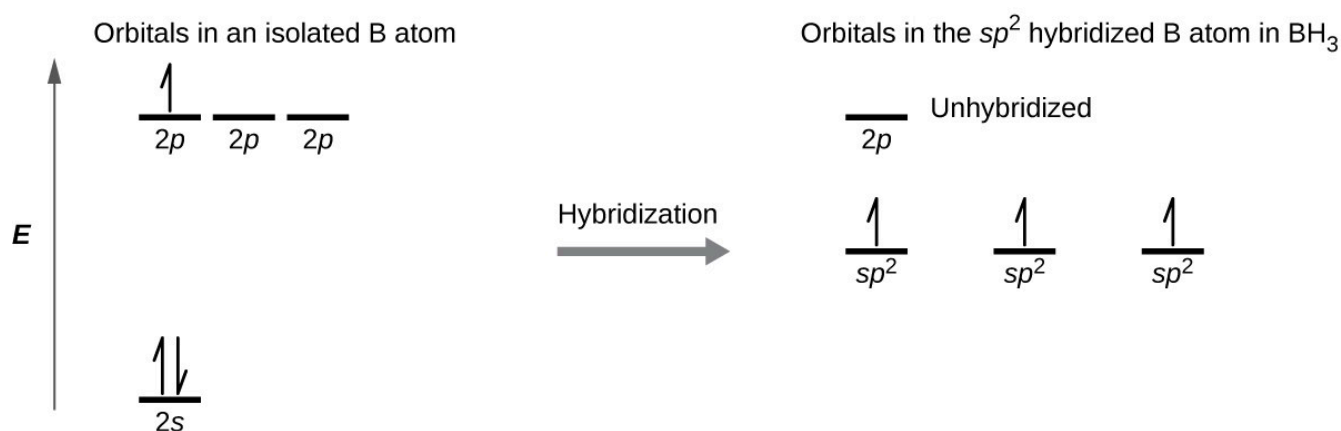


**Figure 5.15** This alternate way of drawing the trigonal planar  $sp^2$  hybrid orbitals is sometimes used in more crowded figures. By: Rice University  
[Openstax CC BY NC SA](#)

The observed structure of the borane molecule,  $BH_3$ , suggests  $sp^2$  hybridization for boron in this compound. The molecule is trigonal planar, and the boron atom is involved in three bonds to hydrogen atoms (**Figure 5.16**). We can illustrate the comparison of orbitals and electron distribution in an isolated boron atom and in the bonded atom in  $BH_3$  as shown in the orbital energy level diagram in **Figure 5.17**. We redistribute the three valence electrons of the boron atom in the three  $sp^2$  hybrid orbitals, and each boron electron pairs with a hydrogen electron when B–H bonds form.

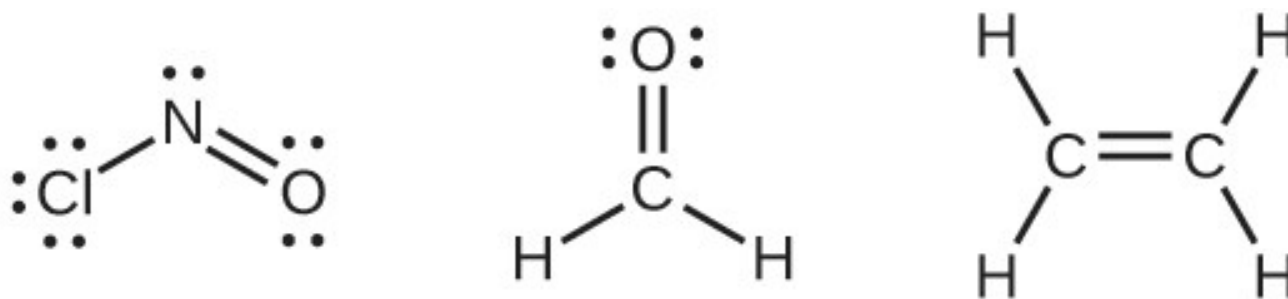


**Figure 5.16**  $BH_3$  is an electron-deficient molecule with a trigonal planar structure. By: Rice University  
[Openstax CC BY NC SA](#)



**Figure 5.17** In an isolated B atom, there are one 2s and three 2p valence orbitals. When boron is in a molecule with three regions of electron density, three of the orbitals hybridize and create a set of three  $sp^2$  orbitals and one unhybridized 2p orbital. The three half-filled hybrid orbitals each overlap with an orbital from a hydrogen atom to form three  $\sigma$  bonds in  $BH_3$ . By: Rice University [Openstax CC BY NC SA](#)

Any central atom surrounded by three regions of electron density will exhibit  $sp^2$  hybridization. This includes molecules with a lone pair on the central atom, such as  $ClNO$  (**Figure 5.18**), or molecules with two single bonds and a double bond connected to the central atom, as in formaldehyde,  $CH_2O$ , and ethene,  $H_2CCH_2$ .

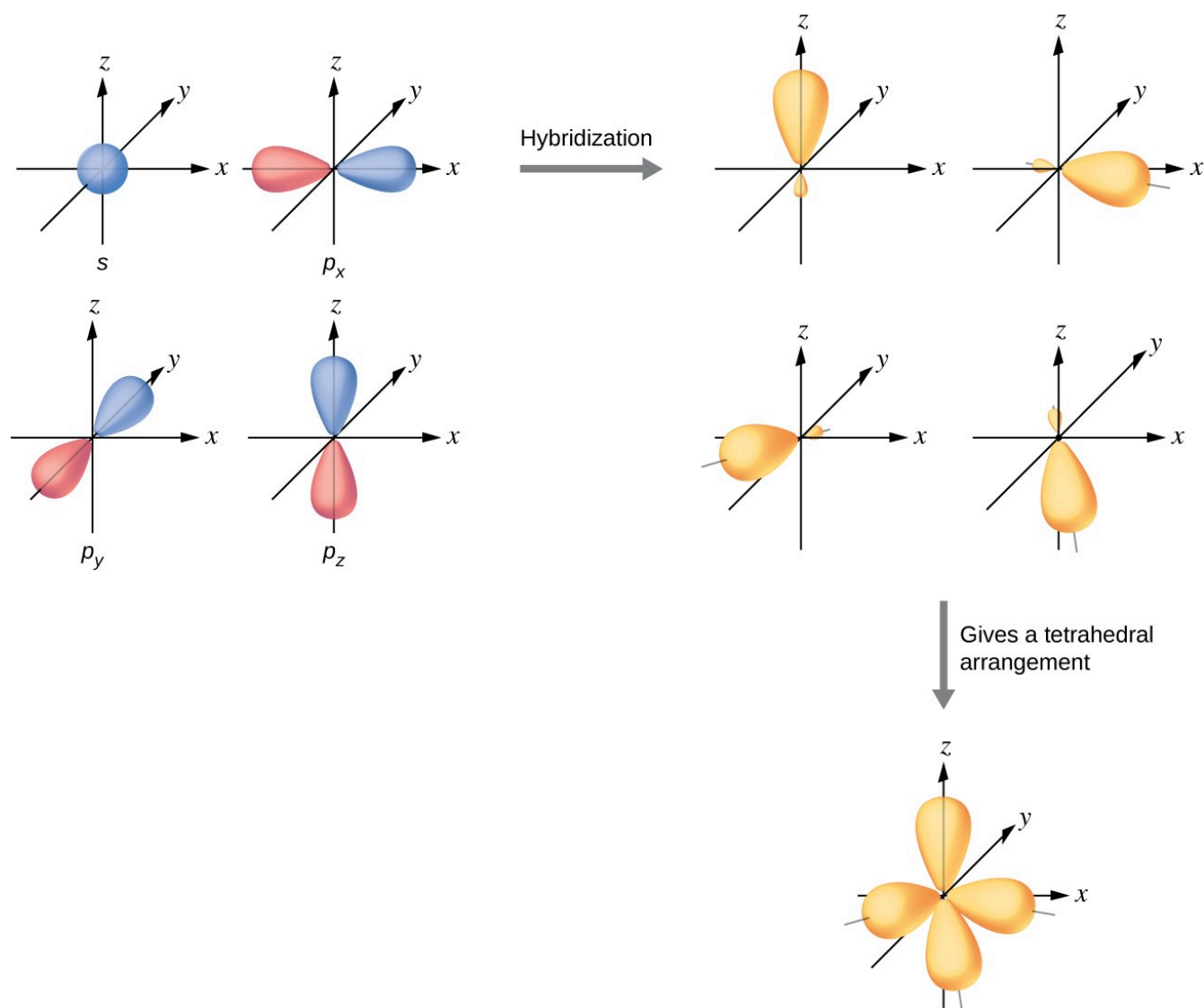


**Figure 5.18** The central atom(s) in each of the structures shown contains three regions of electron density and are  $sp^2$  hybridized. As we know from the discussion of VSEPR theory, a region of electron density contains all of the electrons that point in one direction. A lone pair, an unpaired electron, a single bond, or a multiple bond would each count as one region of electron density. By: Rice University [Openstax CC BY NC SA](#)

## $sp^3$ Hybridization

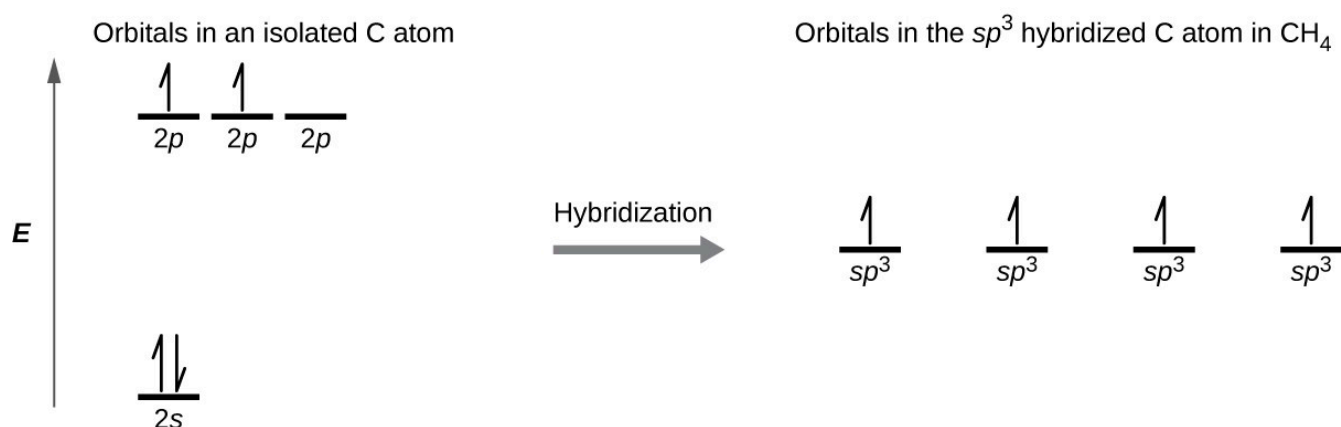
The valence orbitals of an atom surrounded by a tetrahedral arrangement of bonding pairs and lone pairs consist of a set of four  **$sp^3$  hybrid orbitals**. The hybrids result from the mixing of one  $s$  orbital and all three  $p$  orbitals that produces four identical  $sp^3$  hybrid orbitals (**Figure 5.19**). Each of these hybrid orbitals points toward a different corner of a tetrahedron.





**Figure 5.19** The hybridization of an  $s$  orbital (blue) and three  $p$  orbitals (red) produces four equivalent  $sp^3$  hybridized orbitals (yellow) oriented at  $109.5^\circ$  with respect to each other. By: Rice University [Openstax CC BY NC SA](#)

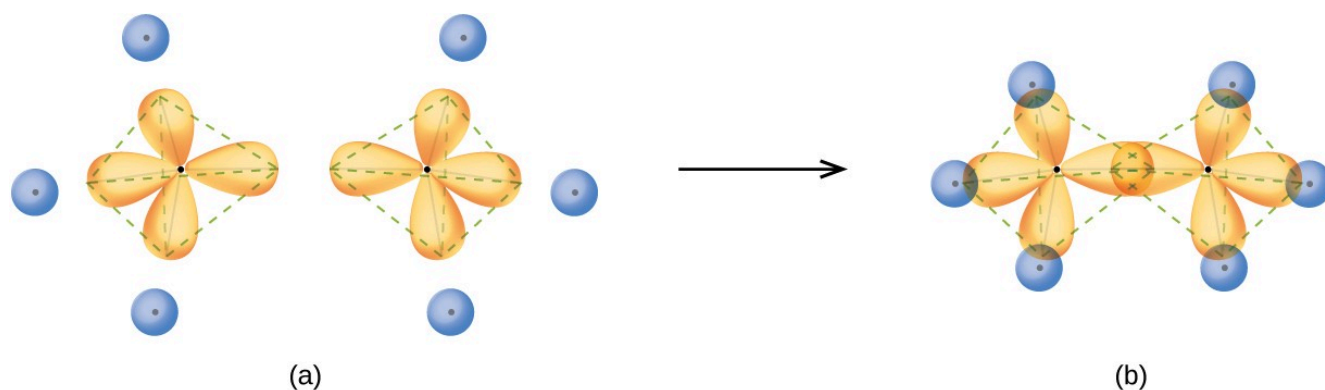
A molecule of methane,  $\text{CH}_4$ , consists of a carbon atom surrounded by four hydrogen atoms at the corners of a tetrahedron. The carbon atom in methane exhibits  $sp^3$  hybridization. We illustrate the orbitals and electron distribution in an isolated carbon atom and in the bonded atom in  $\text{CH}_4$  in **Figure 5.20**. The four valence electrons of the carbon atom are distributed equally in the hybrid orbitals, and each carbon electron pairs with a hydrogen electron when the C–H bonds form.



**Figure 5.20** The four valence atomic orbitals from an isolated carbon atom all hybridize when the carbon bonds in a molecule like  $\text{CH}_4$  with four regions of electron density. This creates four equivalent  $sp^3$  hybridized orbitals. Overlap of each of the hybrid orbitals with a hydrogen orbital creates a C–H  $\sigma$  bond. By: Rice University [Openstax CC BY NC SA](#)

In a methane molecule, the  $1s$  orbital of each of the four hydrogen atoms overlaps with one of the four  $sp^3$  orbitals of the carbon atom to form a sigma ( $\sigma$ ) bond. This results in the formation of four strong, equivalent covalent bonds between the carbon atom and each of the hydrogen atoms to produce the methane molecule,  $\text{CH}_4$ .

The structure of ethane,  $\text{C}_2\text{H}_6$ , is similar to that of methane in that each carbon in ethane has four neighboring atoms arranged at the corners of a tetrahedron—three hydrogen atoms and one carbon atom (**Figure 5.21**). However, in ethane, an  $sp^3$  orbital of one carbon atom overlaps end to end with an  $sp^3$  orbital of a second carbon atom to form a  $\sigma$  bond between the two carbon atoms. Each of the remaining  $sp^3$  hybrid orbitals overlaps with an  $s$  orbital of a hydrogen atom to form carbon–hydrogen  $\sigma$  bonds. The structure and overall outline of the bonding orbitals of ethane are shown in **Figure 5.21**. The orientation of the two  $\text{CH}_3$  groups is not fixed relative to each other. Experimental evidence shows that rotation around  $\sigma$  bonds occurs easily.



**Figure 5.21** (a) In the ethane molecule,  $\text{C}_2\text{H}_6$ , each carbon has four  $sp^3$  orbitals. (b) These four orbitals overlap to form seven  $\sigma$  bonds. By: Rice University [Openstax CC BY NC SA](#)

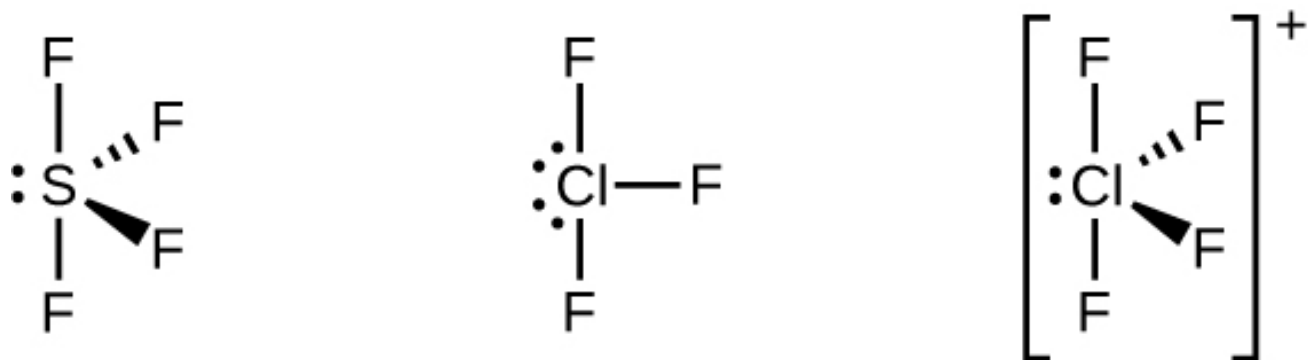
An  $sp^3$  hybrid orbital can also hold a lone pair of electrons. For example, the nitrogen atom in ammonia is surrounded by three bonding pairs and a lone pair of electrons directed to the four corners of a tetrahedron. The nitrogen atom is  $sp^3$  hybridized with one hybrid orbital occupied by the lone pair.

The molecular structure of water is consistent with a tetrahedral arrangement of two lone pairs and two bonding pairs of electrons. Thus we say that the oxygen atom is  $sp^3$  hybridized, with two of the hybrid orbitals occupied by lone pairs and two by bonding pairs. Since lone pairs occupy more space than bonding pairs, structures that contain lone pairs have bond angles slightly distorted from the ideal. Perfect tetrahedra have angles of  $109.5^\circ$ , but the observed angles in ammonia ( $107.3^\circ$ ) and water ( $104.5^\circ$ ) are slightly smaller. Other examples of  $sp^3$  hybridization include  $\text{CCl}_4$ ,  $\text{PCl}_3$ , and  $\text{NCl}_3$ .

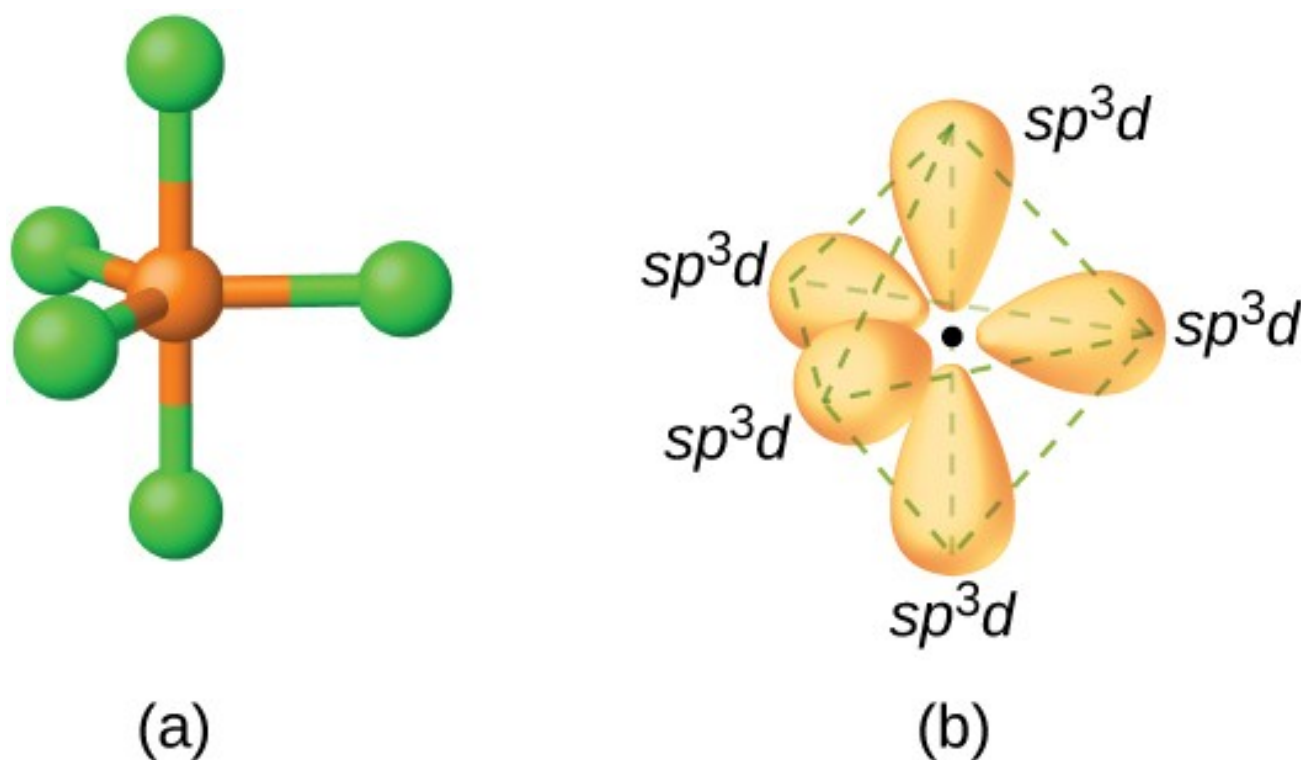
## $sp^3d$ and $sp^3d^2$ Hybridization

To describe the five bonding orbitals in a trigonal bipyramidal arrangement, we must use five of the valence shell atomic orbitals (the  $s$  orbital, the three  $p$  orbitals, and one of the  $d$  orbitals), which gives five  **$sp^3d$  hybrid orbitals**. With an octahedral arrangement of six hybrid orbitals, we must use six valence shell atomic orbitals (the  $s$  orbital, the three  $p$  orbitals, and two of the  $d$  orbitals in its valence shell), which gives six  **$sp^3d^2$  hybrid orbitals**. These hybridizations are only possible for atoms that have  $d$  orbitals in their valence subshells (that is, not those in the first or second period).

In a molecule of phosphorus pentachloride,  $\text{PCl}_5$ , there are five P–Cl bonds (thus five pairs of valence electrons around the phosphorus atom) directed toward the corners of a trigonal bipyramid. We use the  $3s$  orbital, the three  $3p$  orbitals, and one of the  $3d$  orbitals to form the set of five  $sp^3d$  hybrid orbitals (**Figure 5.22**) that are involved in the P–Cl bonds. Other atoms that exhibit  $sp^3d$  hybridization include the sulfur atom in  $\text{SF}_4$  and the chlorine atoms in  $\text{ClF}_3$  and  $\text{ClF}_4^+$ . (The electrons on fluorine atoms are omitted for clarity.)

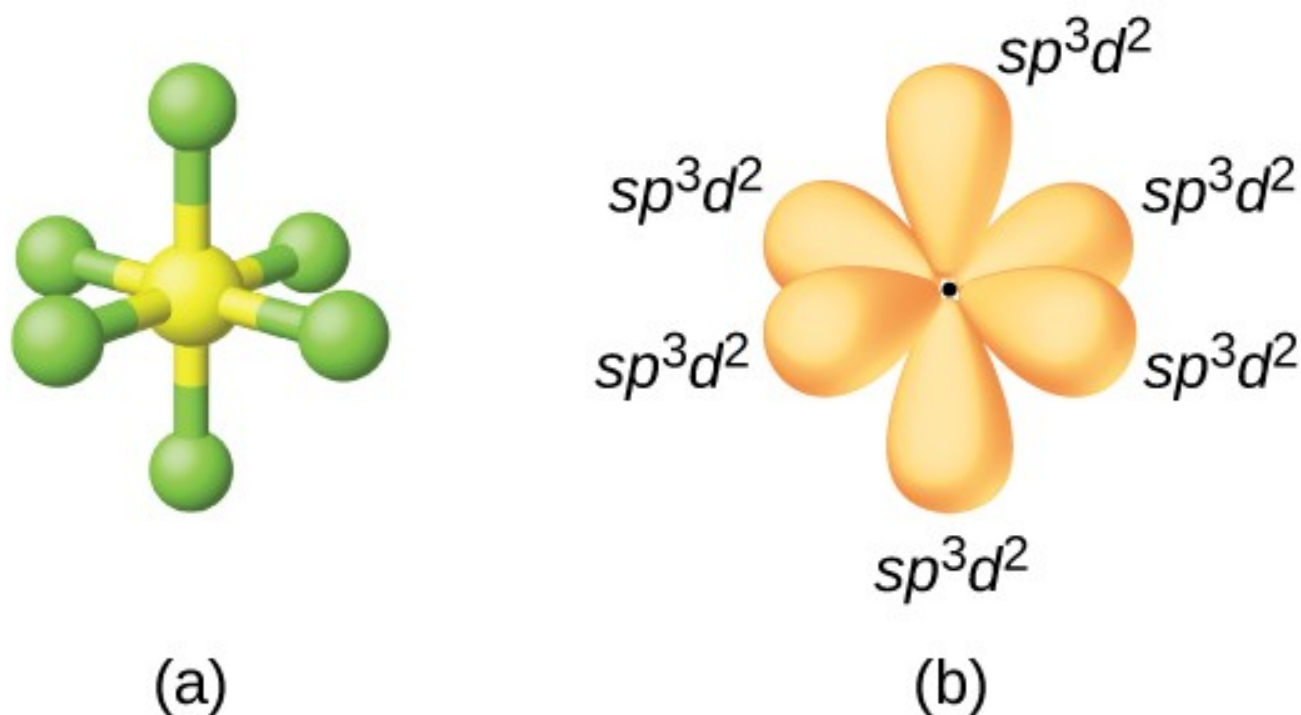


**Figure 5.22** The three compounds pictured exhibit  $sp^3d$  hybridization in the central atom and a trigonal bipyramid form.  $\text{SF}_4$  and  $\text{ClF}_4^+$  have one lone pair of electrons on the central atom, and  $\text{ClF}_3$  has two lone pairs giving it the T-shape shown. By: Rice University [Openstax CC BY NC SA](#)



**Figure 5.23** (a) The five regions of electron density around phosphorus in  $\text{PCl}_5$  require five hybrid  $sp^3d$  orbitals. (b) These orbitals combine to form a trigonal bipyramidal structure with each large lobe of the hybrid orbital pointing at a vertex. As before, there are also small lobes pointing in the opposite direction for each orbital (not shown for clarity). By: Rice University [Openstax CC BY NC SA](#)

The sulfur atom in sulfur hexafluoride,  $\text{SF}_6$ , exhibits  $sp^3d^2$  hybridization. A molecule of sulfur hexafluoride has six bonding pairs of electrons connecting six fluorine atoms to a single sulfur atom. There are no lone pairs of electrons on the central atom. To bond six fluorine atoms, the  $3s$  orbital, the three  $3p$  orbitals, and two of the  $3d$  orbitals form six equivalent  $sp^3d^2$  hybrid orbitals, each directed toward a different corner of an octahedron. Other atoms that exhibit  $sp^3d^2$  hybridization include the phosphorus atom in  $\text{PCl}_6^-$ , the iodine atom in the interhalogens  $\text{IF}_6^+$ ,  $\text{IF}_5$ ,  $\text{ICl}_4^-$ ,  $\text{IF}_4^-$ , and the xenon atom in  $\text{XeF}_4$ .



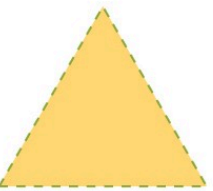
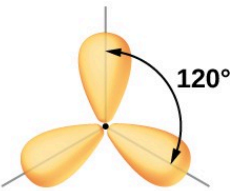
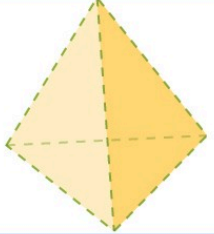
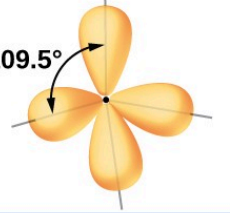
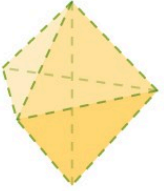
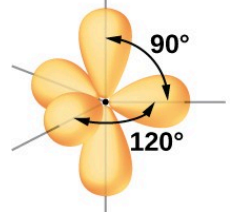
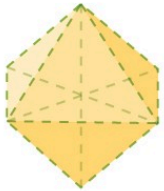
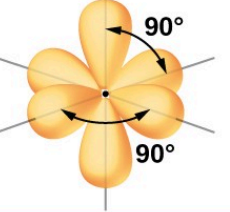


**Figure 5.24** (a) Sulfur hexafluoride,  $\text{SF}_6$ , has an octahedral structure that requires  $sp^3d^2$  hybridization. (b) The six  $sp^3d^2$  orbitals form an octahedral structure around sulfur. Again, the minor lobe of each orbital is not shown for clarity. By: Rice University [Openstax](#) [CC BY NC SA](#)

## Assignment of Hybrid Orbitals to Central Atoms

The hybridization of an atom is determined based on the number of regions of electron density that surround it. The geometrical arrangements characteristic of the various sets of hybrid orbitals are shown in **Figure 5.25**. These arrangements are identical to those of the electron-pair geometries predicted by VSEPR theory. VSEPR theory predicts the shapes of molecules, and hybrid orbital theory provides an explanation for how those shapes are formed. To find the hybridization of a central atom, we can use the following guidelines:

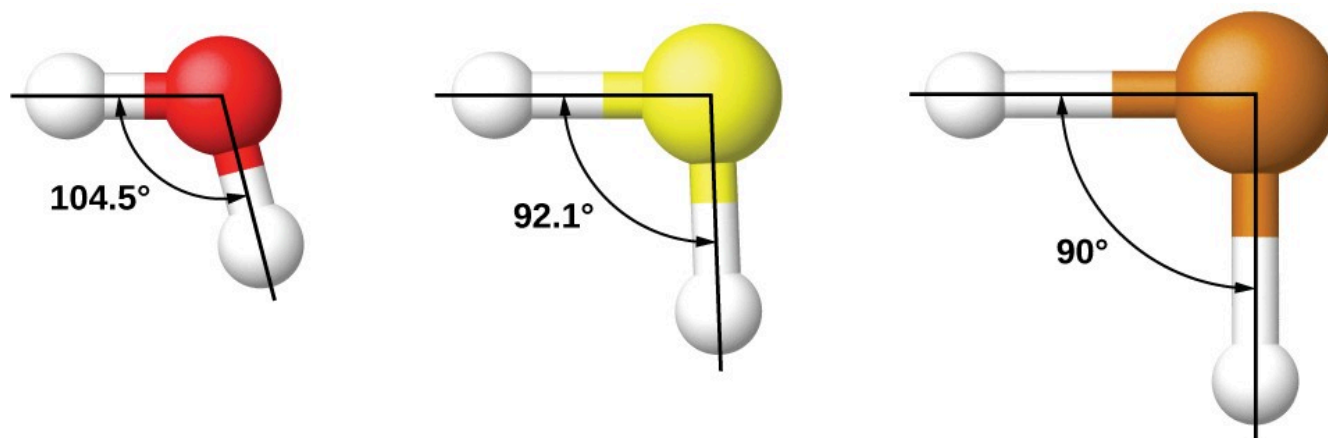
1. Determine the Lewis structure of the molecule.
2. Determine the number of regions of electron density around an atom using VSEPR theory, in which single bonds, multiple bonds, radicals, and lone pairs each count as one region.
3. Assign the set of hybridized orbitals from **Figure 5.25** that corresponds to this geometry.

Regions of Electron Density	Arrangement		Hybridization	
2		linear	$sp$	
3		trigonal planar	$sp^2$	
4		tetrahedral	$sp^3$	
5		trigonal bipyramidal	$sp^3d$	
6		octahedral	$sp^3d^2$	

**Figure 5.25** The shapes of hybridized orbital sets are consistent with the electron-pair geometries. For example, an atom surrounded by three regions of electron density is  $sp^2$  hybridized, and the three  $sp^2$  orbitals are arranged in a trigonal planar fashion. By: Rice University [Openstax CC BY NC SA](#)

It is important to remember that hybridization was devised to rationalize experimentally observed molecular geometries. The model works well for molecules containing small central atoms, in which the valence electron pairs are close together in space. However, for larger central atoms, the valence-shell electron pairs are farther from the nucleus, and there are fewer repulsions. Their compounds exhibit structures that are often not consistent with VSEPR theory, and hybridized orbitals are not necessary to explain the observed data. For example, we have discussed the H–O–H bond angle in  $H_2O$ ,  $104.5^\circ$ , which is more consistent with  $sp^3$  hybrid orbitals ( $109.5^\circ$ ) on the central atom than with  $2p$  orbitals ( $90^\circ$ ). Sulfur is in the same group as oxygen, and

$\text{H}_2\text{S}$  has a similar Lewis structure. However, it has a much smaller bond angle ( $92.1^\circ$ ), which indicates much less hybridization on sulfur than oxygen. Continuing down the group, tellurium is even larger than sulfur, and for  $\text{H}_2\text{Te}$ , the observed bond angle ( $90^\circ$ ) is consistent with the overlap of the  $5p$  orbitals, without invoking hybridization. We invoke hybridization where it is necessary to explain the observed structures.



**Figure 5.26** By: Rice University [Openstax CC BY NC SA](#)

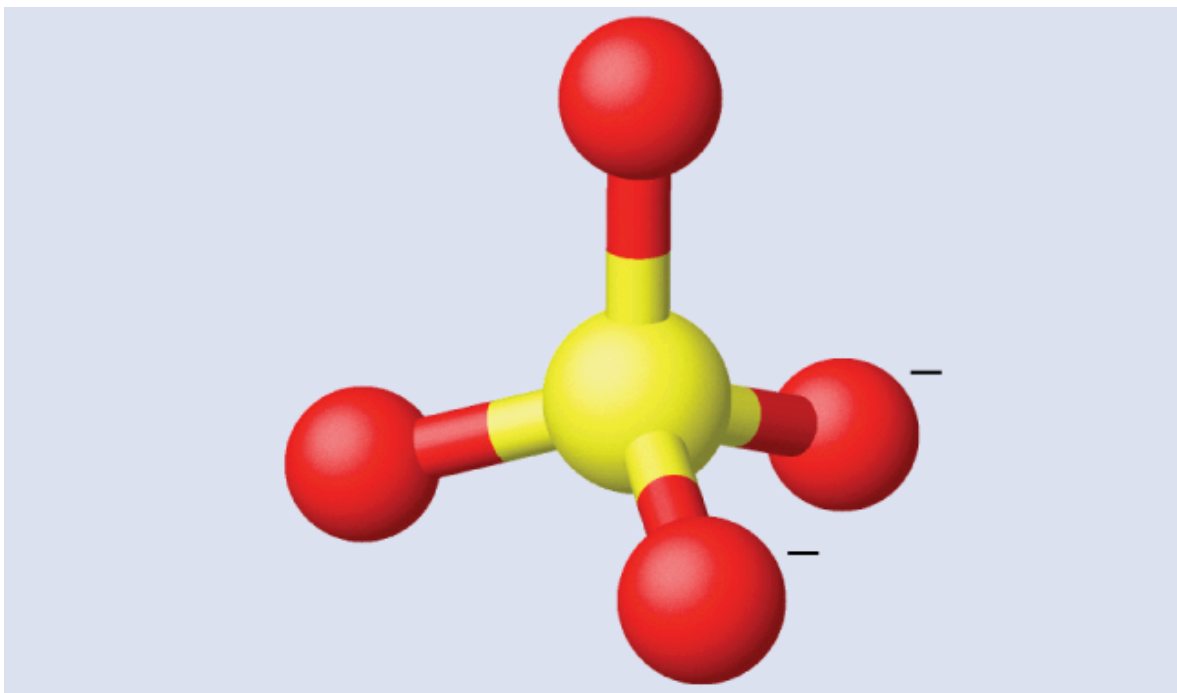
### EXAMPLE 5.3

#### Assigning Hybridization

Ammonium sulfate is important as a fertilizer. What is the hybridization of the sulfur atom in the sulfate ion,  $\text{SO}_4^{2-}$ ?

#### Solution

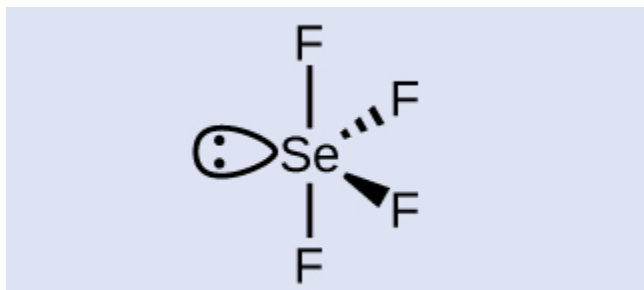
The Lewis structure of sulfate shows there are four regions of electron density. The hybridization is  $sp^3$ .



**Figure 5.27** By: Rice University [Openstax CC BY NC SA](#)

### Check Your Learning

What is the hybridization of the selenium atom in SeF<sub>4</sub>?



**Figure 5.28** By: Rice University [Openstax CC BY NC SA](#)

**Answer:** The selenium atom is  $sp^3d$  hybridized.



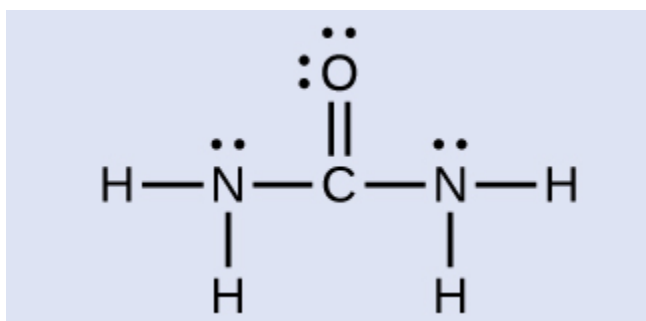
## EXAMPLE 5.4

## Assigning Hybridization

Urea,  $\text{NH}_2\text{C}(\text{O})\text{NH}_2$ , is sometimes used as a source of nitrogen in fertilizers. What is the hybridization of the carbon atom in urea?

## Solution

The Lewis structure of urea is

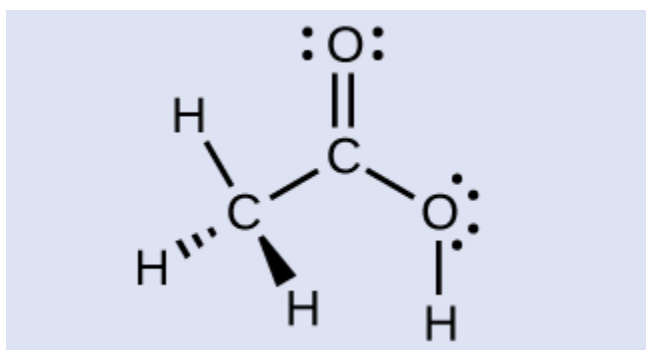


**Figure 5.29** By: Rice University [Openstax CC BY NC SA](#)

The carbon atom is surrounded by three regions of electron density, positioned in a trigonal planar arrangement. The hybridization in a trigonal planar electron pair geometry is  $sp^2$  (**Figure 5.25**), which is the hybridization of the carbon atom in urea.

## Check Your Learning

Acetic acid,  $\text{H}_3\text{CC}(\text{O})\text{OH}$ , is the molecule that gives vinegar its odor and sour taste. What is the hybridization of the two carbon atoms in acetic acid?



**Figure 5.30** By: Rice University [Openstax CC BY NC SA](#)

**Answer:**  $\text{H}_3\text{C}$ ,  $sp^3$ ;  $\text{C}(\text{O})\text{OH}$ ,  $sp^2$



An interactive H5P element has been excluded from this version of the text. You can view it online here:

<https://louis.pressbooks.pub/chemistry1/?p=324#h5p-3>

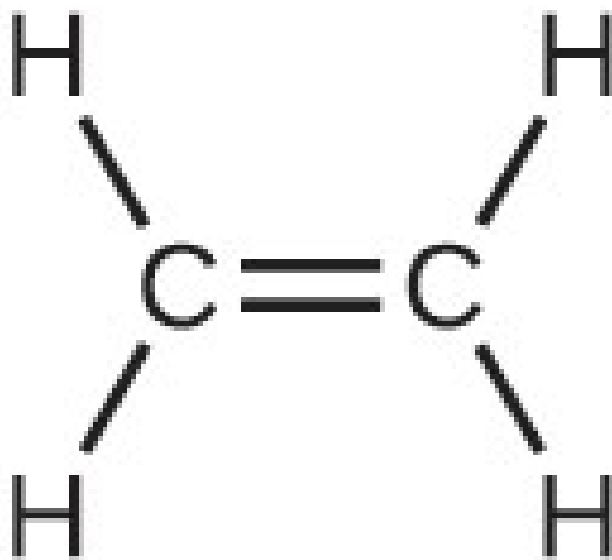
# MULTIPLE BONDS (5.3)

OpenStax

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

- Describe multiple covalent bonding in terms of atomic orbital overlap
- Relate the concept of resonance to  $\pi$ -bonding and electron delocalization

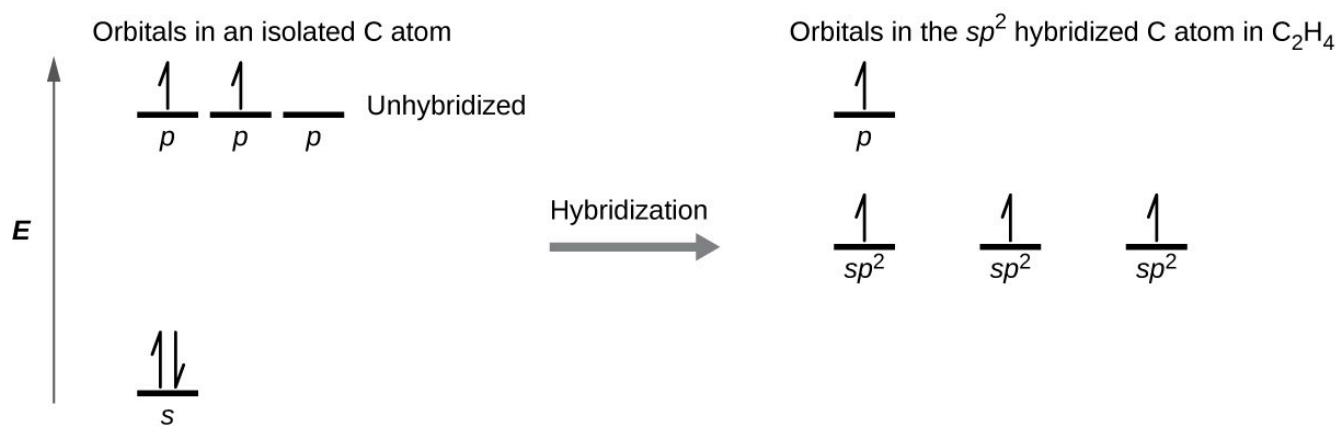
The hybrid orbital model appears to account well for the geometry of molecules involving single covalent bonds. Is it also capable of describing molecules containing double and triple bonds? We have already discussed that multiple bonds consist of  $\sigma$  and  $\pi$  bonds. Next we can consider how we visualize these components and how they relate to hybrid orbitals. The Lewis structure of ethene,  $\text{C}_2\text{H}_4$ , shows us that each carbon atom is surrounded by one other carbon atom and two hydrogen atoms.



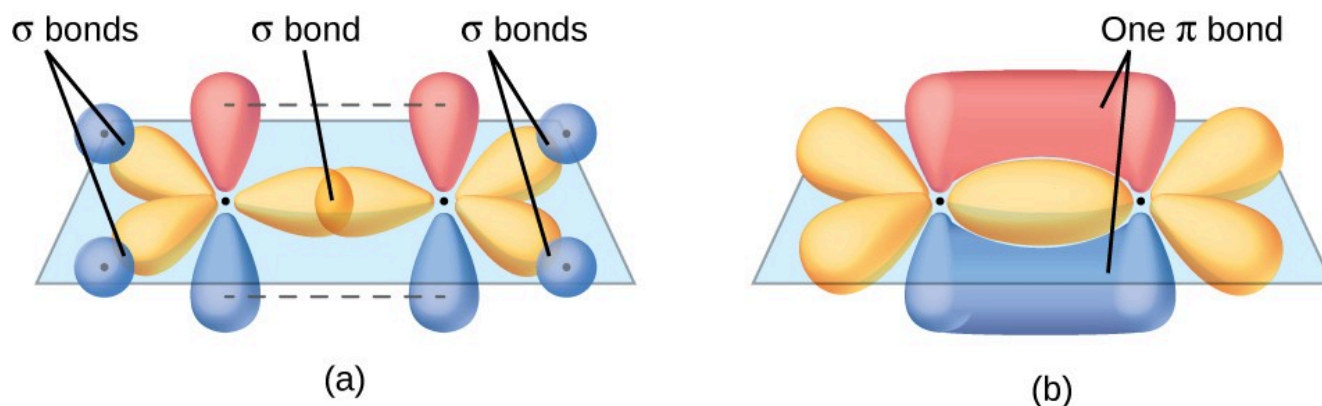
**Figure 5.31** By: Rice University [Openstax CC BY NC SA](#)

The three bonding regions form a trigonal planar electron-pair geometry. Thus we expect the  $\sigma$  bonds from

each carbon atom to be formed using a set of  $sp^2$  hybrid orbitals that result from the hybridization of two of the  $2p$  orbitals and the  $2s$  orbital (**Figure 5.32**). These orbitals form the C–H single bonds and the  $\sigma$  bond in the C = C double bond (**Figure 5.33**). The  $\pi$  bond in the C = C double bond results from the overlap of the third (remaining)  $2p$  orbital on each carbon atom that is not involved in hybridization. This unhybridized  $p$  orbital (lobes shown in red and blue in **Figure 5.33**) is perpendicular to the plane of the  $sp^2$  hybrid orbitals. Thus the unhybridized  $2p$  orbitals overlap in a side-by-side fashion, above and below the internuclear axis (**Figure 5.33**), and form a  $\pi$  bond.



**Figure 5.32** In ethene, each carbon atom is  $sp^2$  hybridized, and the  $sp^2$  orbitals and the  $p$  orbital are singly occupied. The hybrid orbitals overlap to form  $\sigma$  bonds, while the  $p$  orbitals on each carbon atom overlap to form a  $\pi$  bond. By: Rice University [Openstax CC BY NC SA](#)

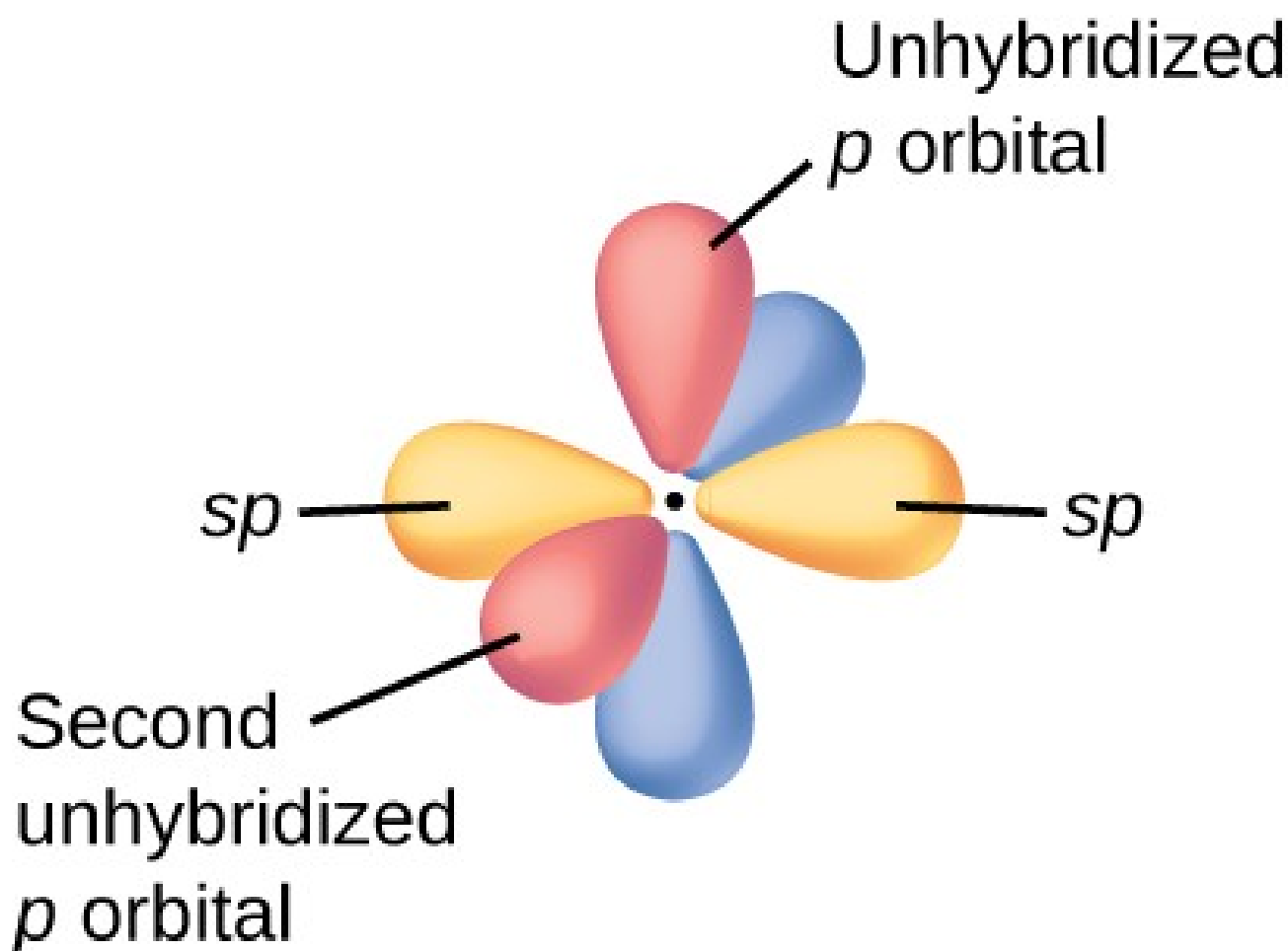


**Figure 5.33** In the ethene molecule,  $C_2H_4$ , there are (a) five  $\sigma$  bonds. One C–C  $\sigma$  bond results from the overlap of  $sp^2$  hybrid orbitals on the carbon atom with one  $sp^2$  hybrid orbital on the other carbon atom. Four C–H bonds result from the overlap between the C atoms'  $sp^2$  orbitals with  $s$  orbitals on the hydrogen atoms. (b) The  $\pi$  bond is formed by the side-by-side overlap of the two unhybridized  $p$  orbitals in the two carbon atoms. The two lobes of the  $\pi$  bond are above and below the plane of the  $\sigma$  system. By: Rice University [Openstax CC BY NC SA](#)

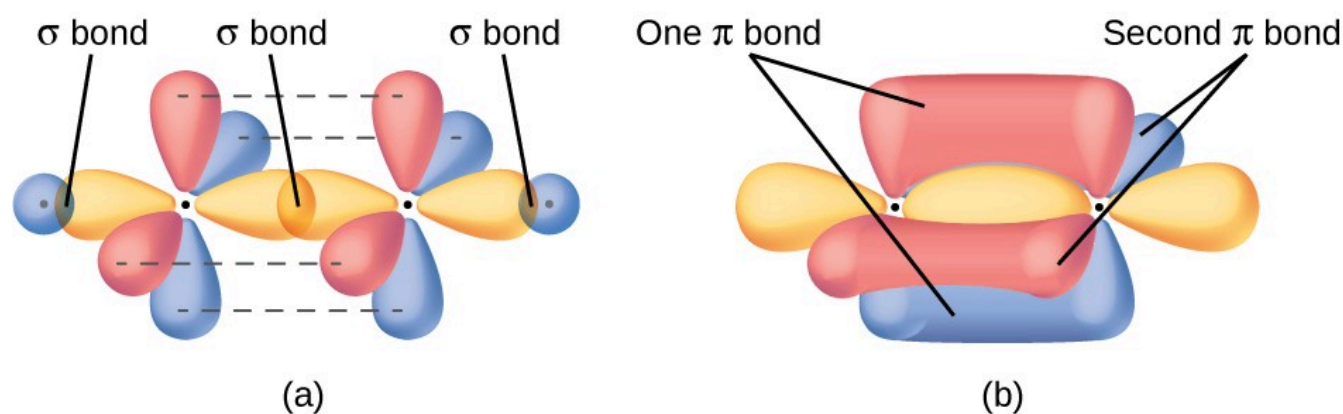
In an ethene molecule, the four hydrogen atoms and the two carbon atoms are all in the same plane. If the two planes of  $sp^2$  hybrid orbitals tilted relative to each other, the  $p$  orbitals would not be oriented to overlap

efficiently to create the  $\pi$  bond. The planar configuration for the ethene molecule occurs because it is the most stable bonding arrangement. This is a significant difference between  $\sigma$  and  $\pi$  bonds; rotation around single ( $\sigma$ ) bonds occurs easily because the end-to-end orbital overlap does not depend on the relative orientation of the orbitals on each atom in the bond. In other words, rotation around the internuclear axis does not change the extent to which the  $\sigma$  bonding orbitals overlap because the bonding electron density is symmetric about the axis. Rotation about the internuclear axis is much more difficult for multiple bonds; however, this would drastically alter the off-axis overlap of the  $\pi$  bonding orbitals, essentially breaking the  $\pi$  bond.

In molecules with  $sp$  hybrid orbitals, two unhybridized  $p$  orbitals remain on the atom (**Figure 5.34**). We find this situation in acetylene,  $\text{H}-\text{C}\equiv\text{C}-\text{H}$ , which is a linear molecule. The  $sp$  hybrid orbitals of the two carbon atoms overlap end to end to form a  $\sigma$  bond between the carbon atoms (**Figure 5.35**). The remaining  $sp$  orbitals form  $\sigma$  bonds with hydrogen atoms. The two unhybridized  $p$  orbitals per carbon are positioned such that they overlap side by side and, hence, form two  $\pi$  bonds. The two carbon atoms of acetylene are thus bound together by one  $\sigma$  bond and two  $\pi$  bonds, giving a triple bond.



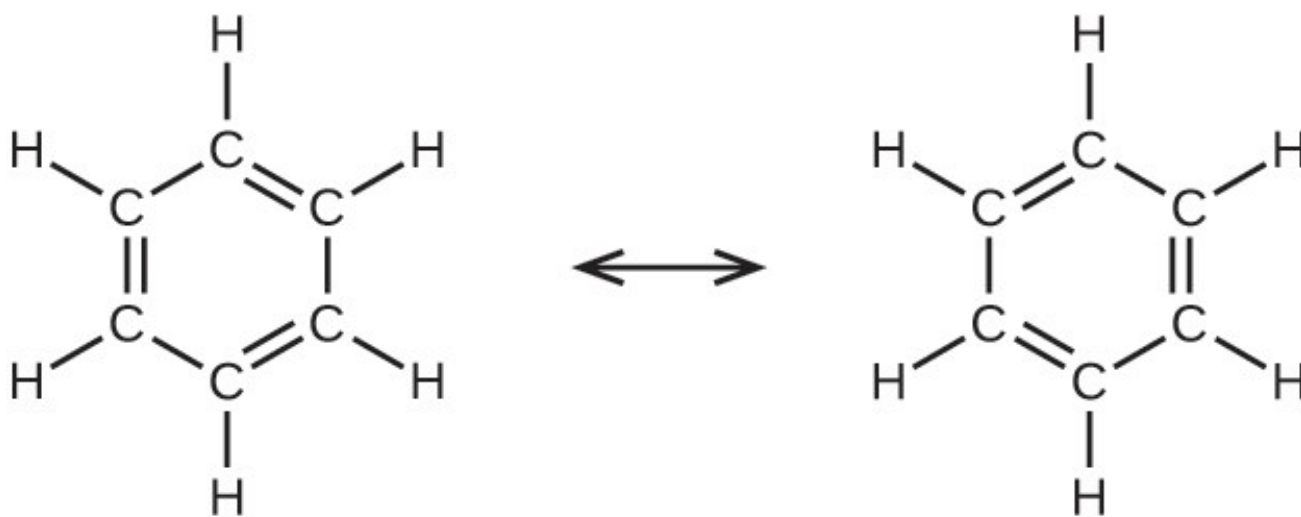
**Figure 5.34** Diagram of the two linear  $sp$  hybrid orbitals of a carbon atom, which lie in a straight line, and the two unhybridized  $p$  orbitals at perpendicular angles. By: Rice University [Openstax CC BY NC SA](#)



**Figure 5.35** (a) In the acetylene molecule,  $\text{C}_2\text{H}_2$ , there are two C-H  $\sigma$  bonds and a  $\text{C} \equiv \text{C}$  triple bond involving one C-C  $\sigma$  bond and two C-C  $\pi$  bonds. The dashed lines, each connecting two lobes, indicate the side-by-side overlap of the four unhybridized  $p$  orbitals. (b) This shows the overall outline of the bonds in  $\text{C}_2\text{H}_2$ . The two lobes of each of the  $\pi$  bonds are positioned across from each other around the line of the C-C  $\sigma$  bond. By: Rice University [Openstax CC BY NC SA](#)

Hybridization involves only  $\sigma$  bonds, lone pairs of electrons, and single unpaired electrons (radicals). Structures that account for these features describe the correct hybridization of the atoms. However, many structures also include resonance forms. Remember that resonance forms occur when various arrangements of  $\pi$  bonds are possible. Since the arrangement of  $\pi$  bonds involves only the unhybridized orbitals, resonance does not influence the assignment of hybridization.

For example, the molecule benzene has two resonance forms (**Figure 5.36**). We can use either of these forms to determine that each of the carbon atoms is bonded to three other atoms with no lone pairs, so the correct hybridization is  $sp^2$ . The electrons in the unhybridized  $p$  orbitals form  $\pi$  bonds. Neither resonance structure completely describes the electrons in the  $\pi$  bonds. They are not located in one position or the other but in reality are delocalized throughout the ring. Valence bond theory does not easily address delocalization. Bonding in molecules with resonance forms is better described by molecular orbital theory. (See the next module.)



**Figure 5.36** Each carbon atom in benzene,  $C_6H_6$ , is  $sp^2$  hybridized, independently of which resonance form is considered. The electrons in the  $\pi$  bonds are not located in one set of p orbitals or the other but rather delocalized throughout the molecule. By: Rice University [Openstax CC BY NC SA](#)

## EXAMPLE 5.5

### Assignment of Hybridization Involving Resonance

Some acid rain results from the reaction of sulfur dioxide with atmospheric water vapor, followed by the formation of sulfuric acid. Sulfur dioxide,  $SO_2$ , is a major component of volcanic gases as well as a product of the combustion of sulfur-containing coal. What is the hybridization of the S atom in  $SO_2$ ?

### Solution

The resonance structures of  $SO_2$  are



**Figure 5.37** By: Rice University [Openstax CC BY NC SA](#)

The sulfur atom is surrounded by two bonds and one lone pair of electrons in either resonance

structure. Therefore, the electron-pair geometry is trigonal planar, and the hybridization of the sulfur atom is  $sp^2$ .

### Check Your Learning

Another acid in acid rain is nitric acid,  $\text{HNO}_3$ , which is produced by the reaction of nitrogen dioxide,  $\text{NO}_2$ , with atmospheric water vapor. What is the hybridization of the nitrogen atom in  $\text{NO}_2$ ? (Note: the lone electron on nitrogen occupies a hybridized orbital just as a lone pair would.)

**Answer:**  $sp^2$



*An interactive H5P element has been excluded from this version of the text. You can view it online here:*

<https://louis.pressbooks.pub/chemistry1/?p=333#h5p-5>



*An interactive H5P element has been excluded from this version of the text. You can view it online here:*

<https://louis.pressbooks.pub/chemistry1/?p=333#h5p-6>



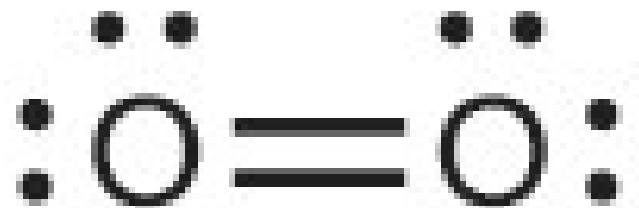
# MOLECULAR ORBITAL THEORY (5.4)

OpenStax

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

- Outline the basic quantum-mechanical approach to deriving molecular orbitals from atomic orbitals
- Describe traits of bonding and antibonding molecular orbitals
- Calculate bond orders based on molecular electron configurations
- Write molecular electron configurations for first- and second-row diatomic molecules
- Relate these electron configurations to the molecules' stabilities and magnetic properties

For almost every covalent molecule that exists, we can now draw the Lewis structure, predict the electron-pair geometry, predict the molecular geometry, and come close to predicting bond angles. However, one of the most important molecules we know, the oxygen molecule  $O_2$ , presents a problem with respect to its Lewis structure. We would write the following Lewis structure for  $O_2$ :

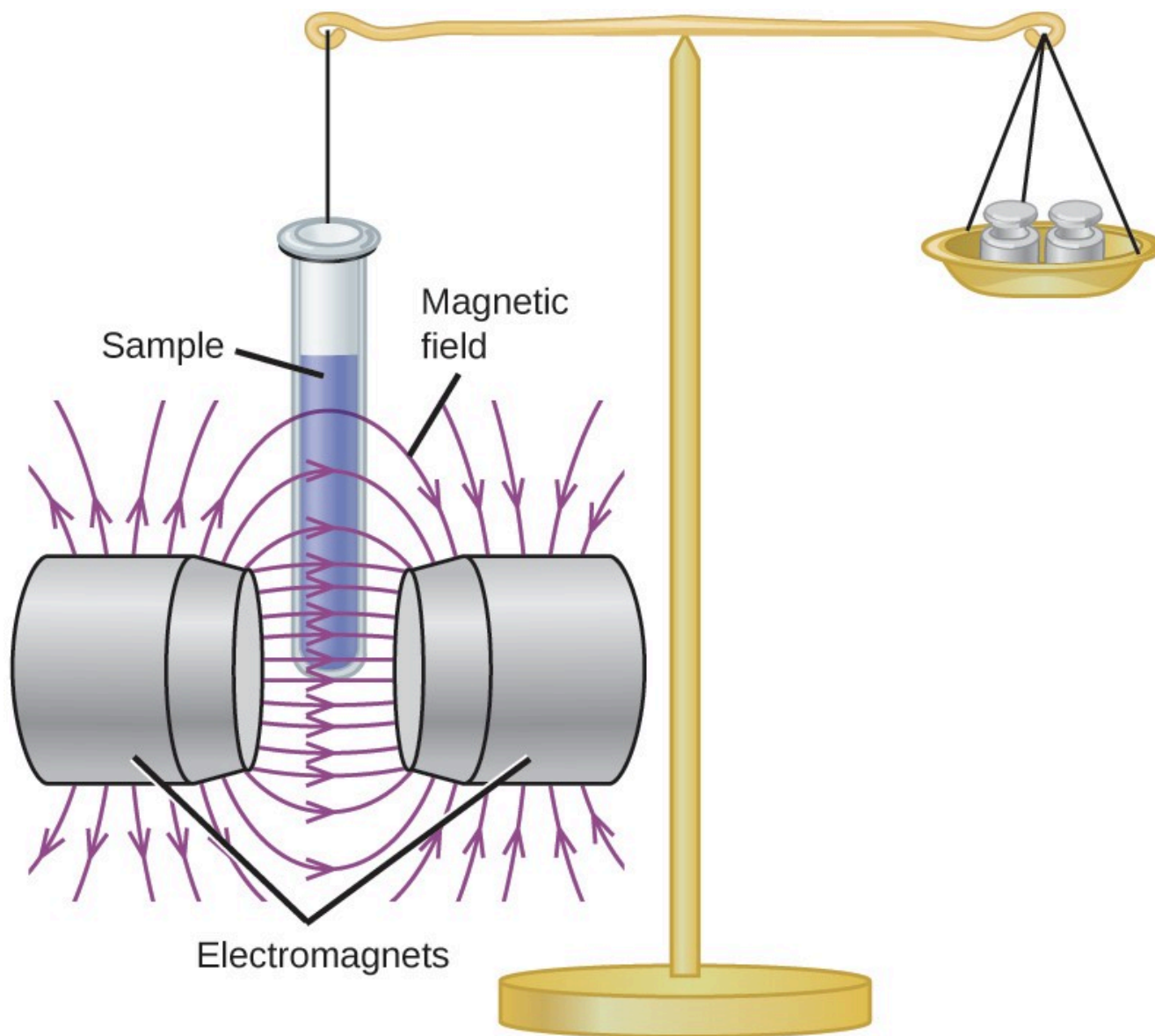


**Figure 5.38** By: Rice University [Openstax CC BY NC SA](#)

This electronic structure adheres to all the rules governing the Lewis theory. There is an  $O=O$  double bond, and each oxygen atom has eight electrons around it. However, this picture is at odds with the magnetic behavior of oxygen. By itself,  $O_2$  is not magnetic, but it is attracted to magnetic fields. Thus, when we pour liquid oxygen past a strong magnet, it collects between the poles of the magnet and defies gravity, as in **Figure 5.1**. Such attraction to a magnetic field is called **paramagnetism**, and it arises in molecules that have unpaired

electrons. And yet, the Lewis structure of  $O_2$  indicates that all electrons are paired. How do we account for this discrepancy?

Magnetic susceptibility measures the force experienced by a substance in a magnetic field. When we compare the weight of a sample to the weight measured in a magnetic field (**Figure 5.39**), paramagnetic samples that are attracted to the magnet will appear heavier because of the force exerted by the magnetic field. We can calculate the number of unpaired electrons based on the increase in weight.



**Figure 5.39** A Gouy balance compares the mass of a sample in the presence of a magnetic field with the mass with the electromagnet turned off to determine the number of unpaired electrons in a sample. By: Rice University [Openstax CC BY NC SA](#)

Experiments show that each  $O_2$  molecule has two unpaired electrons. The Lewis-structure model does not predict the presence of these two unpaired electrons. Unlike oxygen, the apparent weight of most molecules

decreases slightly in the presence of an inhomogeneous magnetic field. Materials in which all of the electrons are paired are **diamagnetic** and weakly repel a magnetic field. Paramagnetic and diamagnetic materials do not act as permanent magnets. Only in the presence of an applied magnetic field do they demonstrate attraction or repulsion.

### Link to Learning

Water, like most molecules, contains all paired electrons. Living things contain a large percentage of water, so they demonstrate diamagnetic behavior. If you place a frog near a sufficiently large magnet, it will levitate. You can see [videos](#) of diamagnetic floating frogs, strawberries, and more.

Molecular orbital theory (MO theory) provides an explanation of chemical bonding that accounts for the paramagnetism of the oxygen molecule. It also explains the bonding in a number of other molecules, such as violations of the octet rule and more molecules with more complicated bonding (beyond the scope of this text) that are difficult to describe with Lewis structures. Additionally, it provides a model for describing the energies of electrons in a molecule and the probable location of these electrons. Unlike valence bond theory, which uses hybrid orbitals that are assigned to one specific atom, MO theory uses the combination of atomic orbitals to yield molecular orbitals that are *delocalized* over the entire molecule rather than being localized on its constituent atoms. MO theory also helps us understand why some substances are electrical conductors, others are semiconductors, and still others are insulators. [Table 5.1](#) summarizes the main points of the two complementary bonding theories. Both theories provide different, useful ways of describing molecular structure.

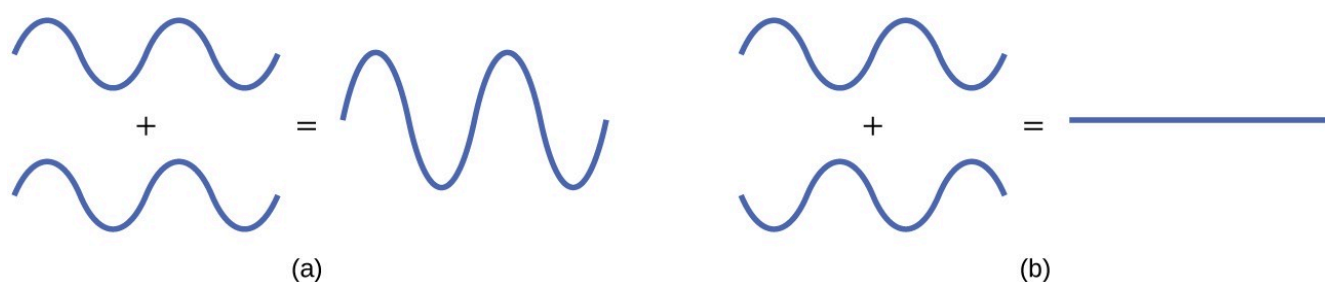
**Table 5.1 Comparison of Bonding Theories By: Rice University** [OpenStax CC BY-NC-SA 4.0](#)

Valence Bond Theory	Molecular Orbital Theory
considers bonds as localized between one pair of atoms	considers electrons delocalized throughout the entire molecule
creates bonds from the overlap of atomic orbitals ( $s$ , $p$ , $d$ ...) and hybrid orbitals ( $sp$ , $sp^2$ , $sp^3$ ...)	combines atomic orbitals to form molecular orbitals ( $\sigma$ , $\sigma^*$ , $\pi$ , $\pi^*$ )
forms $\sigma$ or $\pi$ bonds	creates bonding and antibonding interactions based on which orbitals are filled
predicts molecular shape based on the number of regions of electron density	predicts the arrangement of electrons in molecules
needs multiple structures to describe resonance	<i>No entry</i>

**Molecular orbital theory** describes the distribution of electrons in molecules in much the same way that the distribution of electrons in atoms is described using atomic orbitals. Using quantum mechanics, the behavior of an electron in a molecule is still described by a wave function,  $\Psi$ , analogous to the behavior in an atom. Just like electrons around isolated atoms, electrons around atoms in molecules are limited to discrete (quantized) energies. The region of space in which a valence electron in a molecule is likely to be found is called a **molecular orbital ( $\Psi^2$ )**. Like an atomic orbital, a molecular orbital is full when it contains two electrons with opposite spin.

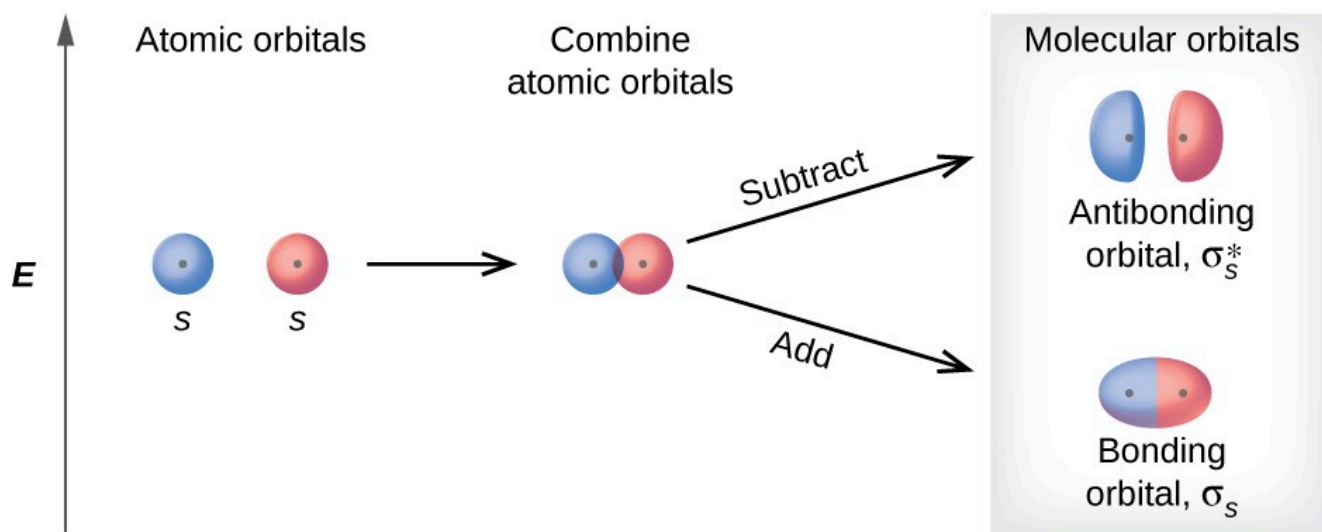
We will consider the molecular orbitals in molecules composed of two identical atoms ( $H_2$  or  $Cl_2$ , for example). Such molecules are called **homonuclear diatomic molecules**. In these diatomic molecules, several types of molecular orbitals occur.

The mathematical process of combining atomic orbitals to generate molecular orbitals is called the **linear combination of atomic orbitals (LCAO)**. The wave function describes the wavelike properties of an electron. Molecular orbitals are combinations of atomic orbital wave functions. Combining waves can lead to constructive interference, in which peaks line up with peaks, or destructive interference, in which peaks line up with troughs (**Figure 5.40**). In orbitals, the waves are three-dimensional, and they combine with in-phase waves producing regions with a higher probability of electron density and out-of-phase waves producing nodes, or regions of no electron density.



**Figure 5.40** (a) When in-phase waves combine, constructive interference produces a wave with greater amplitude. (b) When out-of-phase waves combine, destructive interference produces a wave with less (or no) amplitude. By: Rice University [Openstax CC BY NC SA](#)

There are two types of molecular orbitals that can form from the overlap of two atomic  $s$  orbitals on adjacent atoms. The two types are illustrated in **Figure 5.41**. The in-phase combination produces a lower energy  $\sigma_s$  **molecular orbital** (read as “sigma-s”) in which most of the electron density is directly between the nuclei. The out-of-phase addition (which can also be thought of as subtracting the wave functions) produces a higher energy **molecular orbital** (read as “sigma-s-star”) molecular orbital in which there is a node between the nuclei. The asterisk signifies that the orbital is an antibonding orbital. Electrons in a  $\sigma_s$  orbital are attracted by both nuclei at the same time and are more stable (of lower energy) than they would be in the isolated atoms. Adding electrons to these orbitals creates a force that holds the two nuclei together, so we call these orbitals **bonding orbitals**. Electrons in the  $\sigma_s^*$  orbitals are located well away from the region between the two nuclei. The attractive force between the nuclei and these electrons pulls the two nuclei apart. Hence, these orbitals are called **antibonding orbitals**. Electrons fill the lower-energy bonding orbital before the higher-energy antibonding orbital, just as they fill lower-energy atomic orbitals before they fill higher-energy atomic orbitals.

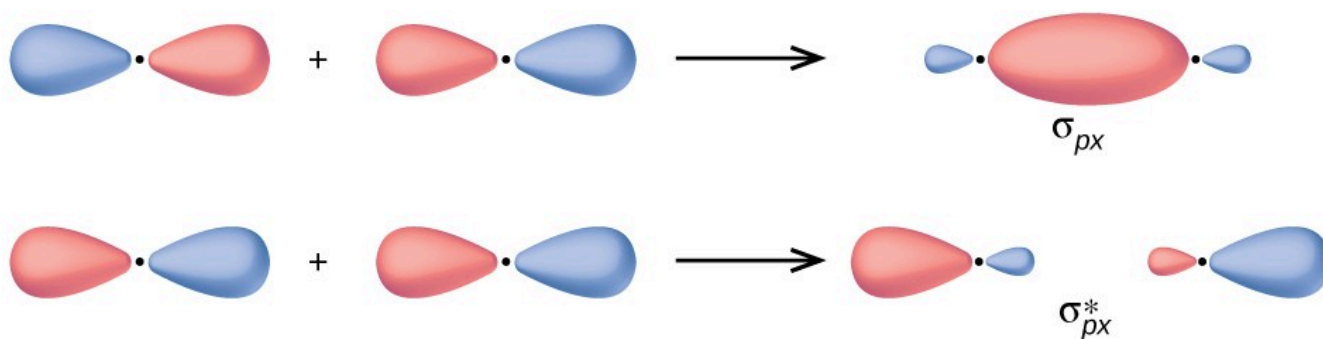


**Figure 5.41** Sigma ( $\sigma$ ) and sigma-star ( $\sigma^*$ ) molecular orbitals are formed by the combination of two  $s$  atomic orbitals. The plus (+) signs indicate the locations of nuclei. By: Rice University [Openstax CC BY NC SA](#)

## Link to Learning

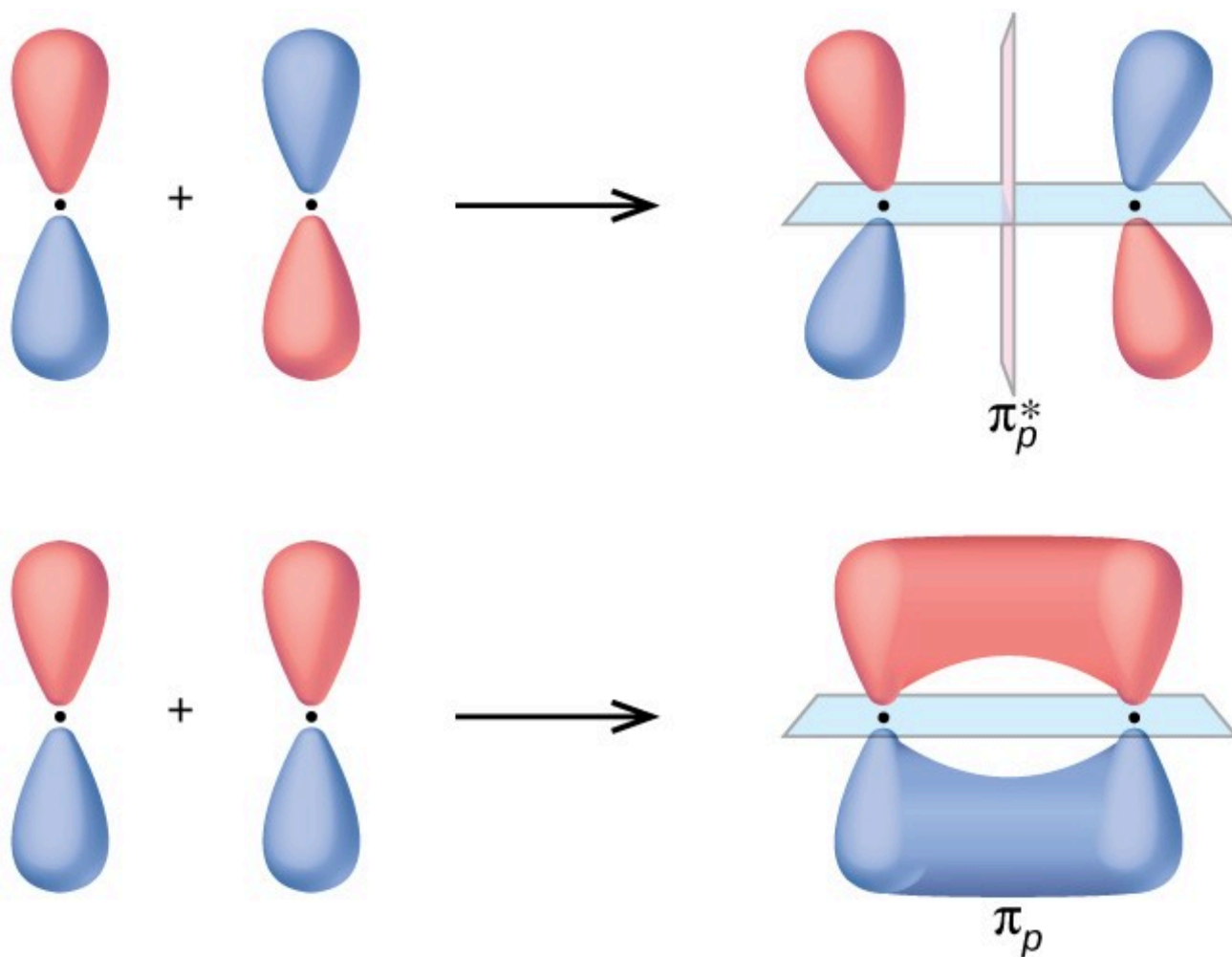
You can watch [animations](#) visualizing the calculated atomic orbitals combining to form various molecular orbitals at the Orbitron website.

In  $p$  orbitals, the wave function gives rise to two lobes with opposite phases, analogous to how a two-dimensional wave has both parts above and below the average. We indicate the phases by shading the orbital lobes different colors. When orbital lobes of the same phase overlap, constructive wave interference increases the electron density. When regions of opposite phases overlap, the destructive wave interference decreases electron density and creates nodes. When  $p$  orbitals overlap end to end, they create  $\sigma$  and  $\sigma^*$  orbitals (**Figure 5.42**). If two atoms are located along the  $x$ -axis in a Cartesian coordinate system, the two  $p_x$  orbitals overlap end to end and form  $\sigma_{px}$  (bonding) and  $\sigma_{px}^*$  (antibonding) (read as “sigma-p-x” and “sigma-p-x star,” respectively). Just as with  $s$ -orbital overlap, the asterisk indicates the orbital with a node between the nuclei, which is a higher-energy, antibonding orbital.



**Figure 5.42** Combining wave functions of two  $p$  atomic orbitals along the internuclear axis creates two molecular orbitals,  $\sigma_p$  and  $\sigma_p^*$ . By: Rice University [Openstax CC BY NC SA](#)

The side-by-side overlap of two  $p$  orbitals gives rise to a **pi ( $\pi$ ) bonding molecular orbital** and a  **$\pi^*$  antibonding molecular orbital**, as shown in **Figure 5.43**. In valence bond theory, we describe  $\pi$  bonds as containing a nodal plane containing the internuclear axis and perpendicular to the lobes of the  $p$  orbitals, with electron density on either side of the node. In molecular orbital theory, we describe the  $\pi$  orbital by this same shape, and a  $\pi$  bond exists when this orbital contains electrons. Electrons in this orbital interact with both nuclei and help hold the two atoms together, making it a bonding orbital. For the out-of-phase combination, there are two nodal planes created, one along the internuclear axis and a perpendicular one between the nuclei.



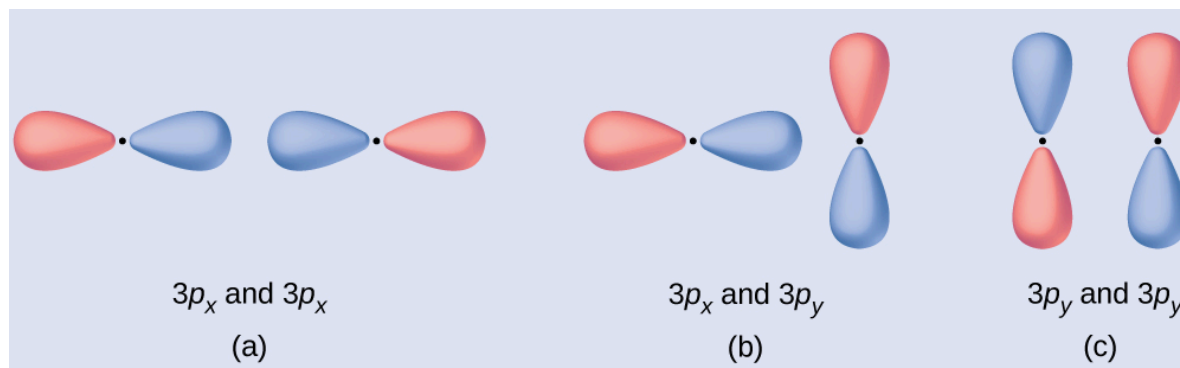
**Figure 5.43** Side-by-side overlap of each two  $p$  orbitals results in the formation of two  $\pi$  molecular orbitals. Combining the out-of-phase orbitals results in an antibonding molecular orbital with two nodes. One contains the internuclear axis, and one is perpendicular to the axis. Combining the in-phase orbitals results in a bonding orbital. There is a node (blue) containing the internuclear axis with the two lobes of the orbital located above and below this node. By: Rice University [Openstax CC BY NC SA](https://openstax.org/r/rice-university)

In the molecular orbitals of diatomic molecules, each atom also has two sets of  $p$  orbitals oriented side by side ( $p_y$  and  $p_z$ ), so these four atomic orbitals combine pairwise to create two  $\pi$  orbitals and two  $\pi^*$  orbitals. The  $\pi_{py}$  and  $\pi^*_{py}$  orbitals are oriented at right angles to the  $\pi_{pz}$  and  $\pi^*_{pz}$  orbitals. Except for their orientation, the  $\pi_{py}$  and  $\pi_{pz}$  orbitals are identical and have the same energy; they are **degenerate orbitals**. The  $\pi^*_{py}$  and  $\pi^*_{pz}$  antibonding orbitals are also degenerate and identical except for their orientation. A total of six molecular orbitals result from the combination of the six atomic  $p$  orbitals in two atoms:  $\sigma_{px}$  and  $\sigma^*_{px}$ ,  $\pi_{py}$  and  $\pi^*_{py}$ ,  $\pi_{pz}$  and  $\pi^*_{pz}$ .

## EXAMPLE 5.6

## Molecular Orbitals

Predict what type (if any) of molecular orbital would result from adding the wave functions so each pair of orbitals shown overlap. The orbitals are all similar in energy.



**Figure 5.44** By: Rice University [Openstax](#) [CC BY NC SA](#)

## Solution

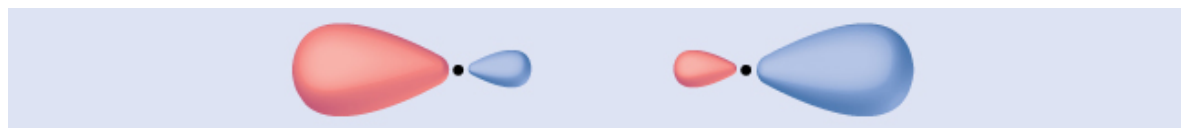
(a) is an in-phase combination, resulting in a  $\sigma_{3p}$  orbital.

(b) will not result in a new orbital because the in-phase component (bottom) and out-of-phase component (top) cancel out. Only orbitals with the correct alignment can combine.

(c) is an out-of-phase combination, resulting in a  $\pi^*_{3p}$  orbital.

## Check Your Learning

Label the molecular orbital shown as  $\sigma$  or  $\pi$ , bonding or antibonding, and indicate where the node occurs.



**Figure 5.45** By: Rice University [Openstax](#) [CC BY NC SA](#)



**Answer:** The orbital is located along the internuclear axis, so it is a  $\sigma$  orbital. There is a node bisecting the internuclear axis, so it is an antibonding orbital.



**Figure 5.46** By: Rice University [Openstax CC BY NC SA](#)

## PORTRAIT OF A CHEMIST

### Walter Kohn: Nobel Laureate

Walter Kohn (**Figure 5.47**) is a theoretical physicist who studies the electronic structure of solids. His work combines the principles of quantum mechanics with advanced mathematical techniques. This technique, called density functional theory, makes it possible to compute properties of molecular orbitals, including their shape and energies. Kohn and mathematician John Pople were awarded the Nobel Prize in Chemistry in 1998 for their contributions to our understanding of electronic structure. Kohn also made significant contributions to the physics of semiconductors.



**Figure 5.47** Walter Kohn developed methods to describe molecular orbitals. By: Rice University [Openstax](#)  
[CC BY NC SA](#)

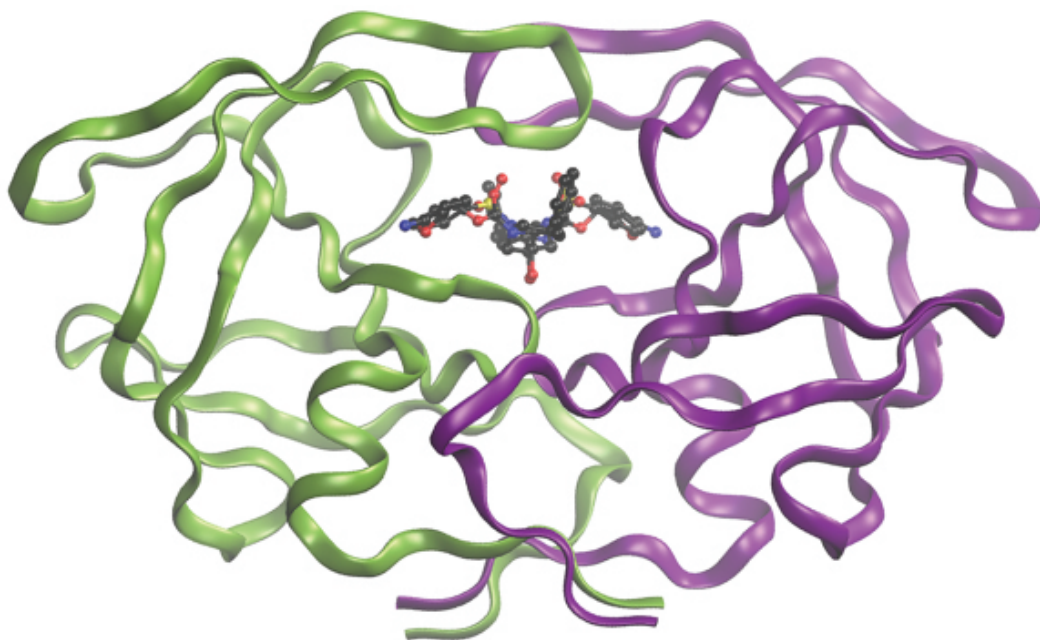
Kohn's biography has been remarkable outside the realm of physical chemistry as well. He was born in Austria, and during World War II, he was part of the Kindertransport program that

rescued 10,000 children from the Nazi regime. His summer jobs included discovering gold deposits in Canada and helping Polaroid explain how its instant film worked. Dr. Kohn passed away in 2016 at the age of 93.

## HOW SCIENCES INTERCONNECT

### Computational Chemistry in Drug Design

While the descriptions of bonding described in this chapter involve many theoretical concepts, they also have many practical, real-world applications. For example, drug design is an important field that uses our understanding of chemical bonding to develop pharmaceuticals. This interdisciplinary area of study uses biology (understanding diseases and how they operate) to identify specific targets, such as a binding site that is involved in a disease pathway. By modeling the structures of the binding site and potential drugs, computational chemists can predict which structures can fit together and how effectively they will bind (see **Figure 5.48**). Thousands of potential candidates can be narrowed down to a few of the most promising candidates. These candidate molecules are then carefully tested to determine side effects, how effectively they can be transported through the body, and other factors. Dozens of important new pharmaceuticals have been discovered with the aid of computational chemistry, and new research projects are underway.



**Figure 5.48** The molecule shown, HIV-1 protease, is an important target for pharmaceutical research. By designing molecules that bind to this protein, scientists are able to drastically inhibit the progress of the disease. By: Rice University [Openstax CC BY NC SA](#)

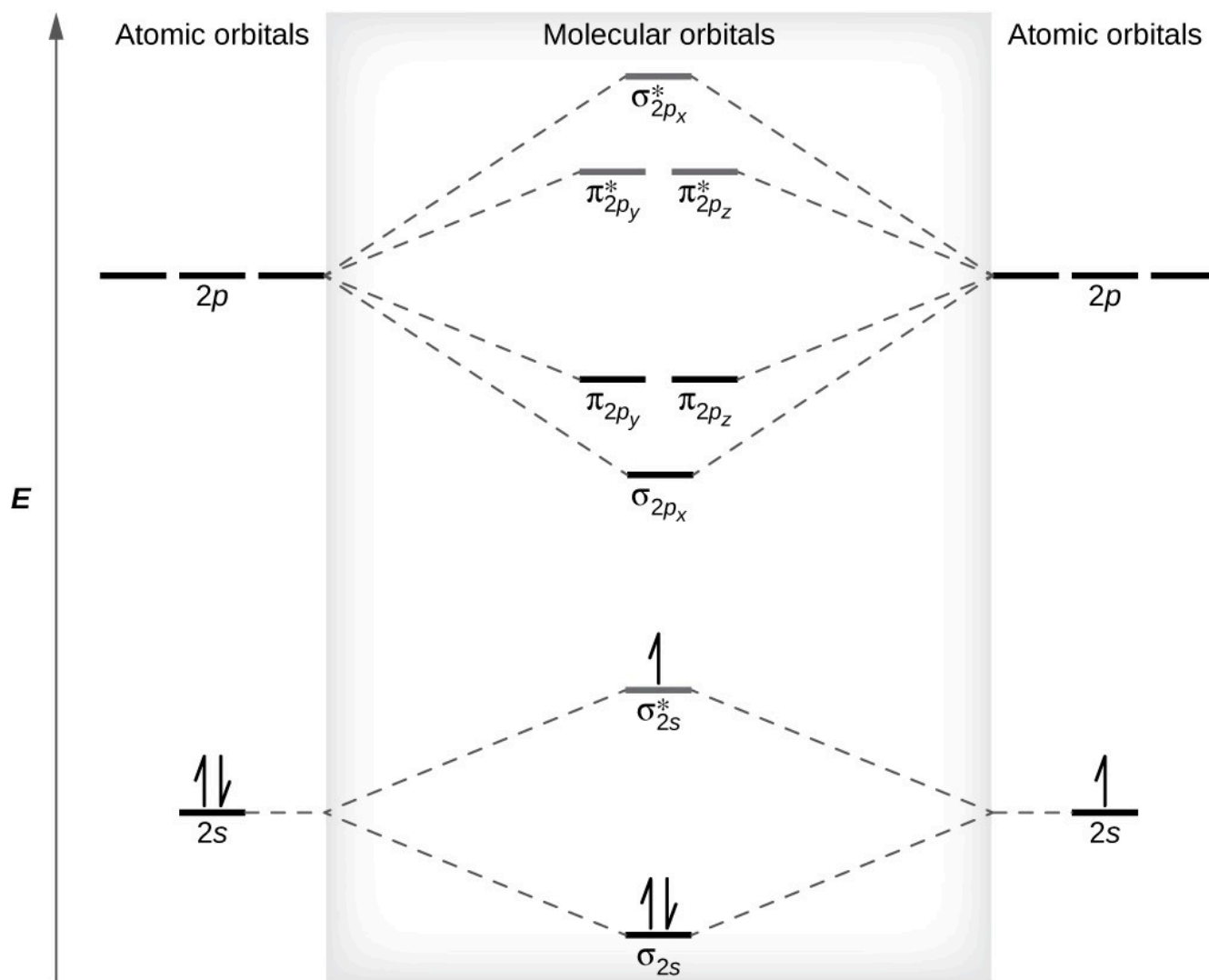
## Molecular Orbital Energy Diagrams

The relative energy levels of atomic and molecular orbitals are typically shown in a **molecular orbital diagram** (**Figure 5.49**). For a diatomic molecule, the atomic orbitals of one atom are shown on the left, and those of the other atom are shown on the right. Each horizontal line represents one orbital that can hold two electrons. The molecular orbitals formed by the combination of the atomic orbitals are shown in the center. Dashed lines show which of the atomic orbitals combine to form the molecular orbitals. For each pair of atomic orbitals that combine, one lower-energy (bonding) molecular orbital and one higher-energy (antibonding) orbital result. Thus we can see that combining the six  $2p$  atomic orbitals results in three bonding orbitals (one  $\sigma$  and two  $\pi$ ) and three antibonding orbitals (one  $\sigma^*$  and two  $\pi^*$ ).

We predict the distribution of electrons in these molecular orbitals by filling the orbitals in the same way that we fill atomic orbitals, by the Aufbau principle. Lower-energy orbitals fill first, electrons spread out among degenerate orbitals before pairing, and each orbital can hold a maximum of two electrons with opposite spins (**Figure 5.49**). Just as we write electron configurations for atoms, we can write the molecular electronic configuration by listing the orbitals with superscripts indicating the number of electrons present. For clarity,

we place parentheses around molecular orbitals with the same energy. In this case, each orbital is at a different energy, so parentheses separate each orbital. Thus we would expect a diatomic molecule or ion containing seven electrons (such as  $\text{Be}_2^+$ ) would have the molecular electron configuration

$(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^1$ . It is common to omit the core electrons from molecular orbital diagrams and configurations and include only the valence electrons.



**Figure 5.49** This is the molecular orbital diagram for the homonuclear diatomic  $\text{Be}_2^+$ , showing the molecular orbitals of the valence shell only. The molecular orbitals are filled in the same manner as atomic orbitals, using the Aufbau principle and Hund's rule. By: Rice University [Openstax CC BY NC SA](#)

## Bond Order

The filled molecular orbital diagram shows the number of electrons in both bonding and antibonding molecular orbitals. The net contribution of the electrons to the bond strength of a molecule is identified by determining the **bond order** that results from the filling of the molecular orbitals by electrons.

When using Lewis structures to describe the distribution of electrons in molecules, we define bond order as the number of bonding pairs of electrons between two atoms. Thus a single bond has a bond order of 1, a double bond has a bond order of 2, and a triple bond has a bond order of 3. We define bond order differently when we use the molecular orbital description of the distribution of electrons, but the resulting bond order is usually the same. The MO technique is more accurate and can handle cases when the Lewis structure method fails, but both methods describe the same phenomenon.

In the molecular orbital model, an electron contributes to a bonding interaction if it occupies a bonding orbital and it contributes to an antibonding interaction if it occupies an antibonding orbital. The bond order is calculated by subtracting the destabilizing (antibonding) electrons from the stabilizing (bonding) electrons. Since a bond consists of two electrons, we divide by two to get the bond order. We can determine bond order with the following equation:

$$\text{bond order} = \frac{(\text{number of bonding electrons}) - (\text{number of antibonding electrons})}{2}$$

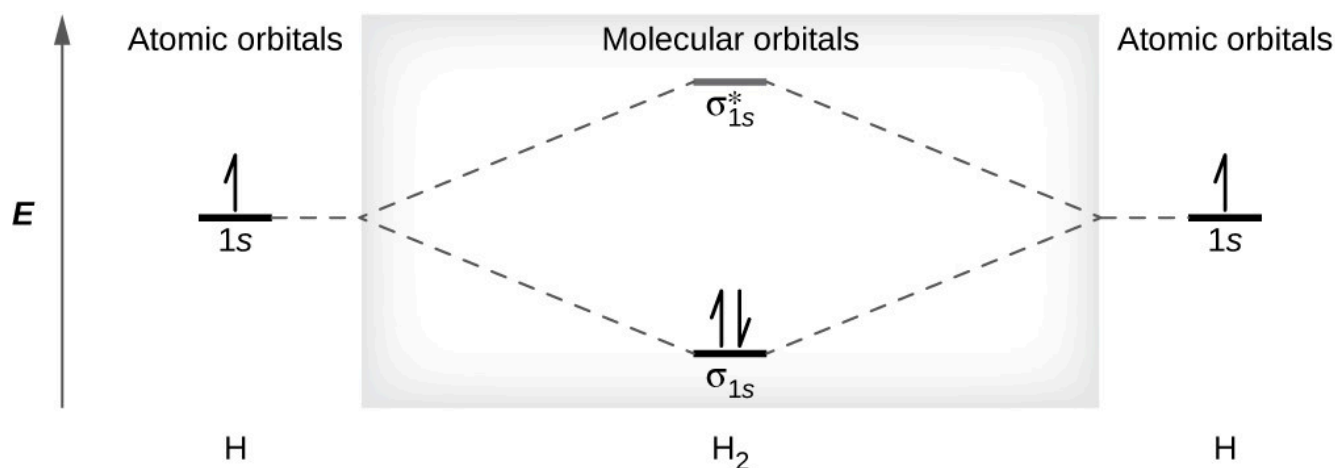
The order of a covalent bond is a guide to its strength; a bond between two given atoms becomes stronger as the bond order increases. If the distribution of electrons in the molecular orbitals between two atoms is such that the resulting bond would have a bond order of zero, a stable bond does not form. We next look at some specific examples of MO diagrams and bond orders.

## Bonding in Diatomic Molecules

A dihydrogen molecule ( $\text{H}_2$ ) forms from two hydrogen atoms. When the atomic orbitals of the two atoms combine, the electrons occupy the molecular orbital of lowest energy, the  $\sigma_{1s}$  bonding orbital. A dihydrogen molecule,  $\text{H}_2$ , readily forms because the energy of an  $\text{H}_2$  molecule is lower than that of two H atoms. The  $\sigma_{1s}$  orbital that contains both electrons is lower in energy than either of the two  $1s$  atomic orbitals.

A molecular orbital can hold two electrons, so both electrons in the  $\text{H}_2$  molecule are in the  $\sigma_{1s}$  bonding orbital; the electron configuration is  $(\sigma_{1s})^2$ . We represent this configuration by a molecular orbital energy diagram (**Figure 5.50**) in which a single upward arrow indicates one electron in an orbital, and two (upward and downward) arrows indicate two electrons of opposite spin.





**Figure 5.50** The molecular orbital energy diagram predicts that  $\text{H}_2$  will be a stable molecule with lower energy than the separated atoms. By: Rice University [Openstax CC BY NC SA](#)

A dihydrogen molecule contains two bonding electrons and no antibonding electrons so we have

$$\text{bond order in } \text{H}_2 = \frac{(2 - 0)}{2} = 1$$

Because the bond order for the H–H bond is equal to 1, the bond is a single bond.

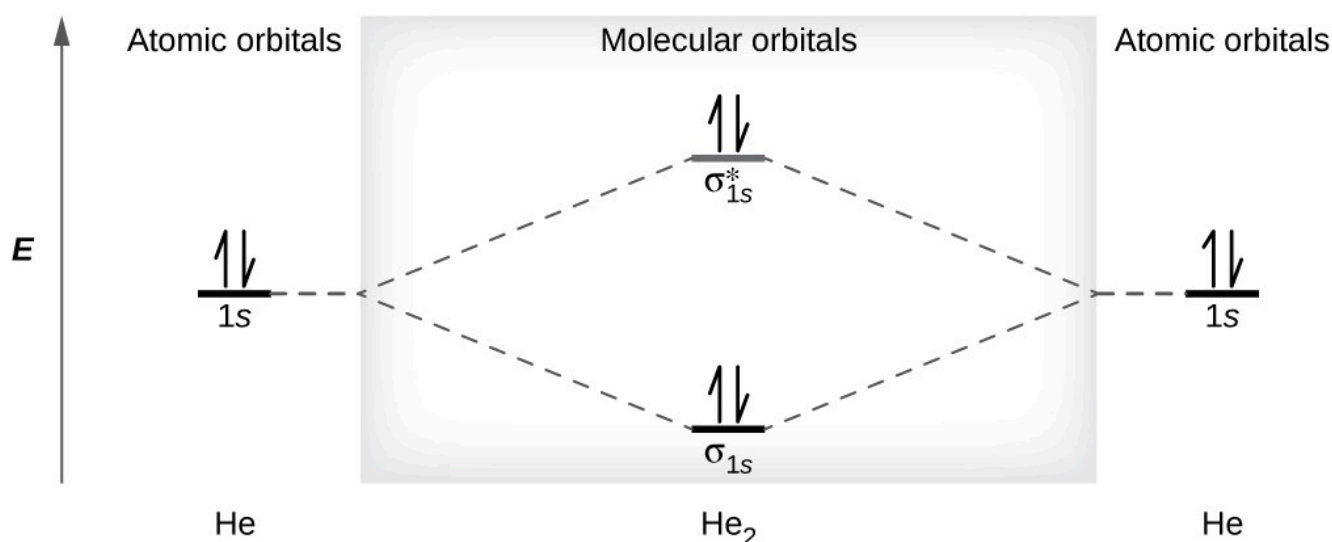
A helium atom has two electrons, both of which are in its  $1s$  orbital. Two helium atoms do not combine to form a dihelium molecule,  $\text{He}_2$ , with four electrons, because the stabilizing effect of the two electrons in the lower-energy bonding orbital would be offset by the destabilizing effect of the two electrons in the higher-energy antibonding molecular orbital. We would write the hypothetical electron configuration of  $\text{He}_2$  as  $(\sigma 1s)^2 (\sigma^* 1s)^2$  as in **Figure 5.51**.

The net energy change would be zero, so there is no driving force for helium atoms to form the diatomic molecule.

In fact, helium exists as discrete atoms rather than as diatomic molecules. The bond order in a hypothetical dihelium molecule would be zero.

$$\text{bond order in } \text{He}_2 = \frac{(2 - 2)}{2} = 0$$

A bond order of zero indicates that no bond is formed between two atoms.



**Figure 5.51** The molecular orbital energy diagram predicts that  $\text{He}_2$  will not be a stable molecule, since it has equal numbers of bonding and antibonding electrons. By: Rice University [Openstax](#) [CC BY NC SA](#)

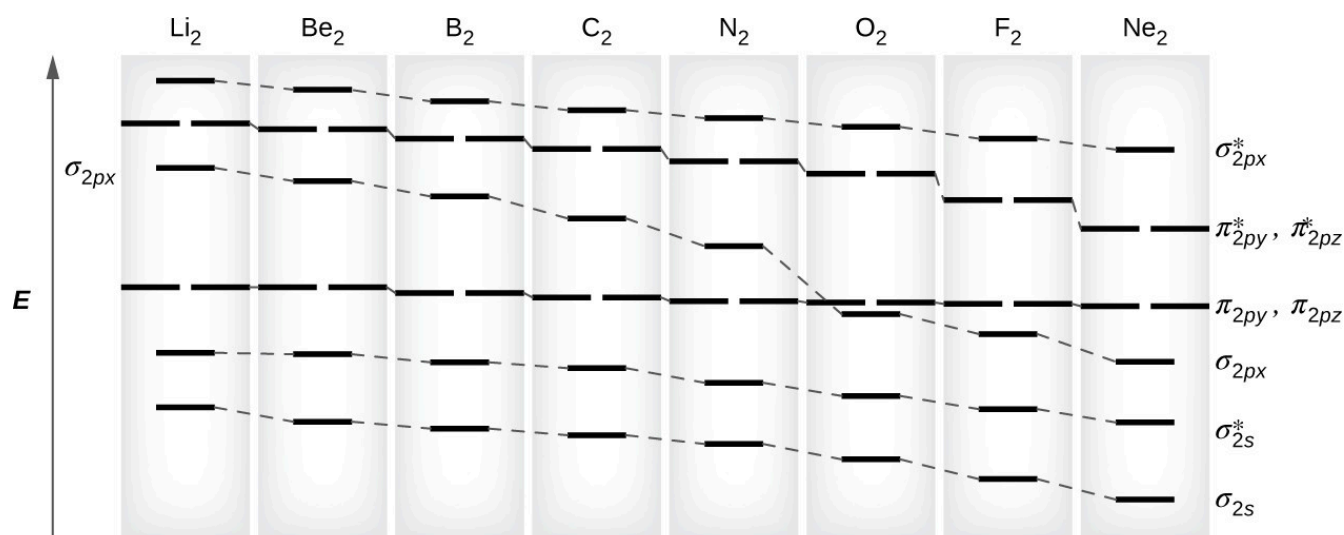
## The Diatomic Molecules of the Second Period

Eight possible homonuclear diatomic molecules might be formed by the atoms of the second period of the periodic table:  $\text{Li}_2$ ,  $\text{Be}_2$ ,  $\text{B}_2$ ,  $\text{C}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{F}_2$ , and  $\text{Ne}_2$ . However, we can predict that the  $\text{Be}_2$  molecule and the  $\text{Ne}_2$  molecule would not be stable. We can see this by a consideration of the molecular electron configurations ([Table 5.2](#)).

We predict valence molecular orbital electron configurations just as we predict electron configurations of atoms. Valence electrons are assigned to valence molecular orbitals with the lowest possible energies. Consistent with Hund's rule, whenever there are two or more degenerate molecular orbitals, electrons fill each orbital of that type singly before any pairing of electrons takes place.

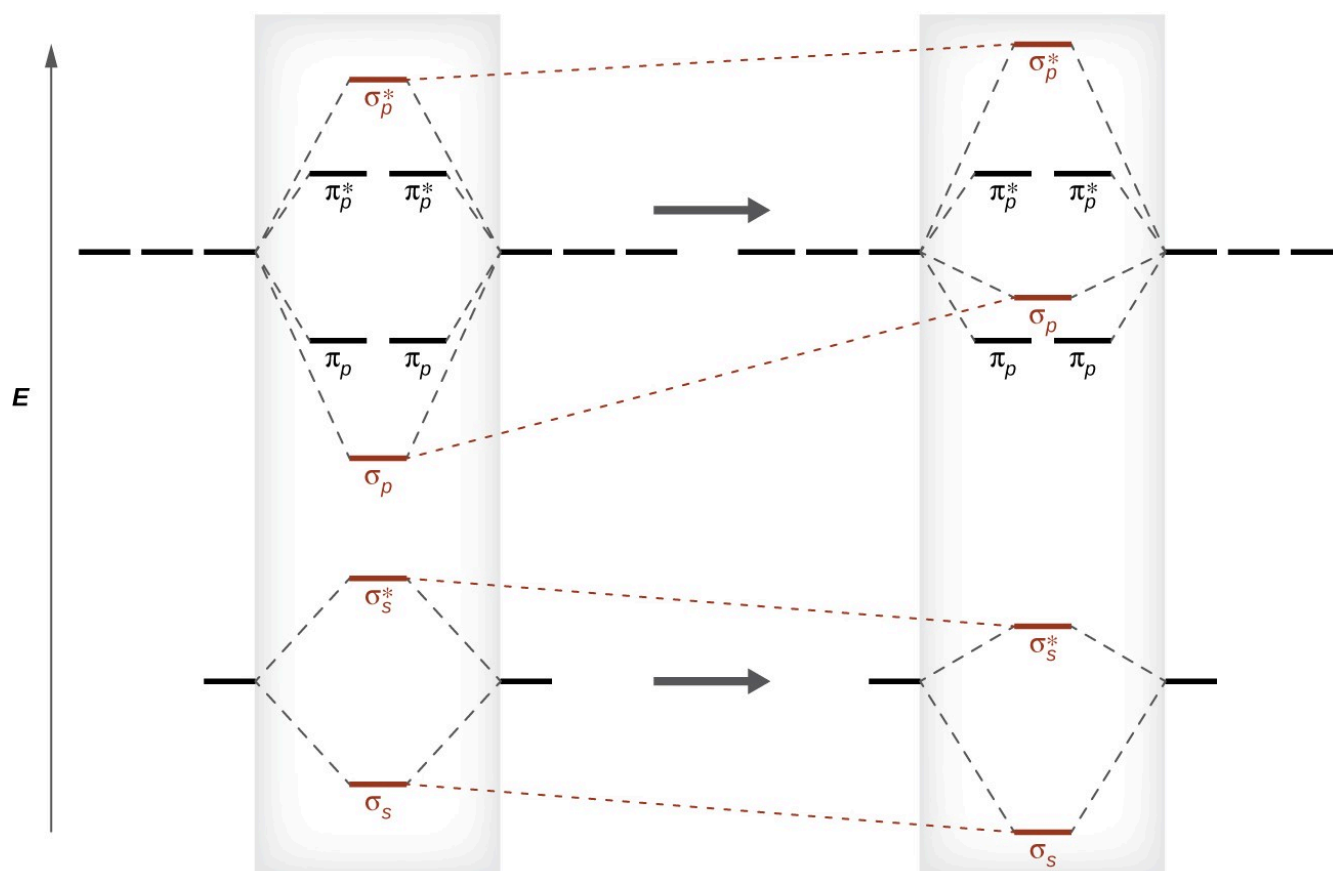
As we saw in valence bond theory,  $\sigma$  bonds are generally more stable than  $\pi$  bonds formed from degenerate atomic orbitals. Similarly, in molecular orbital theory,  $\sigma$  orbitals are usually more stable than  $\pi$  orbitals. However, this is not always the case. The MOs for the valence orbitals of the second period are shown in **Figure 5.52**. Looking at  $\text{Ne}_2$  molecular orbitals, we see that the order is consistent with the generic diagram shown in the previous section. However, for atoms with three or fewer electrons in the  $p$  orbitals (Li through N), we observe a different pattern, in which the  $\sigma_p$  orbital is higher in energy than the  $\pi_p$  set. Obtain the molecular orbital diagram for a homonuclear diatomic ion by adding or subtracting electrons from the diagram for the neutral molecule.





**Figure 5.52** This shows the MO diagrams for each homonuclear diatomic molecule in the second period. The orbital energies decrease across the period as the effective nuclear charge increases and atomic radius decreases. Between  $\text{N}_2$  and  $\text{O}_2$ , the order of the orbitals changes. By: Rice University [Openstax CC BY NC SA](#)

This switch in orbital ordering occurs because of a phenomenon called **s-p mixing**. s-p mixing does not create new orbitals; it merely influences the energies of the existing molecular orbitals. The  $\sigma_s$  wavefunction mathematically combines with the  $\sigma_p$  wavefunction, with the result that the  $\sigma_s$  orbital becomes more stable, and the  $\sigma_p$  orbital becomes less stable (**Figure 5.53**). Similarly, the antibonding orbitals also undergo s-p mixing, with the  $\sigma_s^*$  becoming more stable and the  $\sigma_p^*$  becoming less stable.



**Figure 5.53** Without mixing, the MO pattern occurs as expected, with the  $\sigma_p$  orbital lower in energy than the  $\sigma_p^*$  orbitals. When s-p mixing occurs, the orbitals shift as shown, with the  $\sigma_p$  orbital higher in energy than the  $\pi_p$  orbitals. By: Rice University [Openstax CC BY NC SA](#)

s-p mixing occurs when the  $s$  and  $p$  orbitals have similar energies. The energy difference between  $2s$  and  $2p$  orbitals in O, F, and Ne is greater than that in Li, Be, B, C, and N. Because of this,  $O_2$ ,  $F_2$ , and  $Ne_2$  exhibit negligible s-p mixing (not sufficient to change the energy ordering), and their MO diagrams follow the normal pattern, as shown in **Figure 5.52**. All of the other period 2 diatomic molecules do have s-p mixing, which leads to the pattern where the  $\sigma_p$  orbital is raised above the  $\pi_p$  set.

Using the MO diagrams shown in **Figure 5.52**, we can add in the electrons and determine the molecular electron configuration and bond order for each of the diatomic molecules. As shown in [Table 5.2](#),  $Be_2$  and  $Ne_2$  molecules would have a bond order of 0, and these molecules do not exist.

**Table 5.2 Electron Configuration and Bond Order for Molecular Orbitals in Homonuclear Diatomic Molecules of Period Two Elements By: Rice University [OpenStax CC BY-NC-SA 4.0](#)**

Molecule	Electron Configuration	Bond Order
Li <sub>2</sub>	$(\sigma_{2s})^2$	1
Be <sub>2</sub> (unstable)	$(\sigma_{2s})^2 (\sigma_{2s}^*)^2$	0
B <sub>2</sub>	$(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2py}, \pi_{2pz})^2$	1

**Table 5.3 Electron Configuration and Bond Order for Molecular Orbitals in Homonuclear Diatomic Molecules of Period Two Elements By: Rice University [OpenStax CC BY-NC-SA 4.0](#)**

Molecule	Electron Configuration	Bond Order
C <sub>2</sub>	$(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2py}, \pi_{2pz})^4$	2
N <sub>2</sub>	$(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2py}, \pi_{2pz})^4 (\sigma_{2px})^2$	3
O <sub>2</sub>	$(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2px})^2 (\pi_{2py}, \pi_{2pz})^4 (\pi_{2py}^*, \pi_{2pz}^*)^2$	2
F <sub>2</sub>	$(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2px})^2 (\pi_{2py}, \pi_{2pz})^4 (\pi_{2py}^*, \pi_{2pz}^*)^4$	1
Ne <sub>2</sub> (unstable)	$(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2px})^2 (\pi_{2py}, \pi_{2pz})^4 (\pi_{2py}^*, \pi_{2pz}^*)^4 (\sigma_{2px}^*)^2$	0

The combination of two lithium atoms to form a lithium molecule, Li<sub>2</sub>, is analogous to the formation of H<sub>2</sub>, but the atomic orbitals involved are the valence 2s orbitals. Each of the two lithium atoms has one valence electron. Hence, we have two valence electrons available for the  $\sigma_{2s}$  bonding molecular orbital. Because both valence electrons would be in a bonding orbital, we would predict the Li<sub>2</sub> molecule to be stable. The molecule is, in fact, present in appreciable concentration in lithium vapor at temperatures near the boiling point of the element. All of the other molecules in **Table 5.3** with a bond order greater than zero are also known.

The O<sub>2</sub> molecule has enough electrons to half fill the

$$\left( \pi_{2py}^*, \pi_{2pz}^* \right)$$

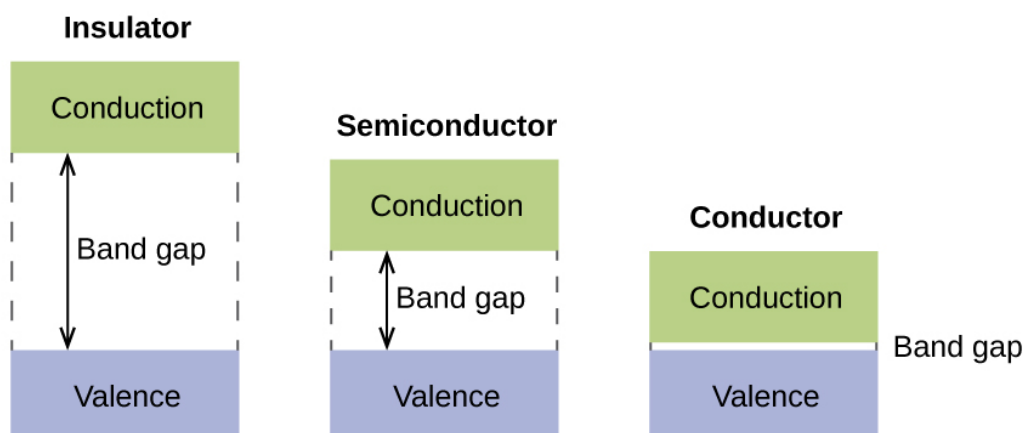
level. We expect the two electrons that occupy these two degenerate orbitals to be unpaired, and this molecular electronic configuration for O<sub>2</sub> is in accord with the fact that the oxygen molecule has two unpaired electrons (**Figure 5.55**). The presence of two unpaired electrons has proved to be difficult to explain using Lewis structures, but the molecular orbital theory explains it quite well. In fact, the unpaired electrons of the oxygen molecule provide a strong piece of support for the molecular orbital theory.

## How Sciences Interconnect

### Band Theory

When two identical atomic orbitals on different atoms combine, two molecular orbitals result (see **Figure 5.29**). The bonding orbital is lower in energy than the original atomic orbitals because the atomic orbitals are in-phase in the molecular orbital. The antibonding orbital is higher in energy than the original atomic orbitals because the atomic orbitals are out-of-phase.

In a solid, similar things happen but on a much larger scale. Remember that even in a small sample, there are a huge number of atoms (typically > 10<sup>23</sup> atoms) and therefore a huge number of atomic orbitals that may be combined into molecular orbitals. When N valence atomic orbitals, all of the same energy and each containing one (1) electron, are combined, N/2 (filled) bonding orbitals and N/2 (empty) antibonding orbitals will result. Each bonding orbital will show an energy lowering as the atomic orbitals are mostly in-phase, but each of the bonding orbitals will be a little different and have slightly different energies. The antibonding orbitals will show an increase in energy as the atomic orbitals are mostly out-of-phase, but each of the antibonding orbitals will also be a little different and have slightly different energies. The allowed energy levels for all the bonding orbitals are so close together that they form a band, called the valence band. Likewise, all the antibonding orbitals are very close together and form a band, called the conduction band. **Figure 5.39** shows the bands for three important classes of materials: insulators, semiconductors, and conductors.



**Figure 5.54** Molecular orbitals in solids are so closely spaced that they are described as bands. The valence band is lower in energy, and the conduction band is higher in energy. The type of solid is determined by the size of the “band gap” between the valence and conduction bands. Only a very small amount of energy is required to move electrons from the valence band to the conduction band in a conductor, and so they conduct electricity well. In an insulator, the band gap is large, so that very few electrons move, and they are poor conductors of electricity. Semiconductors are in between: They conduct electricity better than insulators but not as well as conductors. By: Rice University [Openstax CC BY NC SA](#)

In order to conduct electricity, electrons must move from the filled valence band to the empty conduction band where they can move throughout the solid. The size of the band gap, or the energy difference between the top of the valence band and the bottom of the conduction band, determines how easy it is to move electrons between the bands. Only a small amount of energy is required in a conductor because the band gap is very small. This small energy difference is “easy” to overcome, so they are good conductors of electricity. In an insulator, the band gap is so “large” that very few electrons move into the conduction band; as a result, insulators are poor conductors of electricity. Semiconductors conduct electricity when “moderate” amounts of energy are provided to move electrons out of the valence band and into the conduction band. Semiconductors, such as silicon, are found in many electronics.

## EXAMPLE 5.7

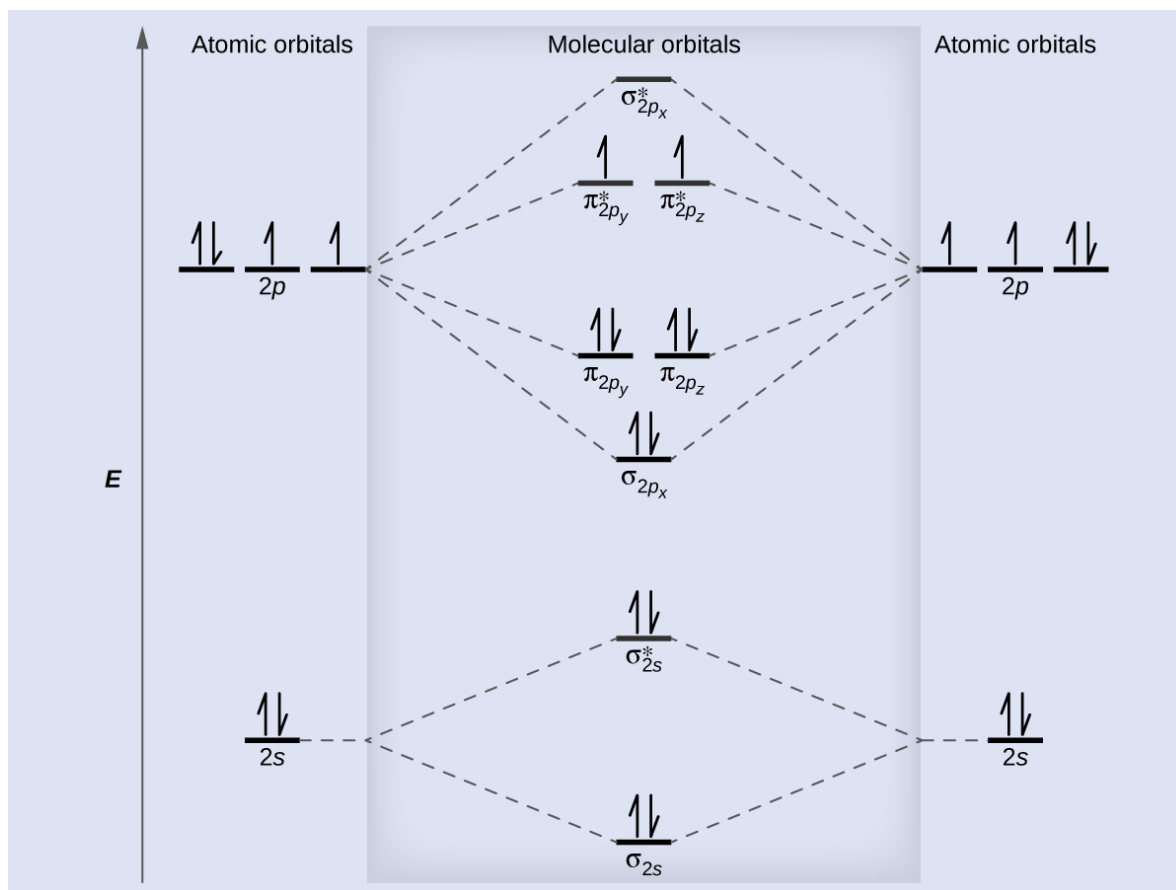
### Molecular Orbital Diagrams, Bond Order, and Number of Unpaired

## Electrons

Draw the molecular orbital diagram for the oxygen molecule,  $O_2$ . From this diagram, calculate the bond order for  $O_2$ . How does this diagram account for the paramagnetism of  $O_2$ ?

## Solution

We draw a molecular orbital energy diagram similar to that shown in **Figure 5.52**. Each oxygen atom contributes six electrons, so the diagram appears as shown in **Figure 5.55**.



**Figure 5.55** The molecular orbital energy diagram for  $O_2$  predicts two unpaired electrons. By: Rice University [Openstax CC BY NC SA](https://openstax.org/r/ncsa)

We calculate the bond order as

$$O_2 = \frac{(8 - 4)}{2} = 2$$

Oxygen's paramagnetism is explained by the presence of two unpaired electrons in the  $(\pi_{2py}, \pi_{2pz})^*$  molecular orbitals.

### Check Your Learning

The main component of air is  $N_2$ . From the molecular orbital diagram of  $N_2$ , predict its bond order and whether it is diamagnetic or paramagnetic.

**Answer:**  $N_2$  has a bond order of 3 and is diamagnetic.

## EXAMPLE 5.8

### Ion Predictions with MO Diagrams

Give the molecular orbital configuration for the valence electrons in  $C_2^{2-}$ . Will this ion be stable?

### Solution

Looking at the appropriate MO diagram, we see that the  $\pi$  orbitals are lower in energy than the  $\sigma_p$  orbital. The valence electron configuration for  $C_2$  is

$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2py}, \pi_{2pz})^4$ . Adding two more electrons to generate the  $C_2^{2-}$  anion will give a valence electron configuration of

$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2py}, \pi_{2pz})^4(\sigma_{2px})^2$ . Since this has six more bonding electrons than antibonding, the bond order will be 3, and the ion should be stable.

### Check Your Learning

How many unpaired electrons would be present on a  $Be_2^{2-}$  ion? Would it be paramagnetic or diamagnetic?

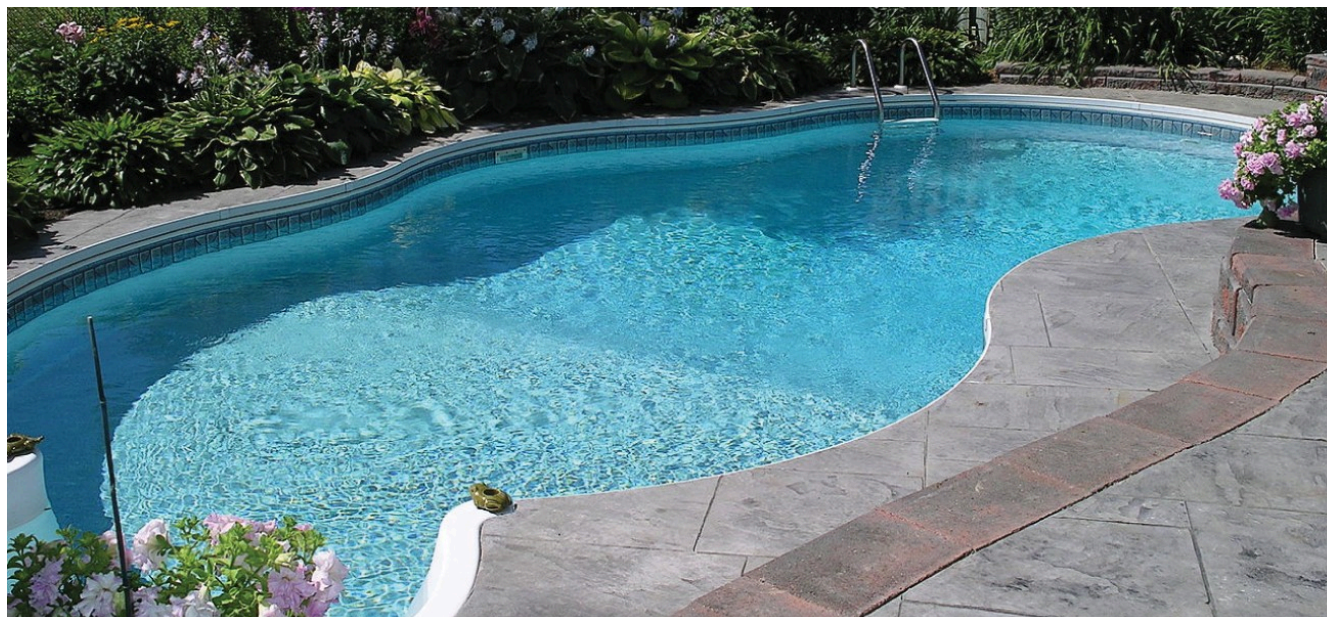
**Answer:** two, paramagnetic

## LINK TO LEARNING

Creating molecular orbital diagrams for molecules with more than two atoms relies on the same basic ideas as the diatomic examples presented here. However, with more atoms, computers are required to calculate how the atomic orbitals combine. See [three-dimensional drawings](#) of the molecular orbitals for  $C_6H_6$ .



# CHAPTER 6: COMPOSITION OF SUBSTANCES AND SOLUTIONS



**Figure 6.1** The water in a swimming pool is a complex mixture of substances whose relative amounts must be carefully maintained to ensure the health and comfort of people using the pool (credit: modification of work by Vic Brincat). By: Rice University [Openstax CC BY NC SA](#)

## Chapter Outline

- Formula Mass
- Determining Empirical and Molecular Formulas
- Molarity
- Other Units for Solution Concentrations

## Introduction

Swimming pools have long been a popular means of recreation, exercise, and physical therapy. Since it is impractical to refill large pools with fresh water on a frequent basis, pool water is regularly treated with chemicals to prevent the growth of harmful bacteria and algae. Proper pool maintenance requires regular additions of various chemical compounds in carefully measured amounts. For example, the relative amount of calcium ion,  $\text{Ca}^{2+}$ , in the water should be maintained within certain limits to prevent eye irritation and avoid

damage to the pool bed and plumbing. To maintain proper calcium levels, calcium cations are added to the water in the form of an ionic compound that also contains anions; thus, it is necessary to know both the relative amount of  $\text{Ca}^{2+}$  in the compound and the volume of water in the pool in order to achieve the proper calcium level. Quantitative aspects of the composition of substances (such as the calcium-containing compound) and mixtures (such as the pool water) are the subject of this chapter.

# FORMULA MASS (6.1)

OpenStax

---

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

- Calculate formula masses for covalent and ionic compounds

Many 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

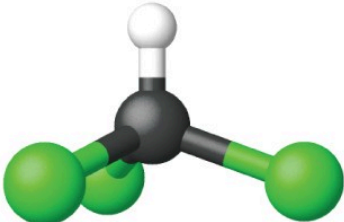
An earlier chapter of this text described the development of the atomic mass unit, the concept of average atomic masses, and the use of chemical formulas to represent the elemental makeup of substances. These ideas can be extended to calculate the **formula mass** of a substance by summing the average 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 ( $\text{CHCl}_3$ ), a covalent compound once used as a surgical anesthetic and now primarily used in the production of 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 6.2** outlines the calculations used to derive the molecular mass of chloroform, which is 119.37 amu.

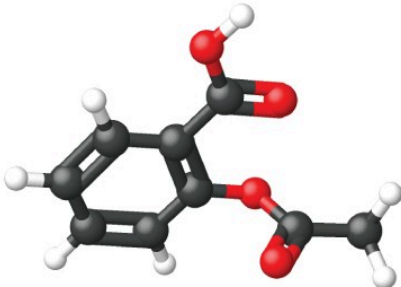
Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	1	×	12.01	=	12.01
H	1	×	1.008	=	1.008
Cl	3	×	35.45	=	106.35
<b>Molecular mass</b>					<b>119.37</b>



**Figure 6.2** The average mass of a chloroform molecule,  $\text{CHCl}_3$ , 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. By: Rice University [Openstax CC BY NC SA](#)

Likewise, the molecular mass of an aspirin molecule,  $\text{C}_9\text{H}_8\text{O}_4$ , 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 6.3**).

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
<b>Molecular mass</b>					<b>180.15</b>



**Figure 6.3** The average mass of an aspirin molecule is 180.15 amu. The model shows the molecular structure of aspirin,  $\text{C}_9\text{H}_8\text{O}_4$ . By: Rice University [Openstax CC BY NC SA](#)

## Example 6.1

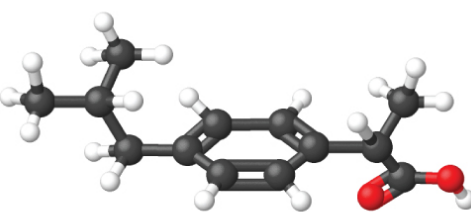
### Computing Molecular Mass for a Covalent Compound

Ibuprofen,  $\text{C}_{13}\text{H}_{18}\text{O}_2$ , 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) of 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	=	18.144
O	2	×	16.00	=	32.00
Molecular mass					206.27



**Figure 6.4** By: Rice University [Openstax CC BY NC SA](#)

## Check Your Learning

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?

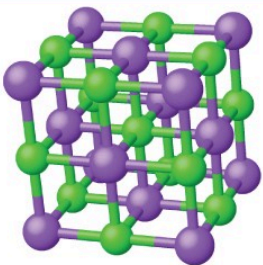
**Answer:** 151.16 amu

## 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 (see **Figure 6.5**).

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



**Figure 6.5** Table salt, NaCl, contains an array of sodium and chloride ions combined in a 1:1 ratio. Its formula mass is 58.44 amu. By: Rice University [Openstax CC BY NC SA](#)

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 6.2

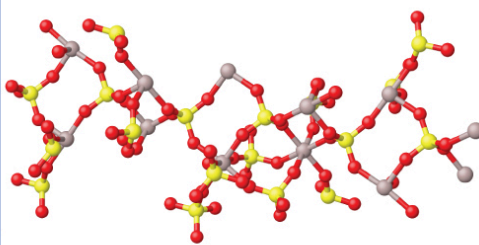
### Computing Formula Mass for an Ionic Compound

Aluminum sulfate,  $\text{Al}_2(\text{SO}_4)_3$ , 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  $\text{Al}^{3+}$  and  $\text{SO}_4^{2-}$  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,  $\text{Al}_2\text{S}_3\text{O}_{12}$ . 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



**Figure 6.6** By: Rice University [OpenstaxCC BY NC SA](https://openstax.org/r/figure6.6)

### Check Your Learning

Calcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ , 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



# DETERMINING EMPIRICAL AND MOLECULAR FORMULAS (6.2)

OpenStax

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

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

The previous section 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, one may 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, these same principles will be applied 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:

$$\begin{aligned}\% \text{ H} &= \frac{\text{mass H}}{\text{mass compound}} \times 100\% \\ \% \text{ C} &= \frac{\text{mass C}}{\text{mass compound}} \times 100\%\end{aligned}$$



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:

$$\begin{aligned}\% \text{ H} &= \frac{2.5 \text{ g H}}{10.0 \text{ g compound}} \times 100\% = 25\% \\ \% \text{ C} &= \frac{7.5 \text{ g C}}{10.0 \text{ g compound}} \times 100\% = 75\%\end{aligned}$$

### EXAMPLE 6.3

#### 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, divide the experimentally derived mass of each element by the overall mass of the compound and then convert it to a percentage:

$$\begin{aligned}\% \text{ C} &= \frac{7.34 \text{ g C}}{12.04 \text{ g compound}} \times 100\% = 61.0\% \\ \% \text{ H} &= \frac{1.85 \text{ g H}}{12.04 \text{ g compound}} \times 100\% = 15.4\% \\ \% \text{ N} &= \frac{2.85 \text{ g N}}{12.04 \text{ g compound}} \times 100\% = 23.7\%\end{aligned}$$

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

#### Check Your Learning

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 Molecular or Empirical

## Formulas

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 ( $\text{NH}_3$ ), ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), and urea ( $\text{CH}_4\text{N}_2\text{O}$ ). 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  $\text{NH}_3$  contains one N atom weighing 14.01 amu and three H atoms weighing a total of  $(3 \times 1.008 \text{ amu}) = 3.024 \text{ amu}$ . The formula mass of ammonia is therefore  $(14.01 \text{ amu} + 3.024 \text{ amu}) = 17.03 \text{ amu}$ , and its percent composition is:

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

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

This same approach may be taken considering a pair of molecules, a dozen molecules, a mole of molecules, and so on. The latter amount is most convenient and would simply involve the use of molar masses instead of atomic and formula masses, as demonstrated in [Example 6.4](#). As long as the molecular or empirical formula of the compound in question is known, the percent composition may be derived from the atomic or molar masses of the compound's elements.

### Example 6.4

#### Determining Percent Composition from a Molecular Formula

Aspirin is a compound with the molecular formula  $\text{C}_9\text{H}_8\text{O}_4$ . What is its percent composition?

#### Solution

To calculate the percent composition, the masses of C, H, and O in a known mass of  $\text{C}_9\text{H}_8\text{O}_4$  are needed. It is convenient to consider 1 mol of  $\text{C}_9\text{H}_8\text{O}_4$  and use its molar mass (180.159 g/mole, determined from the chemical formula) to calculate the percentages of each of its elements:

$$\% \text{ C} = \frac{9 \text{ mol C} \times \text{molar mass C}}{\text{molar mass C}_9\text{H}_8\text{O}_4} \times 100 = \frac{9 \times 12.01 \text{ g/mol}}{180.159 \text{ g/mol}} \times 100 = \frac{108.09 \text{ g/mol}}{180.159 \text{ g/mol}} \times 100$$

$$\% \text{ C} = 60.00\% \text{ C}$$

$$\% \text{ H} = \frac{8 \text{ mol H} \times \text{molar mass H}}{\text{molar mass C}_9\text{H}_8\text{O}_4} \times 100 = \frac{8 \times 1.008 \text{ g/mol}}{180.159 \text{ g/mol}} \times 100 = \frac{8.064 \text{ g/mol}}{180.159 \text{ g/mol}} \times 100$$

$$\% \text{ H} = 4.476\% \text{ H}$$

$$\% \text{ O} = \frac{4 \text{ mol O} \times \text{molar mass O}}{\text{molar mass C}_9\text{H}_8\text{O}_4} \times 100 = \frac{4 \times 16.00 \text{ g/mol}}{180.159 \text{ g/mol}} \times 100 = \frac{64.00 \text{ g/mol}}{180.159 \text{ g/mol}} \times 100$$

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

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

### Check Your Learning

To three significant digits, what is the mass percentage of iron in the compound  $\text{Fe}_2\text{O}_3$ ?

**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, 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. This is accomplished using molar masses to convert the mass of each element to a number of moles. These molar amounts are used to compute whole-number ratios that can be used to derive the empirical formula of the substance. Consider a sample of a compound determined to contain 1.71 g C and 0.287 g H. The corresponding numbers of atoms (in moles) are:

$$1.71 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 0.142 \text{ mol C} \quad \text{Thus, this compound may be represented by the formula}$$

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

$\text{C}_{0.142}\text{H}_{0.248}$ . Per convention, formulas contain whole-number subscripts, which can be achieved by dividing each subscript by the smaller subscript:

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

(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  $\text{CH}_2$ . This may or not be the compound’s *molecular formula* as well; however, additional information is needed to make that determination (as discussed later in this section).

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

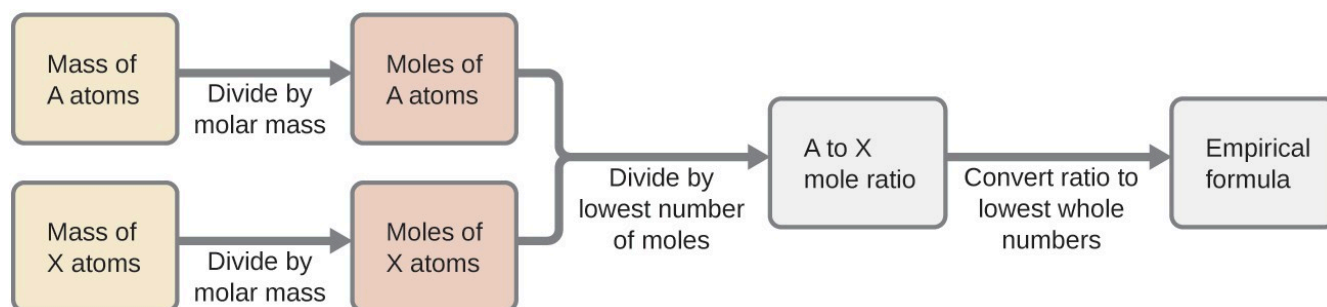
$$\text{Cl}_{0.150}\text{O}_{0.525} = \text{Cl} \frac{0.150}{0.150} \quad \text{O} \frac{0.525}{0.150} = \text{ClO}_{3.5}$$

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, multiply each of the subscripts by two, retaining the same atom ratio and yielding  $\text{Cl}_2\text{O}_7$  as the final empirical formula.

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 6.7** outlines this procedure in flowchart fashion for a substance containing elements A and X.



**Figure 6.7** The empirical formula of a compound can be derived from the masses of all elements in the sample. By: Rice University [Openstax CC BY NC SA](#)

## EXAMPLE 6.5

**Determining a Compound's Empirical Formula from the Masses of Its Elements**

A sample of the black mineral hematite (**Figure 6.8**), 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 6.8** Hematite is an iron oxide that is used in jewelry. By: Rice University [Openstax CC BY NC SA](#)

**Solution**

This problem provides 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 ( $\text{Fe}_1\text{O}_{1.5}$ ). Finally, multiply the ratio by two to get the smallest possible whole-number subscripts while still maintaining the correct iron-to-oxygen ratio:



### Check Your Learning

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

**ANSWER:**



### LINK TO LEARNING

For additional worked examples illustrating the derivation of empirical formulas, watch 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 6.6

### 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 6.9**). What is the empirical formula for this gas?



**Figure 6.9** An oxide of carbon is removed from these fermentation tanks through the large copper pipes at the top. By: Rice University [Openstax CC BY NC SA](https://openstax.org)

## 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:

$$27.29\% \text{ C} = \frac{27.29 \text{ g C}}{100 \text{ g compound}} \quad \text{The molar amounts of carbon and hydrogen in a 100-g}$$

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

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  $\text{CO}_2$ .

## Check Your Learning

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

**Answer:**  $\text{CH}_2\text{O}$



## 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 a 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 the molecular (or molar) mass of the substance is known, it may be divided by the empirical formula mass to yield the number of empirical formula units per molecule ( $n$ ):

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

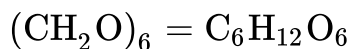
The molecular formula is then obtained by multiplying each subscript in the empirical formula by  $n$ , as shown by the generic empirical formula  $A_xB_y$ :

$$(A_xB_y)_n = A_{nx}B_{ny}$$

For example, consider a covalent compound whose empirical formula is determined to be  $\text{CH}_2\text{O}$ . 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:



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, *one mole* of empirical formula units and molecules is considered, as opposed to single units and molecules.

## EXAMPLE 6.7

**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 the 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:

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

$$(8.710 \text{ g H}) \left( \frac{1 \text{ mol H}}{1.008 \text{ g H}} \right) = 8.641 \text{ mol H}$$

Next, calculate the molar ratios of these

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

elements relative to the least abundant element, N.

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

$$8.641 \text{ mol H} / 1.233 \text{ mol N} = 7$$

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

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

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

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

The C-to-N and H-to-N molar ratios are adequately close to whole numbers, and so the empirical formula is  $\text{C}_5\text{H}_7\text{N}$ . The empirical formula mass for this compound is therefore 81.13 amu/formula unit, or 81.13 g/mol formula unit.

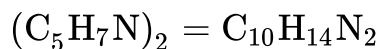
Calculate the molar mass for nicotine from the given mass and molar amount of the compound:

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

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

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

Finally, derive the molecular formula for nicotine from the empirical formula by multiplying each subscript by two:



### Check Your Learning

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:**  $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$

# MOLARITY (6.3)

OpenStax

---

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

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

The preceding sections of this chapter 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 (see **Figure 6.10**). This section will describe one of the most common ways in which the relative compositions of mixtures may be quantified.



**Figure 6.10** 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. By: Rice University [Openstax CC BY NC SA](#)

## Solutions

Solutions have previously been defined 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. A more thorough treatment of solution properties is provided in the chapter on solutions and colloids, but provided here is an introduction to 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:

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

## EXAMPLE 6.8

### 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:

$$M = \frac{\text{mol solute}}{\text{L solution}} = \frac{0.133 \text{ mol}}{355 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}} = 0.375 M$$

#### Check Your Learning

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 6.9

## 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 6.8?

## Solution

Rearrange the definition of molarity to isolate the quantity sought, moles of sugar, then substitute the value for molarity derived in Example 6.8, 0.375 *M*:

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

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

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

## Check Your Learning

What volume (mL) of the sweetened tea described in Example 6.8 contains the same amount of sugar (mol) as 10 mL of the soft drink in this example?

**Answer:** 80 mL

## Example 6.10

## Calculating Molar Concentrations from the Mass of Solute

Distilled white vinegar (**Figure 6.11**) is a solution of acetic acid,  $\text{CH}_3\text{CO}_2\text{H}$ , 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 6.11** Distilled white vinegar is a solution of acetic acid in water. By: Rice University [Openstax CC BY NC SA](#)

### Solution

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

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



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

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

### Check Your Learning

Calculate the molarity of 6.52 g of  $\text{CoCl}_2$  (128.9 g/mol) dissolved in an aqueous solution with a total volume of 75.0 mL.

**Answer:** 0.674 M

## EXAMPLE 6.11

### 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 6.9](#):

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

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

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

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

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

### Check Your Learning

How many grams of  $\text{CaCl}_2$  (110.98 g/mol) are contained in 250.0 mL of a 0.200-*M* solution of calcium chloride?

**Answer:** 5.55 g  $\text{CaCl}_2$

When performing calculations stepwise, as in [Example 6.11](#), it is important to refrain from rounding any intermediate calculation results, which can lead to rounding errors in the final result. In [Example 6.11](#), 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 the guard digit had not been retained, 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, rounding errors may also be avoided by performing computations in a single step (see [Example 6.12](#)). This eliminates intermediate steps so that only the final result is rounded.

### EXAMPLE 6.12

#### Determining the Volume of Solution Containing a Given Mass of Solute

In [Example 6.10](#), the concentration of acetic acid in white vinegar was determined 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:

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

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

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

Combining these two steps into one yields:

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

$$75.6 \text{ g CH}_3\text{CO}_2\text{H} \left( \frac{\text{mol CH}_3\text{CO}_2\text{H}}{60.05 \text{ g}} \right) \left( \frac{\text{L solution}}{0.839 \text{ mol CH}_3\text{CO}_2\text{H}} \right) = 1.50 \text{ L solution}$$

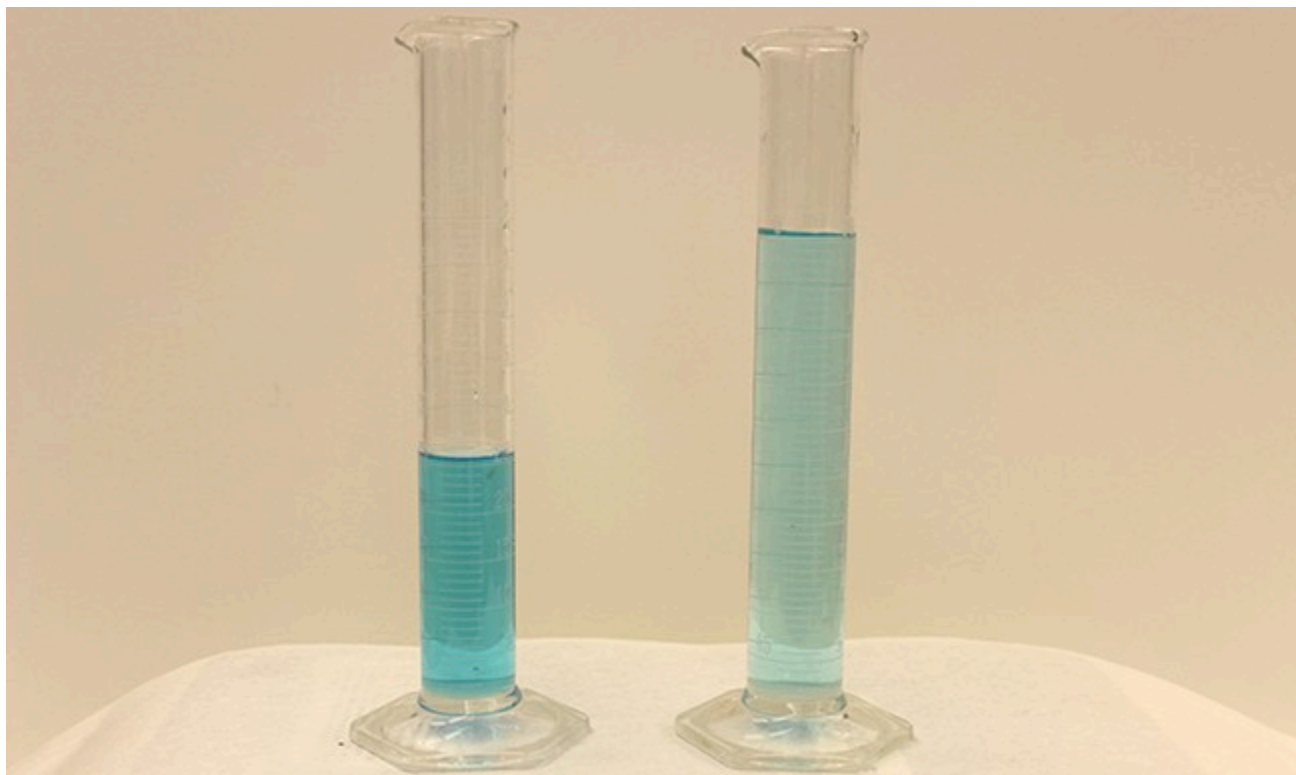
### Check Your Learning

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, 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 6.12](#)).



**Figure 6.12** Both solutions contain the same mass of copper nitrate. The solution on the right is more diluted because the copper nitrate is dissolved in more solvent. By: Rice University [Openstax CC BY NC SA](#)

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*, a solution of lesser concentration may be prepared. 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.

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 ( $n$ ) is equal to the product of the solution's molarity ( $M$ ) and its volume in liters ( $L$ ):

$$n = ML$$

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

$$n_1 = M_1 L_1$$

$$n_2 = M_2 L_2$$

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:

$$M_1 L_1 = M_2 L_2$$

This relation is commonly referred to as the dilution equation. Although this equation uses molarity as the unit of concentration and liters as the unit of volume, other units of concentration and volume may be used as

long as the units properly cancel per the factor-label method. Reflecting this versatility, the dilution equation is often written in the more general form:

$$C_1 V_1 = C_2 V_2$$

where  $C$  and  $V$  are concentration and volume, respectively.

### Link to Learning

[Use the simulation](#) to explore the relations between solute amount, solution volume, and concentration and to confirm the dilution equation.

### Example 6.13

#### Determining the Concentration of a Diluted Solution

If 0.850 L of a 5.00- $M$  solution of copper nitrate,  $\text{Cu}(\text{NO}_3)_2$ , is diluted to a volume of 1.80 L by the addition of water, what is the molarity of the diluted solution?

#### Solution

The stock concentration,  $C_1$ , and volume,  $V_1$ , are provided as well as the volume of the diluted solution,  $V_2$ . Rearrange the dilution equation to isolate the unknown property, the concentration of the diluted solution,  $C_2$ :

$$C_1 V_1 = C_2 V_2$$

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

Since the stock solution is being diluted by more than two-fold (volume is increased from 0.85 L to 1.80 L), the diluted solution's concentration is expected to be less than one-half 5  $M$ . This ballpark estimate will be compared 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:

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

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

### Check Your Learning

What is the concentration of the solution that results from diluting 25.0 mL of a 2.04-*M* solution of CH<sub>3</sub>OH to 500.0 mL?

**Answer:** 0.102 *M* CH<sub>3</sub>OH

## Example 6.14

### 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

Provided are the volume and concentration of a stock solution, *V*<sub>1</sub> and *C*<sub>1</sub>, and the concentration of the resultant diluted solution, *C*<sub>2</sub>. Find the volume of the diluted solution, *V*<sub>2</sub>, by rearranging the dilution equation to isolate *V*<sub>2</sub>:

$$C_1 V_1 = C_2 V_2$$

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

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

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

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

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

### Check Your Learning

A laboratory experiment calls for 0.125 *M* HNO<sub>3</sub>. What volume of 0.125 *M* HNO<sub>3</sub> can be prepared from 0.250 L of 1.88 *M* HNO<sub>3</sub>?

**Answer:** 3.76 L

## EXAMPLE 6.15

### 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

Given are the concentration of a stock solution,  $C_1$ , and the volume and concentration of the resultant diluted solution,  $V_2$  and  $C_2$ . Find the volume of the stock solution,  $V_1$ , by rearranging the dilution equation to isolate  $V_1$ :

$$C_1 V_1 = C_2 V_2$$

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

Since the concentration of the diluted solution 0.100 *M* is roughly one-sixteenth that of the stock solution (1.59 *M*), the volume of the stock solution is expected 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:

$$V_1 = V_2 = \frac{(0.100M)(5.00L)}{(1.59M)}$$

$$V_1 = 0.041 \text{ L}$$

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

### Check Your Learning

What volume of a 0.575-*M* solution of glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ , can be prepared from 50.00 mL of a 3.00-*M* glucose solution?

**Answer:** 0.261 L



# OTHER UNITS FOR SOLUTION CONCENTRATIONS (6.4)

OpenStax

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

- 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

The previous section introduced molarity, a very useful measurement unit for evaluating the concentration of solutions. However, molarity is only one measure of concentration. This section will describe some other units of concentration that are commonly used in various applications, either for convenience or by convention.

## Mass Percentage

Earlier in this chapter, percent composition was introduced 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:

$$\text{mass percentage} = \frac{\text{mass of component}}{\text{mass of solution}} \times 100\%$$

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)%. The 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 6.13**) cites the concentration of its active ingredient, sodium hypochlorite ( $\text{NaOCl}$ ), as being 7.4%. A 100.0-g sample of bleach would therefore contain 7.4 g of  $\text{NaOCl}$ .



**Figure 6.13** Liquid bleach is an aqueous solution of sodium hypochlorite ( $\text{NaOCl}$ ). This brand has a concentration of 7.4%  $\text{NaOCl}$  by mass. By: Rice University [Openstax CC BY NC SA](#)

### Example 6.16

#### 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, the solute mass unit in the numerator was converted from mg to g to match the units in the denominator. Alternatively, the spinal fluid mass unit in the denominator could have been converted 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.

### Check Your Learning

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%

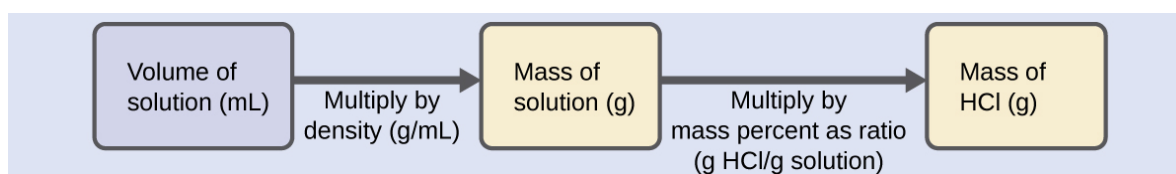
### Example 6.17

#### 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  $5 \times 40 = 200$  g. In order to derive the mass of solute in a solution from its mass percentage, the mass of the solution must be known. Using the solution density given, 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:



**Figure 6.14** By: Rice University [Openstax](#) CC BY NC SA

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.

## Check Your Learning

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)%:

$$\text{volume percentage} = \frac{\text{volume solute}}{\text{volume solution}} \times 100\%$$

## EXAMPLE 6.18

### 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:

$$(355 \text{ mL solution}) \left( \frac{70 \text{ mL isopropyl alcohol}}{100 \text{ mL solution}} \right) \left( \frac{0.785 \text{ g isopropyl alcohol}}{1 \text{ mL isopropyl alcohol}} \right) = 195 \text{ g isopropyl alcohol}$$

### Check Your Learning

Wine is approximately 12% ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) 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 6.15**).





(a)



(b)

**Figure 6.15** “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. By: Rice University [Openstax CC BY NC SA](#)

## 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 the numbers of atoms and molecules.

The mass-based definitions of ppm and ppb are given here:

$$\text{ppm} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^6 \text{ ppm}$$

$$\text{ppb} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^9 \text{ ppb}$$

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 6.16**).



(a)



(b)

**Figure 6.16** (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. By: Rice University [Openstax](#) [CC BY NC SA](#)

## EXAMPLE 6.19

### Calculation of 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 ( $\mu\text{g}$ ) 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 ( $1 \text{ ppm} = 10^3 \text{ ppb}$ ). Thus:

$$15 \text{ ppb} \times \frac{1 \text{ ppm}}{10^3 \text{ ppb}} = 0.015 \text{ ppm}$$

The definition of the ppb unit may be used to calculate the requested mass if the mass of the solution is provided. Since the volume of solution (300 mL) is given, its density must be used to derive the corresponding mass. 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:

$$4.5 \times 10^{-6} \text{ g} \times \frac{1 \mu\text{g}}{10^{-6} \text{ g}} = 4.5 \mu\text{g}$$

### Check Your Learning

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



# CHAPTER 7: STOICHIOMETRY OF CHEMICAL REACTIONS



**Figure 7.1** Many modern rocket fuels are solid mixtures of substances combined in carefully measured amounts and ignited to yield a thrust-generating chemical reaction. By: Rice University [Openstax CC BY NC SA](#)

## Chapter Outline

- Writing and Balancing Chemical Equations
- Classifying Chemical Reactions
- Reaction Stoichiometry
- Reaction Yields
- Quantitative Chemical Analysis

## Introduction

Solid-fuel rockets are a central feature in the world's space exploration programs, including the new Space Launch System being developed by the National Aeronautics and Space Administration (NASA) to replace the retired Space Shuttle fleet (**Figure 7.1**). The engines of these rockets rely on carefully prepared solid

mixtures of chemicals combined in precisely measured amounts. Igniting the mixture initiates a vigorous chemical reaction that rapidly generates large amounts of gaseous products. These gases are ejected from the rocket engine through its nozzle, providing the thrust needed to propel heavy payloads into space. Both the nature of this chemical reaction and the relationships between the amounts of the substances being consumed and produced by the reaction are critically important considerations that determine the success of the technology. This chapter will describe how to symbolize chemical reactions using chemical equations, how to classify some common chemical reactions by identifying patterns of reactivity, and how to determine the quantitative relations between the amounts of substances involved in chemical reactions—that is, the reaction *stoichiometry*.

# WRITING AND BALANCING CHEMICAL EQUATIONS (7.1)

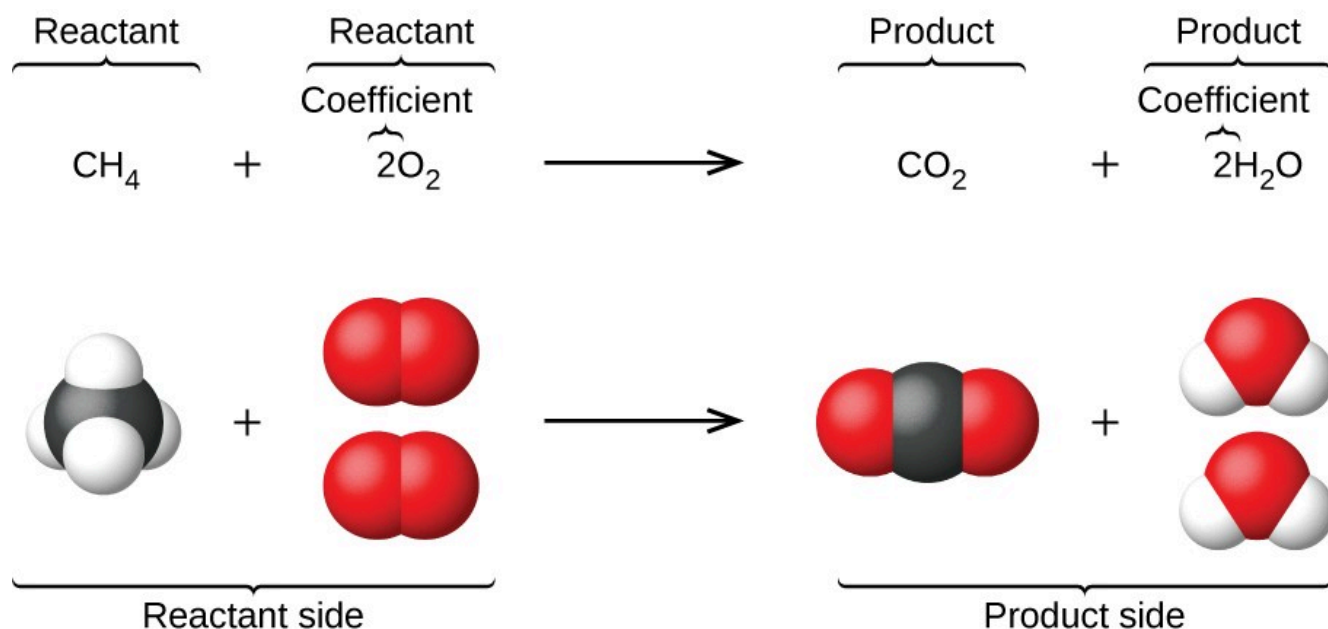
OpenStax

---

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

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

An earlier chapter of this text introduced the use of element symbols to represent individual atoms. When atoms gain or lose electrons to yield ions, or combine with other atoms to form molecules, their symbols are modified or combined to generate chemical formulas that appropriately represent these species. Extending this symbolism to represent both the identities and the relative quantities of substances undergoing a chemical (or physical) change involves writing and balancing a **chemical equation**. Consider as an example the reaction between one methane molecule ( $\text{CH}_4$ ) and two diatomic oxygen molecules ( $\text{O}_2$ ) to produce one carbon dioxide molecule ( $\text{CO}_2$ ) and two water molecules ( $\text{H}_2\text{O}$ ). The chemical equation representing this process is provided in the upper half of **Figure 7.2**, with space-filling molecular models shown in the lower half of the figure.



**Figure 7.2** The reaction between methane and oxygen to yield carbon dioxide and water (shown at the bottom) may be represented by a chemical equation using formulas (top). By: Rice University [Openstax CC BY NC SA](#)

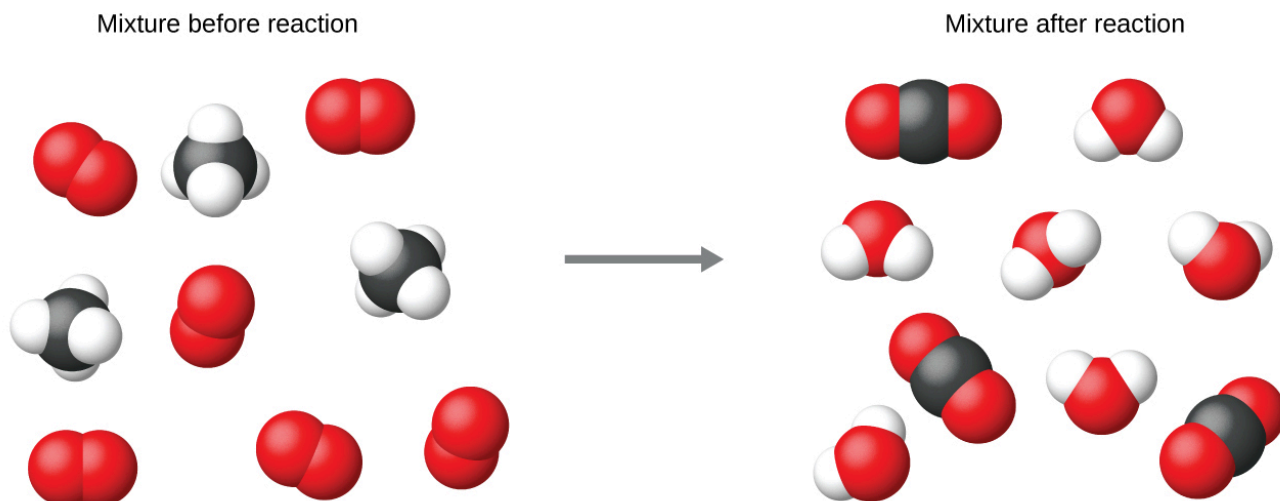
This example illustrates the fundamental aspects of any chemical equation:

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

It is common practice to use the smallest possible whole-number coefficients in a chemical equation, as is done in this example. Realize, however, that these coefficients represent the *relative* numbers of reactants and products, and therefore, they may be correctly interpreted as ratios. Methane and oxygen react to yield carbon dioxide and water in a 1:2:1:2 ratio. This ratio is satisfied if the numbers of these molecules are, respectively, 1-2-1-2, or 2-4-2-4, or 3-6-3-6, and so on (**Figure 7.3**). Likewise, these coefficients may be interpreted with regard to any amount (number) unit, and so this equation may be correctly read in many ways, including:

- *One* methane molecule and *two* oxygen molecules react to yield *one* carbon dioxide molecule and *two* water molecules.

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



**Figure 7.3** Regardless of the absolute numbers of molecules involved, the ratios between the numbers of molecules of each species that react (the reactants) and molecules of each species that form (the products) are the same and are given by the chemical reaction equation. By: Rice University [Openstax CC BY NC SA](#)

## Balancing Equations

The chemical equation described in section 4.1 is **balanced**, meaning that equal numbers of atoms for each element involved in the reaction are represented on the reactant and product sides. This is a requirement the equation must satisfy to be consistent with the law of conservation of matter. It may be confirmed by simply summing the numbers of atoms on either side of the arrow and comparing these sums to ensure they are equal. Note that the number of atoms for a given element is calculated by multiplying the coefficient of any formula containing that element by the element's subscript in the formula. If an element appears in more than one formula on a given side of the equation, the number of atoms represented in each must be computed and then added together. For example, both product species in the example reaction,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , contain the element oxygen, and so the number of oxygen atoms on the product side of the equation is

$$\left( 1 \text{ CO}_2 \text{ molecule} \times \frac{2 \text{ O atoms}}{\text{CO}_2 \text{ molecule}} \right) + \left( 2 \text{ H}_2\text{O molecule} \times \frac{1 \text{ O atom}}{\text{H}_2\text{O molecule}} \right) = 4 \text{ O atoms}$$

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

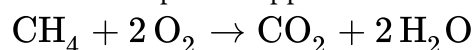
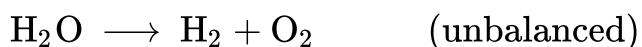


Table 7.1 By: Rice University [OpenStax CC BY-NC-SA 4.0](#)

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

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



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

Table 7.2 By: Rice University [OpenStax CC BY-NC-SA 4.0](#)

Element	Reactants	Products	Balanced?
H	$1 \times 2 = 2$	$1 \times 2 = 2$	$2 = 2$ , yes
O	$1 \times 1 = 1$	$1 \times 2 = 2$	$1 \neq 2$ , no

The numbers of H atoms on the reactant and product sides of the equation are equal, but the numbers of O atoms are not. To achieve balance, the *coefficients* of the equation may be changed as needed. Keep in mind, of course, that the *formula subscripts* define, in part, the identity of the substance, and so these cannot be changed without altering the qualitative meaning of the equation. For example, changing the reactant formula from  $\text{H}_2\text{O}$  to  $\text{H}_2\text{O}_2$  would yield a balance in the number of atoms, but doing so also changes the reactant's identity (it's now hydrogen peroxide and not water). The O atom balance may be achieved by changing the coefficient for  $\text{H}_2\text{O}$  to 2.

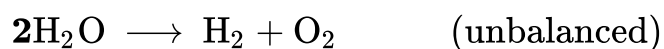
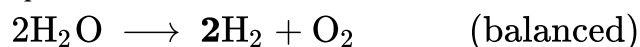


Table 7.3 By: Rice University [OpenStax CC BY-NC-SA 4.0](#)

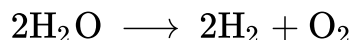
Element	Reactants	Products	Balanced?
H	$2 \times 2 = 4$	$1 \times 2 = 2$	$4 \neq 2$ , no
O	$2 \times 1 = 2$	$1 \times 2 = 2$	$2 = 2$ , yes

The H atom balance was upset by this change, but it was easily reestablished by changing the coefficient for the  $\text{H}_2$  product to 2.


 Table 7.4 By: Rice University [OpenStax CC BY-NC-SA 4.0](#)

Element	Reactants	Products	Balanced?
H	$2 \times 2 = 4$	$2 \times 2 = 4$	$4 = 4$ , yes
O	$2 \times 1 = 2$	$1 \times 2 = 2$	$2 = 2$ , yes

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



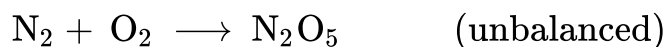
## EXAMPLE 7.1

### Balancing Chemical Equations

Write a balanced equation for the reaction of molecular nitrogen ( $\text{N}_2$ ) and oxygen ( $\text{O}_2$ ) to form dinitrogen pentoxide.

### Solution

First, write the unbalanced equation.

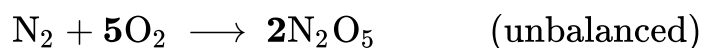


Next, count the number of each type of atom present in the unbalanced equation.

**Table 7.5 By: Rice University [OpenStax CC BY-NC-SA 4.0](#)**

Element	Reactants	Products	Balanced?
N	$1 \times 2 = 2$	$1 \times 2 = 2$	$2 = 2$ , yes
O	$1 \times 2 = 2$	$1 \times 5 = 5$	$2 \neq 5$ , no

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



**Table 7.6 By: Rice University [OpenStax CC BY-NC-SA 4.0](#)**

Element	Reactants	Products	Balanced?
N	$1 \times 2 = 2$	$2 \times 2 = 4$	$2 \neq 4$ , no
O	$5 \times 2 = 10$	$2 \times 5 = 10$	$10 = 10$ , yes

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

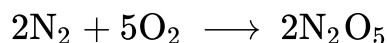




Table 7.7 By: Rice University [OpenStax CC BY-NC-SA 4.0](#)

Element	Reactants	Products	Balanced?
N	$2 \times 2 = 4$	$2 \times 2 = 4$	$4 = 4$ , yes
O	$5 \times 2 = 10$	$2 \times 5 = 10$	$10 = 10$ , yes

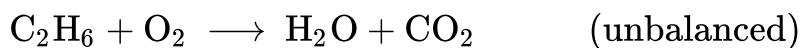
The numbers of N and O atoms on either side of the equation are now equal, and so the equation is balanced.

### Check Your Learning

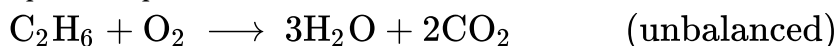
Write a balanced equation for the decomposition of ammonium nitrate to form molecular nitrogen, molecular oxygen, and water. (Hint: Balance oxygen last, since it is present in more than one molecule on the right side of the equation.)

**Answer:**  $2\text{NH}_4\text{NO}_3 \longrightarrow 2\text{N}_2 + \text{O}_2 + 4\text{H}_2\text{O}$

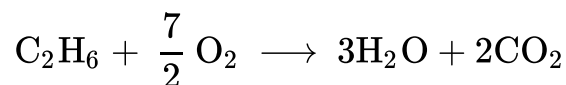
It is sometimes convenient to use fractions instead of integers as intermediate coefficients in the process of balancing a chemical equation. When balance is achieved, all the equation's coefficients may then be multiplied by a whole number to convert the fractional coefficients to integers without upsetting the atom balance. For example, consider the reaction of ethane ( $\text{C}_2\text{H}_6$ ) with oxygen to yield  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , represented by the unbalanced equation:



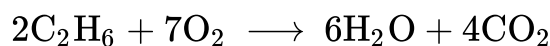
Following the usual inspection approach, one might first balance C and H atoms by changing the coefficients for the two product species, as shown:



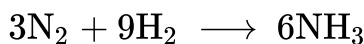
This results in seven O atoms on the product side of the equation, an odd number—no integer coefficient can be used with the  $\text{O}_2$  reactant to yield an odd number, so a fractional coefficient,  $\frac{7}{2}$ , is used instead to yield a provisional balanced equation:



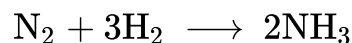
A conventional balanced equation with integer-only coefficients is derived by multiplying each coefficient by 2:



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



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

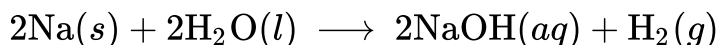


### Link to Learning

[Use this interactive](#) tutorial for additional practice balancing equations.

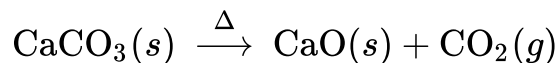
## Additional Information in Chemical Equations

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



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

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

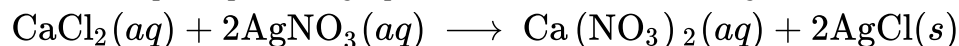


Other examples of these special conditions will be encountered in more depth in later chapters.

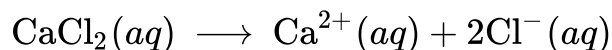
## Equations for Ionic Reactions

Given the abundance of water on earth, it stands to reason that a great many chemical reactions take place in aqueous media. When ions are involved in these reactions, the chemical equations may be written with

various levels of detail appropriate to their intended use. To illustrate this, consider a reaction between ionic compounds taking place in an aqueous solution. When aqueous solutions of  $\text{CaCl}_2$  and  $\text{AgNO}_3$  are mixed, a reaction takes place, producing aqueous  $\text{Ca}(\text{NO}_3)_2$  and solid  $\text{AgCl}$ :

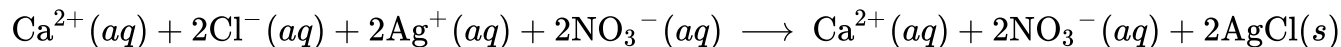


This balanced equation, derived in the usual fashion, is called a **molecular equation** because it doesn't explicitly represent the ionic species that are present in the solution. When ionic compounds dissolve in water, they may *dissociate* into their constituent ions, which are subsequently dispersed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

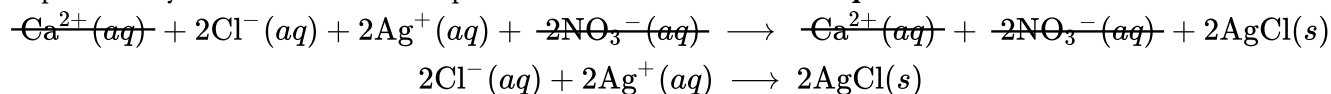


Unlike these three ionic compounds,  $\text{AgCl}$  does not dissolve in water to a significant extent, as signified by its physical state notation, *s*.

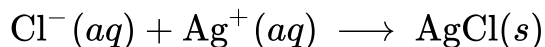
Explicitly representing all dissolved ions results in a **complete ionic equation**. In this particular case, the formulas for the dissolved ionic compounds are replaced by formulas for their dissociated ions:



Examining this equation shows that two chemical species are present in identical form on both sides of the arrow,  $\text{Ca}^{2+}(aq)$  and  $\text{NO}_3^-(aq)$ . These **spectator ions**—ions whose presence is required to maintain charge neutrality—are neither chemically nor physically changed by the process, and so they may be eliminated from the equation to yield a more succinct representation called a **net ionic equation**:



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



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

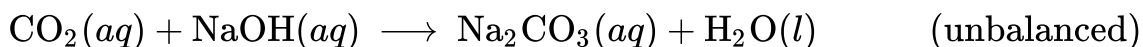
## EXAMPLE 7.2

## Molecular and Ionic Equations

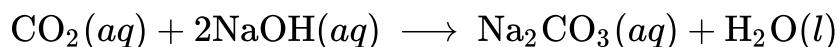
When carbon dioxide is dissolved in an aqueous solution of sodium hydroxide, the mixture reacts to yield aqueous sodium carbonate and liquid water. Write balanced molecular, complete ionic, and net ionic equations for this process.

## Solution

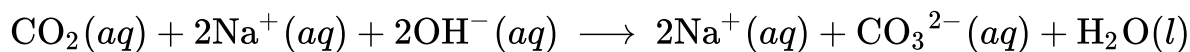
Begin by identifying formulas for the reactants and products and arranging them properly in chemical equation form:



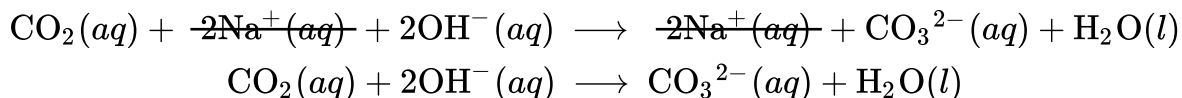
Balance is achieved easily in this case by changing the coefficient for NaOH to 2, resulting in the molecular equation for this reaction:



The two dissolved ionic compounds, NaOH and Na<sub>2</sub>CO<sub>3</sub>, can be represented as dissociated ions to yield the complete ionic equation:

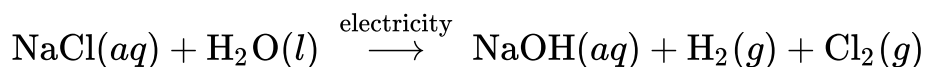


Finally, identify the spectator ion(s), in this case Na<sup>+</sup>(aq), and remove it from each side of the equation to generate the net ionic equation:



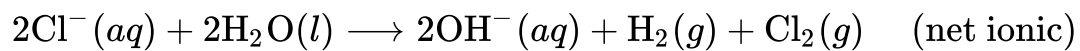
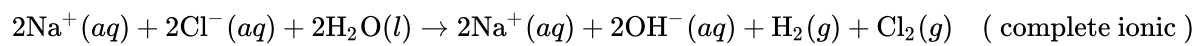
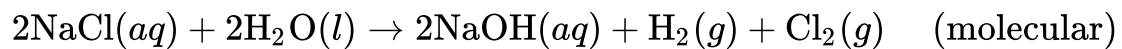
## Check Your Learning

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



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

**Answer:**



# CLASSIFYING CHEMICAL REACTIONS (7.2)

OpenStax

---

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

- Define three common types of chemical reactions (precipitation, acid-base, and oxidation-reduction)
- Classify chemical reactions as one of these three types given appropriate descriptions or chemical equations
- Identify common acids and bases
- Predict the solubility of common inorganic compounds by using solubility rules
- Compute the oxidation states for elements in compounds

Humans interact with one another in various and complex ways, and we classify these interactions according to common patterns of behavior. When two humans exchange information, we say they are communicating. When they exchange blows with their fists or feet, we say they are fighting. Faced with a wide range of varied interactions between chemical substances, scientists have likewise found it convenient (or even necessary) to classify chemical interactions by identifying common patterns of reactivity. This module will provide an introduction to three of the most prevalent types of chemical reactions: precipitation, acid-base, and oxidation-reduction.

## Precipitation Reactions and Solubility Rules

A **precipitation reaction** is one in which dissolved substances react to form one (or more) solid products. Many reactions of this type involve the exchange of ions between ionic compounds in aqueous solution and are sometimes referred to as *double displacement*, *double replacement*, or *metathesis* reactions. These reactions are common in nature and are responsible for the formation of coral reefs in ocean waters and kidney stones in animals. They are used widely in industry for the production of a number of commodity and specialty chemicals. Precipitation reactions also play a central role in many chemical analysis techniques, including spot

tests used to identify metal ions and *gravimetric methods* for determining the composition of matter (see the last module of this chapter).

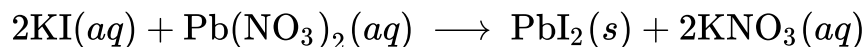
The extent to which a substance may be dissolved in water, or any solvent, is quantitatively expressed as its **solubility**, defined as the maximum concentration of a substance that can be achieved under specified conditions. Substances with relatively large solubilities are said to be **soluble**. A substance will **precipitate** when solution conditions are such that its concentration exceeds its solubility. Substances with relatively low solubilities are said to be **insoluble**, and these are the substances that readily precipitate from solution. More information on these important concepts is provided in a later chapter on solutions. For purposes of predicting the identities of solids formed by precipitation reactions, one may simply refer to patterns of solubility that have been observed for many ionic compounds (**Table 7.8**).

**T**  
**a**  
**b**  
**l**  
**e**  
**7**  
**.**  
**8**  
**B**  
**y**  
**:**  
**R**  
**i**  
**c**  
**e**  
**U**  
**n**  
**i**  
**v**  
**e**  
**r**  
**s**  
**i**  
**t**  
**y**  
**O**  
**p**  
**e**  
**n**  
**S**  
**t**  
**a**  
**x**  
**C**  
**C**  
**B**  
**Y**  
**=**  
**N**  
**C**  
**=**  
**S**  
**A**  
**4**  
**.**  
**0**



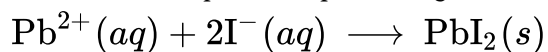
<b>Soluble Ionic Compounds</b>	contain these ions	exceptions
	$\text{NH}_4^+$ group I cations: $\text{Li}^+$ $\text{Na}^+$ $\text{K}^+$ $\text{Rb}^+$ $\text{Cs}^+$	none
	$\text{Cl}^-$ $\text{Br}^-$ $\text{I}^-$	compounds with $\text{Ag}^+$ , $\text{Hg}_2^{2+}$ , and $\text{Pb}^{2+}$
	$\text{F}^-$	compounds with group 2 metal cations, $\text{Pb}^{2+}$ , and $\text{Fe}^{3+}$
	$\text{C}_2\text{H}_3\text{O}_2^-$ $\text{HCO}_3^-$ $\text{NO}_3^-$ $\text{ClO}_3^-$	none
	$\text{SO}_4^{2-}$	compounds with $\text{Ag}^+$ , $\text{Ba}^{2+}$ , $\text{Ca}^{2+}$ , $\text{Hg}_2^{2+}$ , $\text{Pb}^{2+}$ , and $\text{Sr}^{2+}$
<b>Insoluble Ionic Compounds</b>	contain these ions	exceptions
	$\text{CO}_3^{2-}$ $\text{CrO}_4^{2-}$ $\text{PO}_4^{3-}$ $\text{S}^{2-}$	compounds with group 1 cations and $\text{NH}_4^+$
	$\text{OH}^-$	compounds with group 1 cations and $\text{Ba}^{2+}$

A vivid example of precipitation is observed when solutions of potassium iodide and lead nitrate are mixed, resulting in the formation of solid lead iodide:

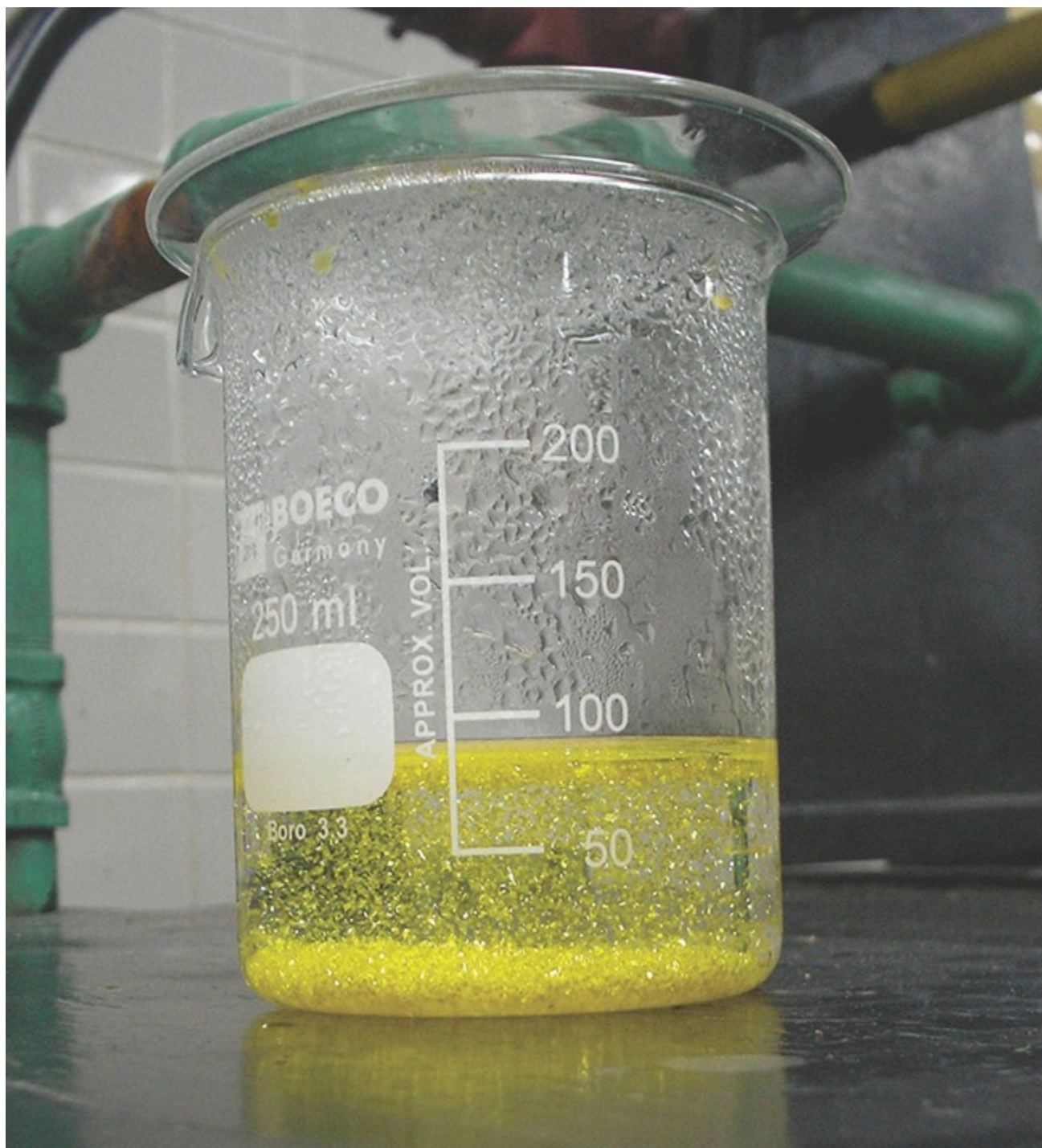


This observation is consistent with the solubility guidelines: The only insoluble compound among all those involved is lead iodide, one of the exceptions to the general solubility of iodide salts.

The net ionic equation representing this reaction is:



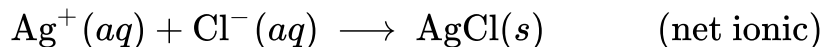
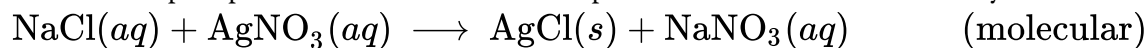
Lead iodide is a bright-yellow solid that was formerly used as an artist's pigment known as iodine yellow (**Figure 7.4**). The properties of pure  $\text{PbI}_2$  crystals make them useful for the fabrication of X-ray and gamma-ray detectors.



**Figure 7.4** A precipitate of  $\text{PbI}_2$  forms when solutions containing  $\text{Pb}^{2+}$  and  $\text{I}^-$  are mixed. By: Rice University [Openstax CC BY NC SA](#)

The solubility guidelines in **Table 7.8** may be used to predict whether a precipitation reaction will occur when solutions of soluble ionic compounds are mixed together. One merely needs to identify all the ions present in the solution and then consider if possible cation/anion pairing could result in an insoluble compound. For example, mixing solutions of silver nitrate and sodium fluoride will yield a solution containing  $\text{Ag}^+$ ,  $\text{NO}_3^-$ ,

$\text{Na}^+$ , and  $\text{F}^-$  ions. Aside from the two ionic compounds originally present in the solutions,  $\text{AgNO}_3$  and  $\text{NaF}$ , two additional ionic compounds may be derived from this collection of ions:  $\text{NaNO}_3$  and  $\text{AgF}$ . The solubility guidelines indicate all nitrate salts are soluble but that  $\text{AgF}$  is one of the exceptions to the general solubility of fluoride salts. A precipitation reaction, therefore, is predicted to occur, as described by the following equations:



## EXAMPLE 7.3

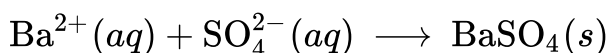
### Predicting Precipitation Reactions

Predict the result of mixing reasonably concentrated solutions of the following ionic compounds. If precipitation is expected, write a balanced net ionic equation for the reaction.

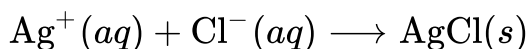
- (a) potassium sulfate and barium nitrate
- (b) lithium chloride and silver acetate
- (c) lead nitrate and ammonium carbonate

### Solution

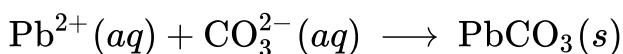
(a) The two possible products for this combination are  $\text{KNO}_3$  and  $\text{BaSO}_4$ . The solubility guidelines indicate  $\text{BaSO}_4$  is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is



(b) The two possible products for this combination are  $\text{LiC}_2\text{H}_3\text{O}_2$  and  $\text{AgCl}$ . The solubility guidelines indicate  $\text{AgCl}$  is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is



(c) The two possible products for this combination are  $\text{PbCO}_3$  and  $\text{NH}_4\text{NO}_3$ . The solubility guidelines indicate  $\text{PbCO}_3$  is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is



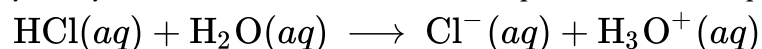
### Check Your Learning

Which solution could be used to precipitate the barium ion,  $\text{Ba}^{2+}$ , in a water sample: sodium chloride, sodium hydroxide, or sodium sulfate? What is the formula for the expected precipitate?

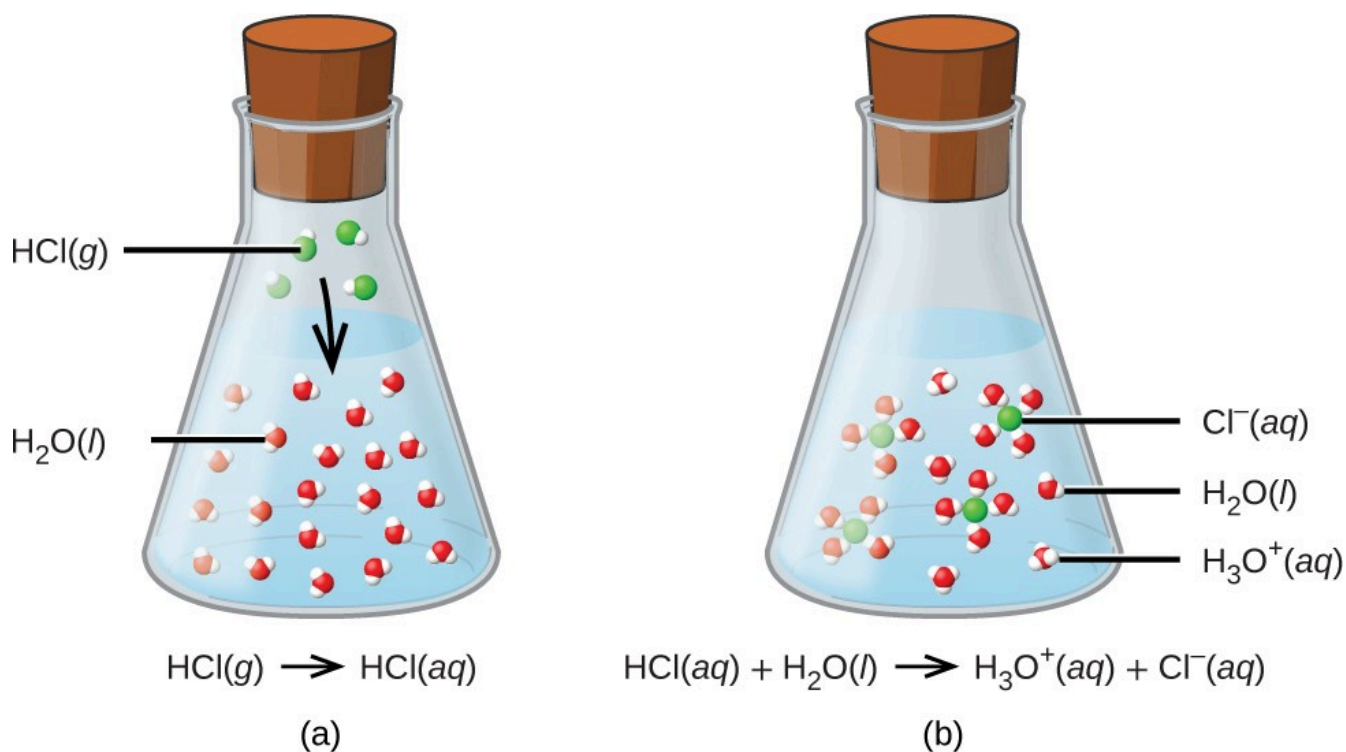
**Answer:** sodium sulfate,  $\text{BaSO}_4$

## Acid-Base Reactions

An **acid-base reaction** is one in which a hydrogen ion,  $\text{H}^+$ , is transferred from one chemical species to another. Such reactions are of central importance to numerous natural and technological processes, ranging from the chemical transformations that take place within cells and the lakes and oceans to the industrial-scale production of fertilizers, pharmaceuticals, and other substances essential to society. The subject of acid-base chemistry, therefore, is worthy of thorough discussion, and a full chapter is devoted to this topic later in the text. For purposes of this brief introduction, we will consider only the more common types of acid-base reactions that take place in aqueous solutions. In this context, an **acid** is a substance that will dissolve in water to yield hydronium ions,  $\text{H}_3\text{O}^+$ . As an example, consider the equation shown here:

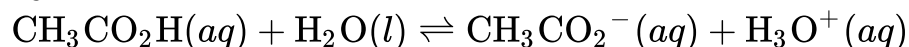


The process represented by this equation confirms that hydrogen chloride is an acid. When dissolved in water,  $\text{H}_3\text{O}^+$  ions are produced by a chemical reaction in which  $\text{H}^+$  ions are transferred from  $\text{HCl}$  molecules to  $\text{H}_2\text{O}$  molecules (**Figure 7.5**).



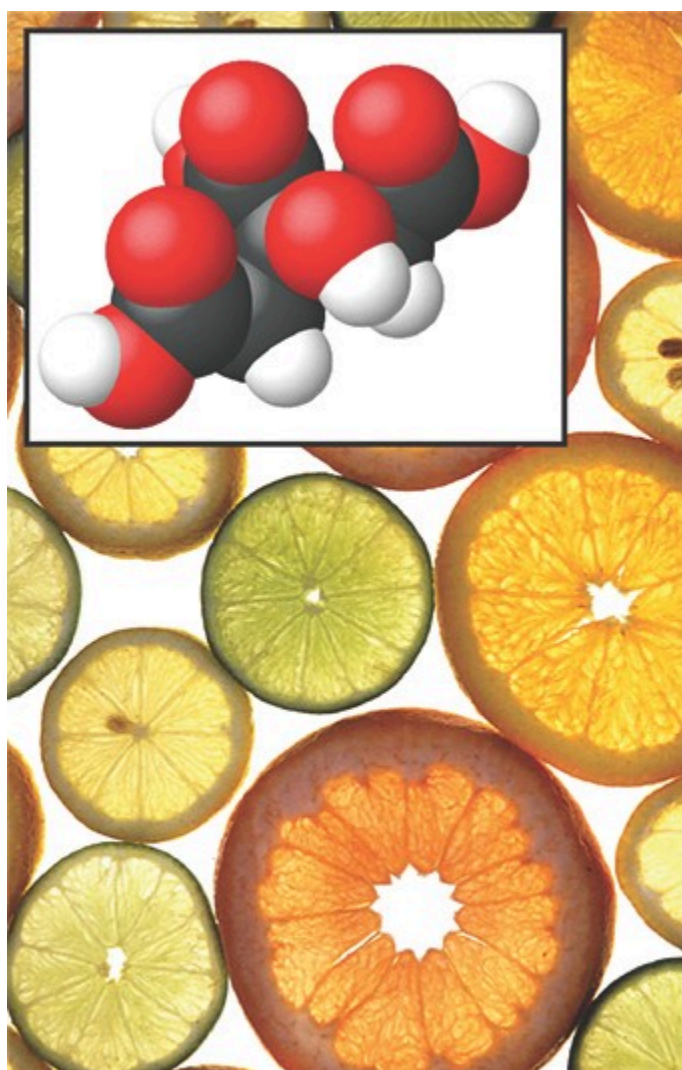
**Figure 7.5** When hydrogen chloride gas dissolves in water, (a) it reacts as an acid, transferring protons to water molecules to yield (b) hydronium ions (and solvated chloride ions). By: Rice University [Openstax CC BY-NC-SA](#)

The nature of HCl is such that its reaction with water as just described is essentially 100% efficient: Virtually every HCl molecule that dissolves in water will undergo this reaction. Acids that completely react in this fashion are called **strong acids**, and HCl is one among just a handful of common acid compounds that are classified as strong (**Table 7.2**). A far greater number of compounds behave as **weak acids** and only partially react with water, leaving a large majority of dissolved molecules in their original form and generating a relatively small amount of hydronium ions. Weak acids are commonly encountered in nature, being the substances partly responsible for the tangy taste of citrus fruits, the stinging sensation of insect bites, and the unpleasant smells associated with body odor. A familiar example of a weak acid is acetic acid, the main ingredient in food vinegars:



When dissolved in water under typical conditions, only about 1% of acetic acid molecules are present in the ionized form,  $\text{CH}_3\text{CO}_2^-$  (**Figure 7.6**). (The use of a double-arrow in the equation above denotes the partial reaction aspect of this process, a concept addressed fully in the chapters on chemical equilibrium.)





(a)



(b)

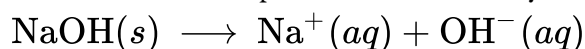
**Figure 7.6** (a) Fruits such as oranges, lemons, and grapefruit contain the weak acid citric acid. (b) Vinegars contain the weak acid acetic acid. By: Rice University [OpenStax CC BY NC SA](#)

**Table 7.9 Common Strong Acids** By: Rice University [OpenStax CC BY-NC-SA 4.0](#)

Compound Formula	Name in Aqueous Solution
HBr	hydrobromic acid
HCl	hydrochloric acid
HI	hydroiodic acid
HNO <sub>3</sub>	nitric acid
HClO <sub>4</sub>	perchloric acid
H <sub>2</sub> SO <sub>4</sub>	sulfuric acid

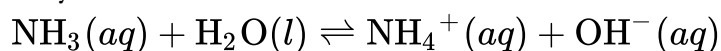
A **base** is a substance that will dissolve in water to yield hydroxide ions,  $\text{OH}^-$ . The most common bases are ionic compounds composed of alkali or alkaline earth metal cations (groups 1 and 2) combined with the hydroxide ion—for example,  $\text{NaOH}$  and  $\text{Ca}(\text{OH})_2$ . Unlike the acid compounds discussed previously, these compounds do not react chemically with water; instead, they dissolve and dissociate, releasing hydroxide ions directly into the solution. For example,  $\text{KOH}$  and  $\text{Ba}(\text{OH})_2$  dissolve in water and dissociate completely to produce cations ( $\text{K}^+$  and  $\text{Ba}^{2+}$ , respectively) and hydroxide ions,  $\text{OH}^-$ . These bases, along with other hydroxides that completely dissociate in water, are considered **strong bases**.

Consider as an example the dissolution of lye (sodium hydroxide) in water:



This equation confirms that sodium hydroxide is a base. When dissolved in water,  $\text{NaOH}$  dissociates to yield  $\text{Na}^+$  and  $\text{OH}^-$  ions. This is also true for any other ionic compound containing hydroxide ions. Since the dissociation process is essentially complete when ionic compounds dissolve in water under typical conditions,  $\text{NaOH}$  and other ionic hydroxides are all classified as strong bases.

Unlike ionic hydroxides, some compounds produce hydroxide ions when dissolved by chemically reacting with water molecules. In all cases, these compounds react only partially and so are classified as **weak bases**. These types of compounds are also abundant in nature and important commodities in various technologies. For example, global production of the weak base ammonia is typically well over 100 metric tons annually, being widely used as an agricultural fertilizer, a raw material for the chemical synthesis of other compounds and an active ingredient in household cleaners (**Figure 7.7**). When dissolved in water, ammonia reacts partially to yield hydroxide ions, as shown here:



This is, by definition, an acid-base reaction, in this case involving the transfer of  $\text{H}^+$  ions from water molecules to ammonia molecules. Under typical conditions, only about 1% of the dissolved ammonia is present as  $\text{NH}_4^+$  ions.



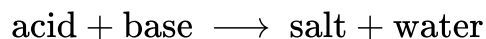
(a)



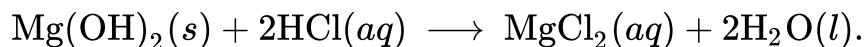
(b)

**Figure 7.7** Ammonia is a weak base used in a variety of applications. (a) Pure ammonia is commonly applied as an agricultural fertilizer. (b) Dilute solutions of ammonia are effective household cleansers. By: Rice University [Openstax CC BY NC SA](#)

A **neutralization reaction** is a specific type of acid-base reaction in which the reactants are an acid and a base (but not water), and the products are often a **salt** and water:



To illustrate a neutralization reaction, consider what happens when a typical antacid such as milk of magnesia (an aqueous suspension of solid  $\text{Mg}(\text{OH})_2$ ) is ingested to ease symptoms associated with excess stomach acid ( $\text{HCl}$ ):



Note that in addition to water, this reaction produces a salt, magnesium chloride.

## EXAMPLE 7.4

### Writing Equations for Acid-Base Reactions

Write balanced chemical equations for the acid-base reactions described here:

- (a) the weak acid hydrogen hypochlorite reacts with water
- (b) a solution of barium hydroxide is neutralized with a solution of nitric acid

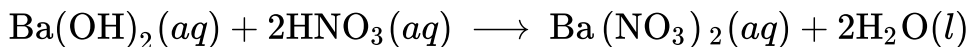
#### Solution

(a) The two reactants are provided,  $\text{HOCl}$  and  $\text{H}_2\text{O}$ . Since the substance is reported to be an acid, its reaction with water will involve the transfer of  $\text{H}^+$  from  $\text{HOCl}$  to  $\text{H}_2\text{O}$  to generate hydronium ions,  $\text{H}_3\text{O}^+$  and hypochlorite ions,  $\text{OCl}^-$



A double-arrow is appropriate in this equation because it indicates the  $\text{HOCl}$  is a weak acid that has not reacted completely.

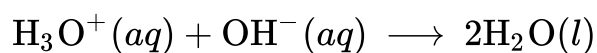
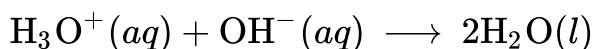
(b) The two reactants are provided,  $\text{Ba}(\text{OH})_2$  and  $\text{HNO}_3$ . Since this is a neutralization reaction, the two products will be water and a salt composed of the cation of the ionic hydroxide ( $\text{Ba}^{2+}$ ) and the anion generated when the acid transfers its hydrogen ion ( $\text{NO}_3^-$ ).



### Check Your Learning

Write the net ionic equation representing the neutralization of any strong acid with an ionic hydroxide. (Hint: Consider the ions produced when a strong acid is dissolved in water.)



**Answer:**

## Chemistry in Everyday Life

### Stomach Antacids

Our stomachs contain a solution of roughly 0.03 M HCl, which helps us digest the food we eat. The burning sensation associated with heartburn is a result of the acid of the stomach leaking through the muscular valve at the top of the stomach into the lower reaches of the esophagus. The lining of the esophagus is not protected from the corrosive effects of stomach acid the way the lining of the stomach is, and the results can be very painful. When we have heartburn, it feels better if we reduce the excess acid in the esophagus by taking an antacid. As you may have guessed, antacids are bases. One of the most common antacids is calcium carbonate,  $\text{CaCO}_3$ . The reaction,

$\text{CaCO}_3(s) + 2\text{HCl}(aq) \rightleftharpoons \text{CaCl}_2(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g)$  not only neutralizes stomach acid, it also produces  $\text{CO}_2(g)$ , which may result in a satisfying belch.

Milk of Magnesia is a suspension of the sparingly soluble base magnesium hydroxide,  $\text{Mg}(\text{OH})_2$ . It works according to the reaction:

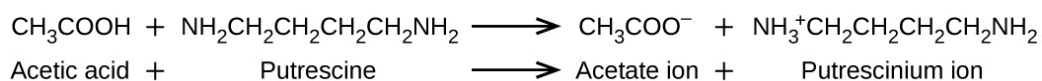
$\text{Mg}(\text{OH})_2(s) \rightleftharpoons \text{Mg}^{2+}(aq) + 2\text{OH}^-(aq)$  The hydroxide ions generated in this equilibrium then go on to react with the hydronium ions from the stomach acid, so that:

$\text{H}_3\text{O}^+ + \text{OH}^- \rightleftharpoons 2\text{H}_2\text{O}(l)$  This reaction does not produce carbon dioxide, but magnesium-containing antacids can have a laxative effect. Several antacids have aluminum hydroxide,  $\text{Al}(\text{OH})_3$ , as an active ingredient. The aluminum hydroxide tends to cause constipation, and some antacids use aluminum hydroxide in concert with magnesium hydroxide to balance the side effects of the two substances.

## Chemistry in Everyday Life

### Culinary Aspects of Chemistry

Examples of acid-base chemistry are abundant in the culinary world. One example is the use of baking soda, or sodium bicarbonate in baking.  $\text{NaHCO}_3$  is a base. When it reacts with an acid such as lemon juice, buttermilk, or sour cream in a batter, bubbles of carbon dioxide gas are formed from the decomposition of the resulting carbonic acid, and the batter “rises.” Baking powder is a combination of sodium bicarbonate, and one or more acid salts that react when the two chemicals come in contact with water in the batter. Many people like to put lemon juice or vinegar, both of which are acids, on cooked fish (**Figure 7.8**). It turns out that fish have volatile amines (bases) in their systems, which are neutralized by the acids to yield involatile ammonium salts. This reduces the odor of the fish and also adds a “sour” taste that we seem to enjoy.



**Figure 7.8** A neutralization reaction takes place between citric acid in lemons or acetic acid in vinegar and the bases in the flesh of fish. By: Rice University [Openstax CC BY NC SA](#)

Pickling is a method used to preserve vegetables using a naturally produced acidic environment.

The vegetable, such as a cucumber, is placed in a sealed jar submerged in a brine solution. The brine solution favors the growth of beneficial bacteria and suppresses the growth of harmful bacteria. The beneficial bacteria feed on starches in the cucumber and produce lactic acid as a waste product in a process called fermentation. The lactic acid eventually increases the acidity of the brine to a level that kills any harmful bacteria, which require a basic environment. Without the harmful bacteria consuming the cucumbers, they are able to last much longer than if they were unprotected. A byproduct of the pickling process changes the flavor of the vegetables with the acid making them taste sour.

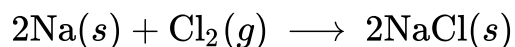
### Link to Learning

[Explore the microscopic view](#) of strong and weak acids and bases.

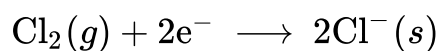
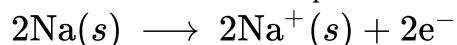
## Oxidation-Reduction Reactions

Earth's atmosphere contains about 20% molecular oxygen,  $O_2$ , a chemically reactive gas that plays an essential role in the metabolism of aerobic organisms and in many environmental processes that shape the world. The term **oxidation** was originally used to describe chemical reactions involving  $O_2$ , but its meaning has evolved to refer to a broad and important reaction class known as *oxidation-reduction (redox) reactions*. A few examples of such reactions will be used to develop a clear picture of this classification.

Some redox reactions involve the transfer of electrons between reactant species to yield ionic products, such as the reaction between sodium and chlorine to yield sodium chloride:



It is helpful to view the process with regard to each individual reactant, that is, to represent the fate of each reactant in the form of an equation called a **half-reaction**:



These equations show that Na atoms *lose electrons* while Cl atoms (in the  $Cl_2$  molecule) *gain electrons*, the “s” subscripts for the resulting ions signifying they are present in the form of a solid ionic compound. For redox reactions of this sort, the loss and gain of electrons define the complementary processes that occur:

**oxidation** = loss of electrons

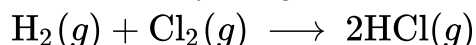
**reduction** = gain of electrons

In this reaction, then, sodium is *oxidized*, and chlorine undergoes **reduction**. Viewed from a more active perspective, sodium functions as a **reducing agent (reductant)**, since it provides electrons to (or reduces) chlorine. Likewise, chlorine functions as an **oxidizing agent (oxidant)**, as it effectively removes electrons from (oxidizes) sodium.

**reducing agent** = species that is oxidized

**oxidizing agent** = species that is reduced

Some redox processes, however, do not involve the transfer of electrons. Consider, for example, a reaction similar to the one yielding NaCl:



The product of this reaction is a covalent compound, so the transfer of electrons in the explicit sense is not involved. To clarify the similarity of this reaction to the previous one and permit an unambiguous definition of redox reactions, a property called *oxidation number* has been defined. The **oxidation number** (or **oxidation state**) of an element in a compound is the charge its atoms would possess *if the compound was ionic*. The following guidelines are used to assign oxidation numbers to each element in a molecule or ion.

- The oxidation number of an atom in an elemental substance is zero.
- The oxidation number of a monatomic ion is equal to the ion's charge.
- Oxidation numbers for common nonmetals are usually assigned as follows:
  - Hydrogen: +1 when combined with nonmetals, −1 when combined with metals
  - Oxygen: −2 in most compounds, sometimes −1 (so-called peroxides,  $\text{O}_2^{2-}$ ), very rarely  $-\frac{1}{2}$  (so-called superoxides,  $\text{O}_2^-$ ) positive values when combined with F (values vary)
  - Halogens: −1 for F always, −1 for other halogens except when combined with oxygen or other halogens (positive oxidation numbers in these cases, varying values)
- The sum of oxidation numbers for all atoms in a molecule or polyatomic ion equals the charge on the molecule or ion.

Note: The proper convention for reporting charge is to write the number first, followed by the sign (e.g., 2+), while the oxidation number is written with the reversed sequence, the sign followed by the number (e.g., +2). This convention aims to emphasize the distinction between these two related properties.

## EXAMPLE 7.5

## Assigning Oxidation Numbers

Follow the guidelines in this section of the text to assign oxidation numbers to all the elements in the following species:

(a)  $\text{H}_2\text{S}$

(b)  $\text{SO}_3^{2-}$

(c)  $\text{Na}_2\text{SO}_4$

## Solution

(a) According to guideline 1, the oxidation number for H is +1.

Using this oxidation number and the compound's formula, guideline 4 may then be used to calculate the oxidation number for sulfur:

$$\text{charge on H}_2\text{S} = 0 = (2 \times +1) + (1 \times x) \quad \text{(b) Guideline 3 suggests the oxidation}$$

$$x = 0 - (2 \times +1) = -2$$

number for oxygen is -2.

Using this oxidation number and the ion's formula, guideline 4 may then be used to calculate the oxidation number for sulfur:

$$\text{charge on SO}_3^{2-} = -2 = (3 \times -2) + (1 \times x) \quad \text{(c) For ionic compounds, it's}$$

$$x = -2 - (3 \times -2) = +4$$

convenient to assign oxidation numbers for the cation and anion separately.

According to guideline 2, the oxidation number for sodium is +1.

Assuming the usual oxidation number for oxygen (-2 per guideline 3), the oxidation number for sulfur is calculated as directed by guideline 4:

$$\text{charge on SO}_4^{2-} = -2 = (4 \times -2) + (1 \times x)$$

$$x = -2 - (4 \times -2) = +6$$

### Check Your Learning

Assign oxidation states to the elements whose atoms are underlined in each of the following compounds or ions:



**Answer:** (a) N, +5; (b) Al, +3; (c) N, –3; (d) P, +5

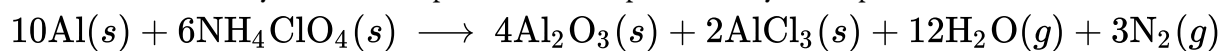
Using the oxidation number concept, an all-inclusive definition of redox reaction has been established. **Oxidation-reduction (redox) reactions** are those in which one or more elements involved undergo a change in oxidation number. (While the vast majority of redox reactions involve changes in oxidation number for two or more elements, a few interesting exceptions to this rule do exist **Example 7.6.**) Definitions for the complementary processes of this reaction class are correspondingly revised as shown here:

**oxidation** = increase in oxidation number

**reduction** = decrease in oxidation number

Returning to the reactions used to introduce this topic, they may now both be identified as redox processes. In the reaction between sodium and chlorine to yield sodium chloride, sodium is oxidized (its oxidation number increases from 0 in Na to +1 in NaCl), and chlorine is reduced (its oxidation number decreases from 0 in  $\text{Cl}_2$  to –1 in NaCl). In the reaction between molecular hydrogen and chlorine, hydrogen is oxidized (its oxidation number increases from 0 in  $\text{H}_2$  to +1 in HCl), and chlorine is reduced (its oxidation number decreases from 0 in  $\text{Cl}_2$  to –1 in HCl).

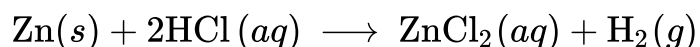
Several subclasses of redox reactions are recognized, including **combustion reactions** in which the reductant (also called a *fuel*) and oxidant (often, but not necessarily, molecular oxygen) react vigorously and produce significant amounts of heat, and often light, in the form of a flame. Solid rocket-fuel reactions such as the one depicted in **Figure 7.1** are combustion processes. A typical propellant reaction in which solid aluminum is oxidized by ammonium perchlorate is represented by this equation:



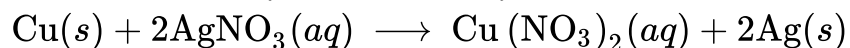
## Link to Learning

[Watch a brief video](#) showing the test firing of a small-scale, prototype, hybrid rocket engine planned for use in the new Space Launch System being developed by NASA. The first engines firing at 3 s (green flame) use a liquid fuel/oxidant mixture, and the second, more powerful engines firing at 4 s (yellow flame) use a solid mixture.

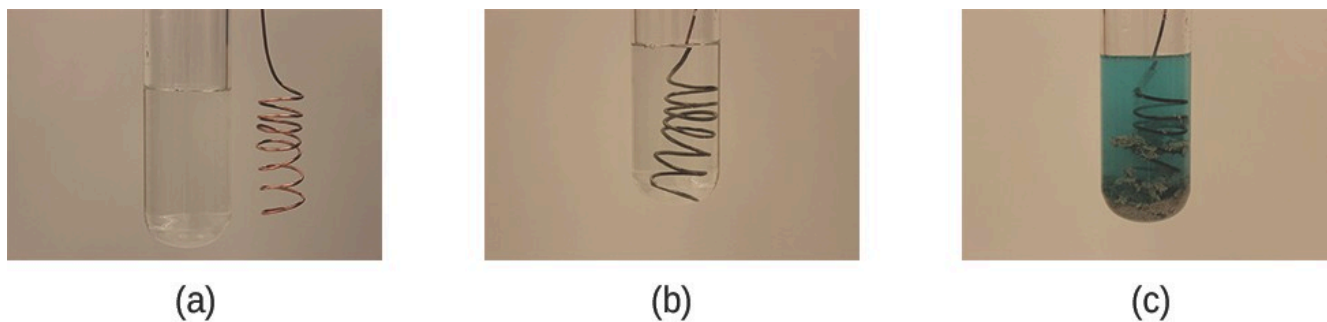
**Single-displacement (replacement) reactions** are redox reactions in which an ion in solution is displaced (or replaced) via the oxidation of a metallic element. One common example of this type of reaction is the acid oxidation of certain metals:



Metallic elements may also be oxidized by solutions of other metal salts; for example:



This reaction may be observed by placing copper wire in a solution containing a dissolved silver salt. Silver ions in solution are reduced to elemental silver at the surface of the copper wire, and the resulting  $\text{Cu}^{2+}$  ions dissolve in the solution to yield a characteristic blue color (**Figure 7.9**).



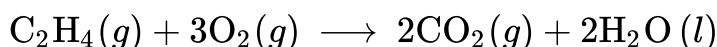
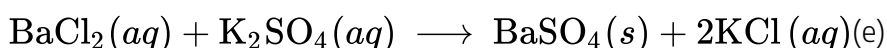
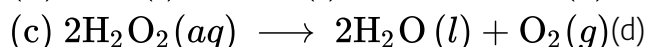
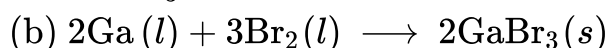
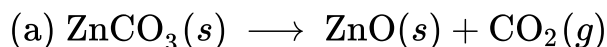
**Figure 7.9** (a) A copper wire is shown next to a solution containing silver(I) ions. (b) Displacement of dissolved silver ions by copper ions results in (c) accumulation of gray-colored silver metal on the wire and development of a blue color in the solution, due to dissolved copper ions. By: Rice University [Openstax CC BY-NC-SA](#)



## EXAMPLE 7.6

## Describing Redox Reactions

Identify which equations represent redox reactions, providing a name for the reaction if appropriate. For those reactions identified as redox, name the oxidant and reductant.



## Solution

Redox reactions are identified per definition if one or more elements undergo a change in oxidation number.

(a) This is not a redox reaction, since oxidation numbers remain unchanged for all elements.

(b) This is a redox reaction. Gallium is oxidized, its oxidation number increasing from 0 in  $\text{Ga}(l)$  to +3 in  $\text{GaBr}_3(s)$ . The reducing agent is  $\text{Ga}(l)$ . Bromine is reduced, its oxidation number decreasing from 0 in  $\text{Br}_2(l)$  to -1 in  $\text{GaBr}_3(s)$ . The oxidizing agent is  $\text{Br}_2(l)$ .

(c) This is a redox reaction. It is a particularly interesting process, as it involves the same element, oxygen, undergoing both oxidation and reduction (a so-called *disproportionation reaction*). Oxygen is oxidized, its oxidation number increasing from -1 in  $\text{H}_2\text{O}_2(aq)$  to 0 in  $\text{O}_2(g)$ . Oxygen is also reduced, its oxidation number decreasing from -1 in  $\text{H}_2\text{O}_2(aq)$  to -2 in  $\text{H}_2\text{O}(l)$ . For disproportionation reactions, the same substance functions as an oxidant and a reductant.

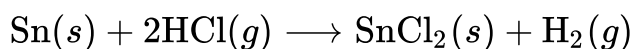
(d) This is not a redox reaction, since oxidation numbers remain unchanged for all elements.

(e) This is a redox reaction (combustion). Carbon is oxidized, its oxidation number increasing from -2 in  $\text{C}_2\text{H}_4(g)$  to +4 in  $\text{CO}_2(g)$ . The reducing agent (fuel) is  $\text{C}_2\text{H}_4(g)$ . Oxygen is reduced, its oxidation number decreasing from 0 in  $\text{O}_2(g)$  to -2 in  $\text{H}_2\text{O}(l)$ . The oxidizing agent is  $\text{O}_2(g)$ .

## Check Your Learning

This equation describes the production of tin(II) chloride:





Is this a redox reaction? If so, provide a more specific name for the reaction if appropriate, and identify the oxidant and reductant.

**Answer:** Yes, a single-replacement reaction.  $\text{Sn}(s)$  is the reductant,  $\text{HCl}(g)$  is the oxidant.

### Balancing Redox Reactions via the Half-Reaction Method

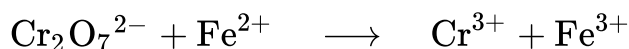
Redox reactions that take place in aqueous media often involve water, hydronium ions, and hydroxide ions as reactants or products. Although these species are not oxidized or reduced, they do participate in chemical change in other ways (e.g., by providing the elements required to form oxyanions). Equations representing these reactions are sometimes very difficult to balance by inspection, so systematic approaches have been developed to assist in the process. One very useful approach is to use the method of half-reactions, which involves the following steps:

1. Write the two half-reactions representing the redox process.
2. Balance all elements except oxygen and hydrogen.
3. Balance oxygen atoms by adding  $\text{H}_2\text{O}$  molecules.
4. Balance hydrogen atoms by adding  $\text{H}^+$  ions.
5. Balance charge by adding electrons.
6. If necessary, multiply each half-reaction's coefficients by the smallest possible integers to yield equal numbers of electrons in each.
7. Add the balanced half-reactions together and simplify by removing species that appear on both sides of the equation.
8. For reactions occurring in basic media (excess hydroxide ions), carry out these additional steps:
  - Add  $\text{OH}^-$  ions to both sides of the equation in numbers equal to the number of  $\text{H}^+$  ions.
  - On the side of the equation containing both  $\text{H}^+$  and  $\text{OH}^-$  ions, combine these ions to yield water molecules.
  - Simplify the equation by removing any redundant water molecules.
9. Finally, check to see that both the number of atoms and the total charges<sup>1</sup> are balanced.

## EXAMPLE 7.7

## Balancing Redox Reactions in Acidic Solution

Write a balanced equation for the reaction between dichromate ion and iron(II) to yield iron(III) and chromium(III) in an acidic solution.

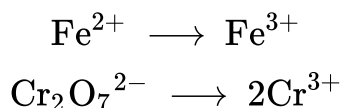


## Solution

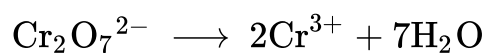
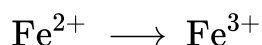
Step 1. *Write the two half-reactions.*

Each half-reaction will contain one reactant and one product with one element in common.

$\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+}$   
 $\text{Cr}_2\text{O}_7^{2-} \longrightarrow \text{Cr}^{3+}$  Step 2. *Balance all elements except oxygen and hydrogen.* The iron half-reaction is already balanced, but the chromium half-reaction shows two Cr atoms on the left and one Cr atom on the right. Changing the coefficient on the right side of the equation to 2 achieves balance with regard to Cr atoms.

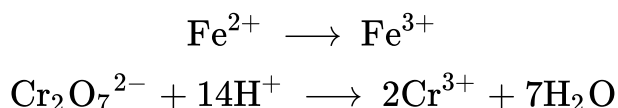


Step 3. *Balance oxygen atoms by adding H<sub>2</sub>O molecules.* The iron half-reaction does not contain O atoms. The chromium half-reaction shows seven O atoms on the left and none on the right, so seven water molecules are added to the right side.



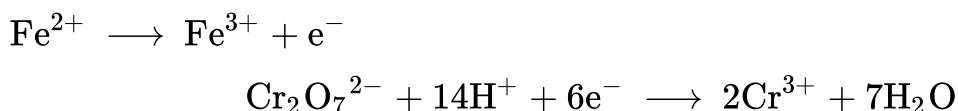
1. The requirement of “charge balance” is just a specific type of “mass balance” in which the species in question are electrons. An equation must represent equal numbers of electrons on the reactant and product sides, and so both atoms and charges must be balanced.

Step 4. *Balance hydrogen atoms by adding H<sup>+</sup> ions.* The iron half-reaction does not contain H atoms. The chromium half-reaction shows 14 H atoms on the right and none on the left, so 14 hydrogen ions are added to the left side.

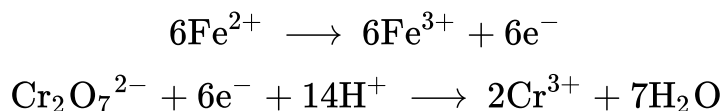


Step 5. *Balance charge by adding electrons.* The iron half-reaction shows a total charge of 2+ on the left side (1 Fe<sup>2+</sup> ion) and 3+ on the right side (1 Fe<sup>3+</sup> ion). Adding one electron to the right side brings that side's total charge to (3+) + (1-) = 2+, and charge balance is achieved.

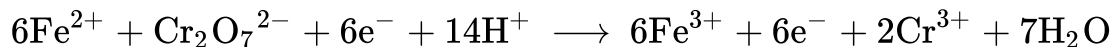
The chromium half-reaction shows a total charge of (1 x 2-) + (14 x 1+) = 12+ on the left side (1 Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> ion and 14 H<sup>+</sup> ions). The total charge on the right side is (2 x 3+) = 6+ (2 Cr<sup>3+</sup> ions). Adding six electrons to the left side will bring that side's total charge to (12+ + 6-) = 6+, and charge balance is achieved.



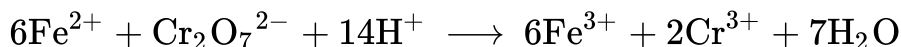
Step 6. *Multiply the two half-reactions so the number of electrons in one reaction equals the number of electrons in the other reaction.* To be consistent with mass conservation, and the idea that redox reactions involve the transfer (not creation or destruction) of electrons, the iron half-reaction's coefficient must be multiplied by 6.



Step 7. *Add the balanced half-reactions and cancel species that appear on both sides of the equation.*



Only the six electrons are redundant species. Removing them from each side of the equation yields the simplified, balanced equation here:



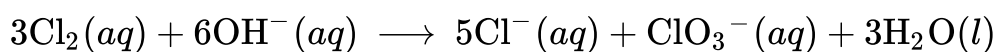
A final check of atom and charge balance confirms the equation is balanced.

	Reactants	Products
Fe	6	6
Cr	2	2
O	7	7
H	14	14
charge	24+	24+

### Check Your Learning

In basic solution, molecular chlorine,  $\text{Cl}_2$ , reacts with hydroxide ions,  $\text{OH}^-$ , to yield chloride ions,  $\text{Cl}^-$ , and chlorate ions,  $\text{ClO}_3^-$ . HINT: This is a *disproportionation reaction* in which the element chlorine is both oxidized and reduced. Write a balanced equation for this reaction.

**Answer:**



# REACTION STOICHIOMETRY (7.3)

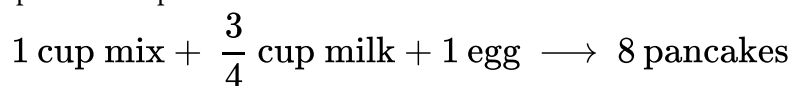
OpenStax

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

- Explain the concept of stoichiometry as it pertains to chemical reactions
- Use balanced chemical equations to derive stoichiometric factors relating to 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 the 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. Food preparation, for example, offers an appropriate comparison. 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

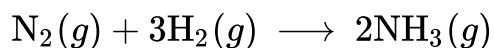


If two dozen pancakes are needed for a big family breakfast, the ingredient amounts must be increased proportionally according to the amounts given in the recipe. For example, the number of eggs required to make 24 pancakes is

$$24 \text{ ~~pancakes~~} \times \frac{1 \text{ egg}}{8 \text{ ~~pancakes~~}} = 3 \text{ eggs}$$

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 the computation of the desired quantity. To illustrate this idea, consider the production of ammonia by reaction of hydrogen and nitrogen:



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

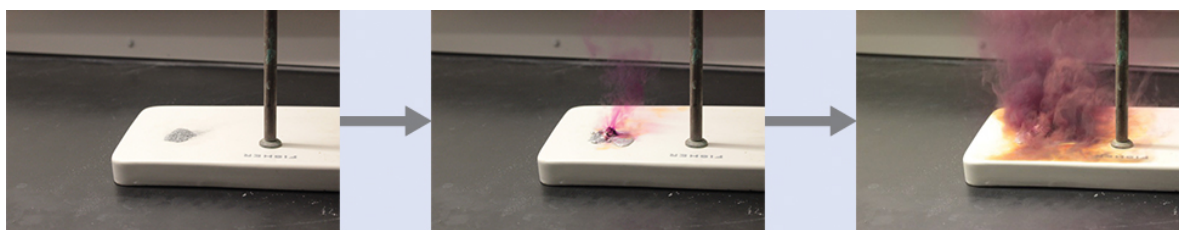
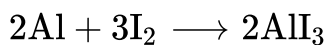
$$\frac{2\text{NH}_3 \text{ molecules}}{3\text{H}_2 \text{ molecules}} \text{ or } \frac{2 \text{ doz NH}_3 \text{ molecules}}{3 \text{ doz H}_2 \text{ molecules}} \text{ or } \frac{2 \text{ mol NH}_3 \text{ molecules}}{3 \text{ mol H}_2 \text{ molecules}}$$

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 7.8

### Moles of Reactant Required in a Reaction

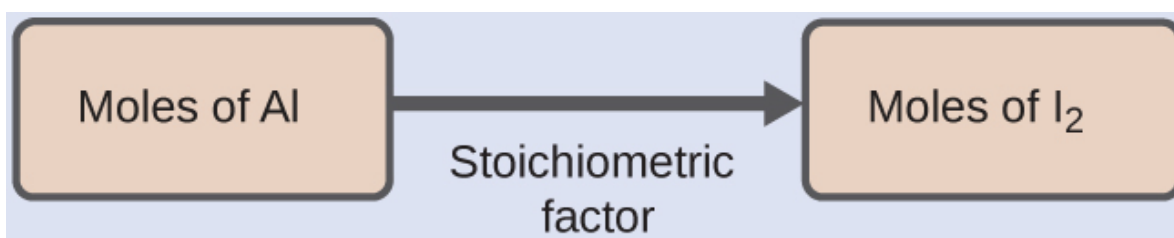
How many moles of  $\text{I}_2$  are required to react with 0.429 mol of Al according to the following equation (see **Figure 7.10**)?



**Figure 7.10** Aluminum and iodine react to produce aluminum iodide. The heat of the reaction vaporizes some of the solid iodine as a purple vapor. By: Rice University [Openstax CC BY NC SA](#)

### Solution

Referring to the balanced chemical equation, the stoichiometric factor relating the two substances of interest is  $\frac{3 \text{ mol I}_2}{2 \text{ mol Al}}$ . The molar amount of iodine is derived by multiplying the provided molar amount of aluminum by this factor:

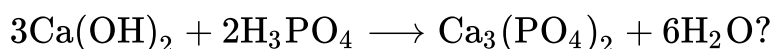


**Figure 7.11** By: Rice University [OpenstaxCC BY NC SA](https://openstax.org/r/by-nc-sa)

$$\begin{aligned}\text{mol I}_2 &= 0.429 \cancel{\text{mol Al}} \times \frac{3 \text{ mol I}_2}{2 \cancel{\text{mol Al}}} \\ &= 0.644 \text{ mol I}_2\end{aligned}$$

### Check Your Learning

How many moles of  $\text{Ca}(\text{OH})_2$  are required to react with 1.36 mol of  $\text{H}_3\text{PO}_4$  to produce  $\text{Ca}_3(\text{PO}_4)_2$  according to the equation:

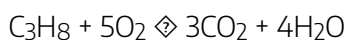


**Answer:** 2.04 mol

## EXAMPLE 7.9

### 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?



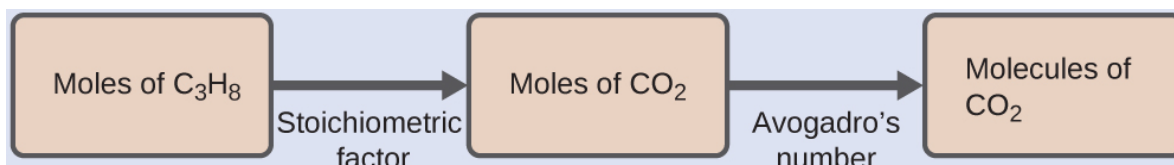
### Solution

The approach here is the same as for Example 7.8, though the absolute number of molecules is requested, not the number of moles of molecules. This will simply require the 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:

$$\frac{3 \text{ mol } CO_2}{1 \text{ mol } C_3H_8}$$

Using this stoichiometric factor, the provided molar amount of propane, and Avogadro's number,



**Figure 7.12** By: Rice University [OpenstaxCC BY NC SA](#)

$$0.76 \text{ mol } C_3H_8 \times \frac{3 \cancel{\text{ mol } CO_2}}{1 \cancel{\text{ mol } C_3H_8}} \times \frac{6.022 \times 10^{23} \text{ CO}_2 \text{ molecules}}{\cancel{\text{ mol } CO_2}} = 1.4 \times 10^{24} \text{ CO}_2 \text{ molecules}$$

### Check Your Learning

How many  $NH_3$  molecules are produced by the reaction of 4.0 mol of  $Ca(OH)_2$  according to the following equation:



**Answer:**  $4.8 \times 10^{24}$   $NH_3$  molecules

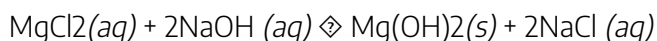
These examples illustrate the ease with which the amounts of substances involved in a chemical reaction of known stoichiometry may be related. Directly measuring numbers of atoms and molecules is, however, not an easy task, and the practical application of stoichiometry requires that we use the more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



## EXAMPLE 7.10

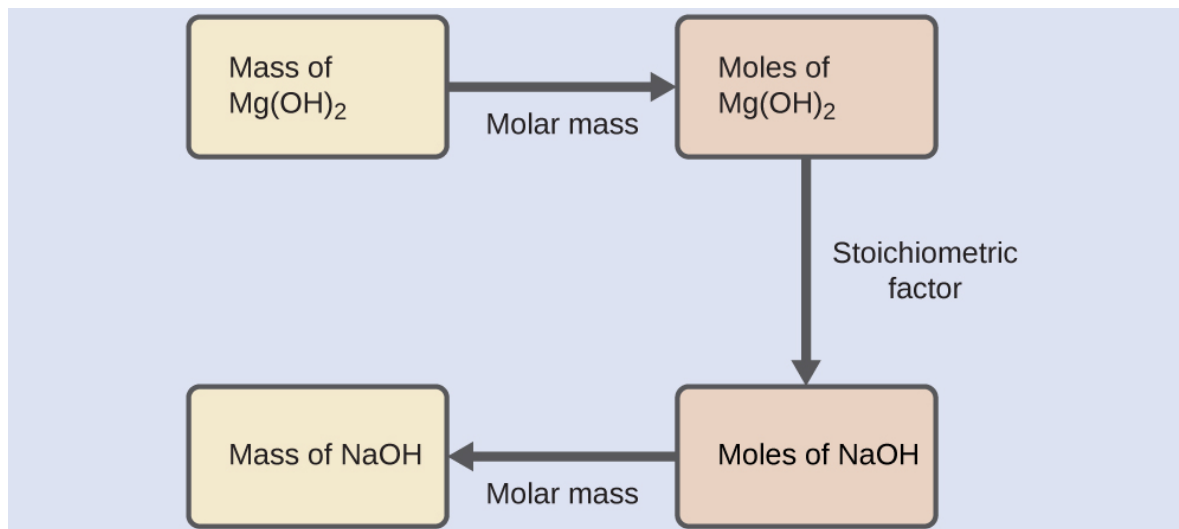
## Relating Masses of Reactants and Products

What mass of sodium hydroxide, NaOH, would be required to produce 16 g of the antacid milk of magnesia [magnesium hydroxide, Mg(OH)<sub>2</sub>] by the following reaction?



## Solution

The approach used previously in Example 7.8 and Example 7.9 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:



**Figure 7.13** By: Rice University [OpenstaxCC BY NC SA](#)

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

### Check Your Learning

What mass of gallium oxide,  $\text{Ga}_2\text{O}_3$ , can be prepared from 29.0 g of gallium metal? The equation for the reaction is

**Answer:** 39.0 g

### EXAMPLE 7.11

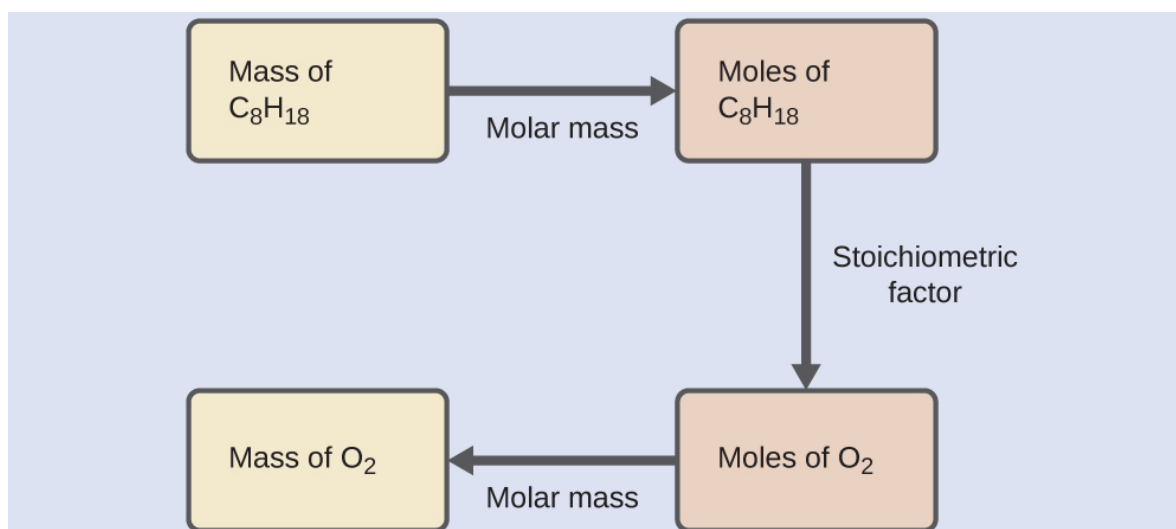
#### Relating Masses of Reactants

What mass of oxygen gas,  $\text{O}_2$ , from the air is consumed in the combustion of 702 g of octane,  $\text{C}_8\text{H}_{18}$ , one of the principal components of gasoline?



#### Solution

The approach required here is the same as for the approach in [Example 7.10](#), differing only in that the provided and requested masses are both for reactant species.

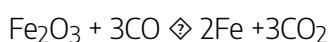


**Figure 7.14** By: Rice University [OpenstaxCC BY NC SA](#)

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

### Check Your Learning

What mass of CO is required to react with 25.13 g OF  $\text{Fe}_2\text{O}_3$  according to the equation:

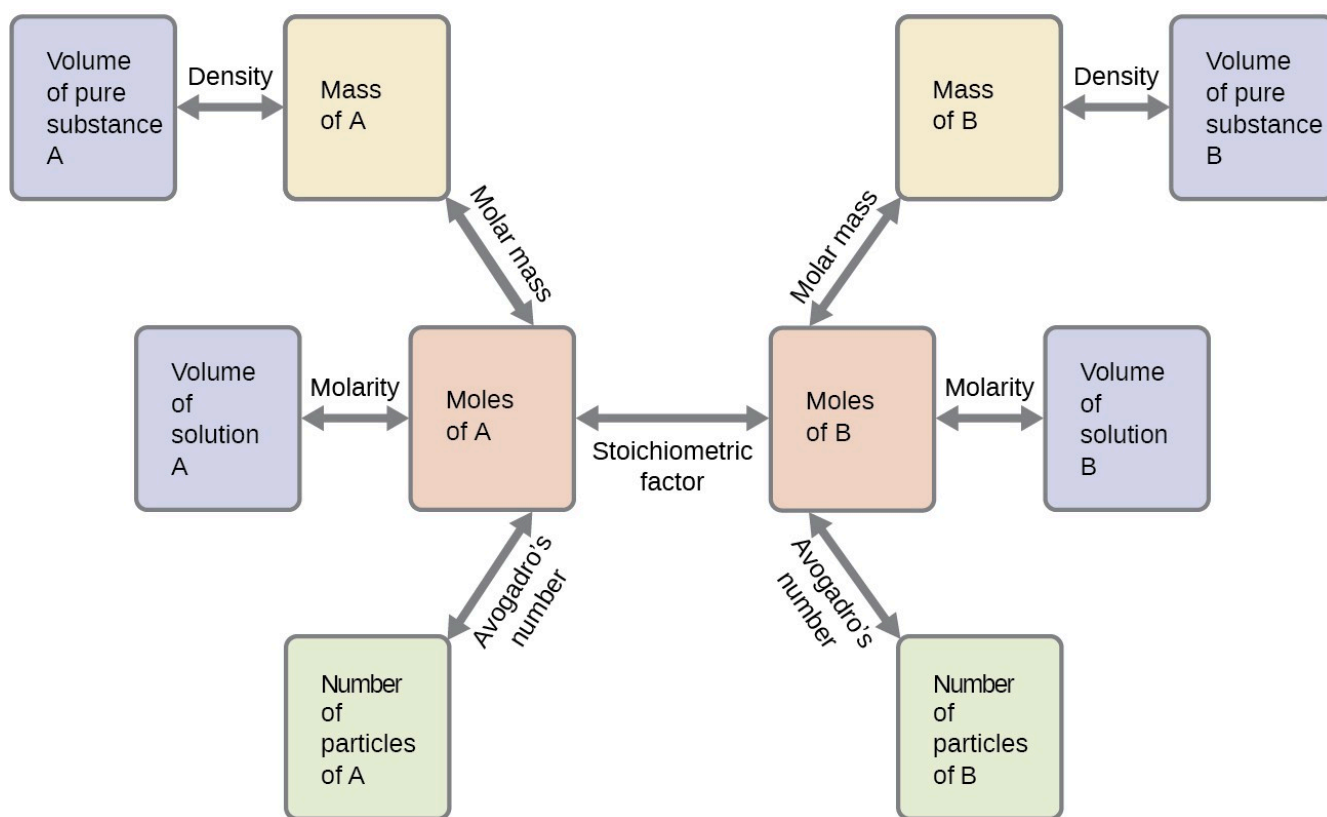


**Formula does not parse**

**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 7.15**

- provides a general outline of the various computational steps associated with many reaction stoichiometry calculations.

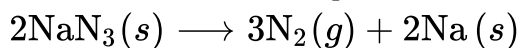


**Figure 7.15** The flowchart depicts the various computational steps involved in most reaction stoichiometry calculations. By: Rice University [OpenstaxCC BY NC SA](#)

## CHEMISTRY IN EVERYDAY LIFE

### Airbags

Airbags (**Figure 7.16**) 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,  $\text{NaN}_3$ . When sensors in the vehicle detect a collision, an electrical current is passed through a carefully measured amount of  $\text{NaN}_3$  to initiate its decomposition:



This reaction is very rapid, generating gaseous nitrogen that can deploy and fully inflate a typical airbag in a fraction of a second ( $\sim 0.03$ – $0.1$  s). Among many engineering considerations, the amount of sodium azide used must be appropriate for generating enough nitrogen gas to fully inflate the airbag and ensure its proper function. For example, a small mass ( $\sim 100$  g) of  $\text{NaN}_3$  will generate approximately 50 L of  $\text{N}_2$ .



**Figure 7.16** Airbags deploy upon impact to minimize serious injuries to passengers. By: Rice University  
[OpenstaxCC BY NC SA](#)

# REACTION YIELDS (7.4)

OpenStax

---

## Reaction Yields

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

- 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 the 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 7.17**):

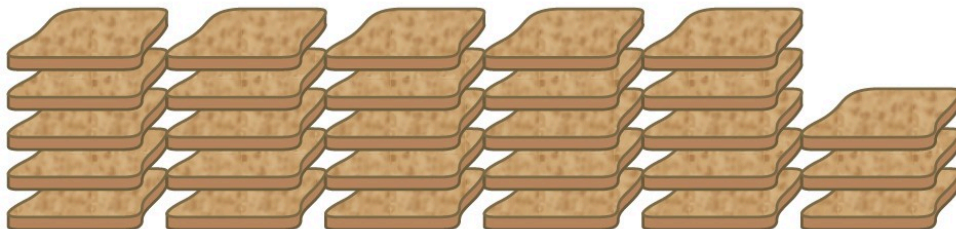
1 slice of cheese + 2 slices of bread  $\rightarrow$  1 sandwich

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*.

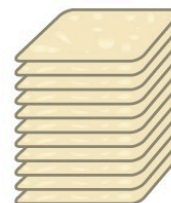
1 sandwich = 2 slices of bread + 1 slice of cheese



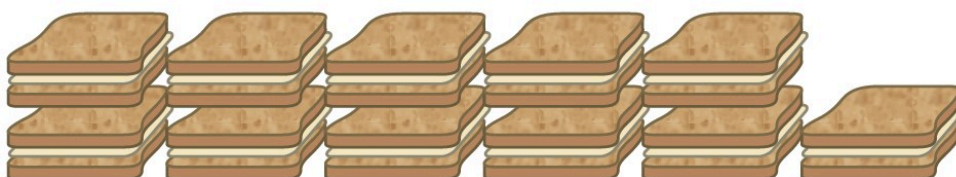
Provided with: 28 slices of bread



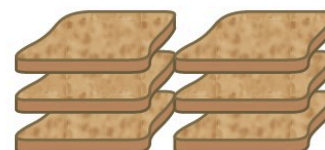
+ 11 slices of cheese



We can make: 11 sandwiches

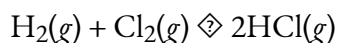


+ 6 slices bread left over



**Figure 7.17** Sandwich making can illustrate the concepts of limiting and excess reactants. By: Rice University [Openstax CC BY NC SA](https://openstax.org/r/CC-BY-NC-SA)

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



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 3 moles of  $\text{H}_2$  and 2 moles of  $\text{Cl}_2$ . This represents a 3:2 (or 1.5:1) ratio of hydrogen to chlorine present for reaction, which is greater than the stoichiometric ratio of 1:1. Hydrogen, therefore, is present in excess, and chlorine is the limiting reactant. The reaction of all the provided chlorine (2 mol) will consume 2 mol of the 3 mol of hydrogen provided, leaving 1 mol of hydrogen unreacted.

An alternative approach to 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, a complete reaction of the hydrogen would yield

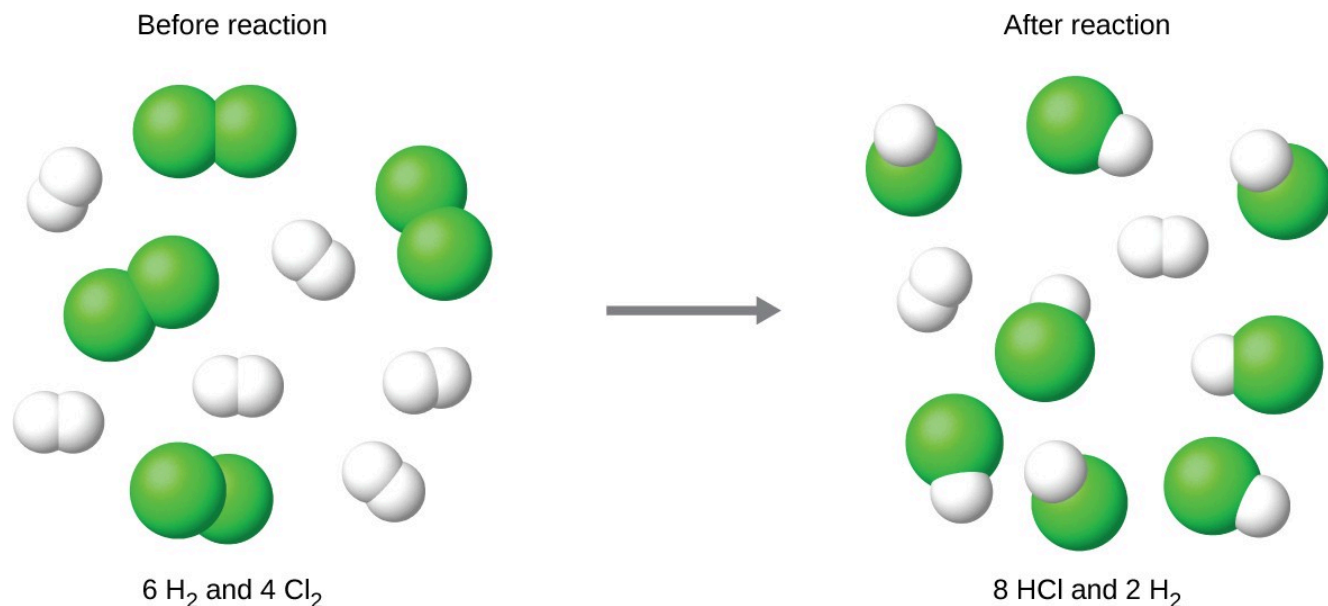


$$\text{mol HCl produced} = 3\text{mol H}_2 \times \frac{2\text{mol HCl}}{1\text{mol H}_2} = 6\text{mol HCl}$$

A complete reaction of the provided chlorine would produce

$$\text{mol HCl produced} = 2\text{mol Cl}_2 \times \frac{2\text{mol HCl}}{1\text{mol Cl}_2} = 4\text{mol HCl}$$

The chlorine will be completely consumed once 4 moles of HCl have been produced. Since enough hydrogen was provided to yield 6 moles of HCl, there will be unreacted hydrogen remaining once this reaction is complete. Chlorine, therefore, is the limiting reactant, and hydrogen is the excess reactant (**Figure 7.18**).



**Figure 7.18** When H<sub>2</sub> and Cl<sub>2</sub> 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. By: Rice University [Openstax CC BY NC SA](#)

## Link to Learning

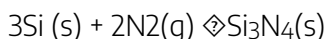
[View this](#) interactive simulation illustrating the concepts of limiting and excess reactants.



## EXAMPLE 7.12

## 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:



Which is the limiting reactant when 2.00 g of Si and 1.50 g of N<sub>2</sub> react?

## Solution

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

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

$$\text{mol N}_2 = 1.50 \text{ g N}_2 \times \frac{1 \text{ mol N}_2}{28.02 \text{ g N}_2} = 0.0535 \text{ mol N}_2$$

The provided Si:N<sub>2</sub> 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<sub>2</sub> 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

$$\text{mol Si}_3\text{N}_4 \text{ produced} = 0.0712 \text{ mol Si} \times \frac{1 \text{ mol Si}_3\text{N}_4}{3 \text{ mol Si}} = 0.0237 \text{ mol Si}_3\text{N}_4$$

while the 0.0535 moles of nitrogen would produce

$$\text{molSi}_3\text{N}_4 \text{ produced} = 0.0535\text{molN}_2 \times \frac{1\text{molSi}_3\text{N}_4}{2\text{molN}_2} = 0.0268\text{molSi}_3\text{N}_4$$

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

### Check Your Learning

Which is the limiting reactant when 5.00 g of H<sub>2</sub> and 10.0 g of O<sub>2</sub> react and form water?

**Answer:** O<sub>2</sub>

## 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 chapter). 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**:

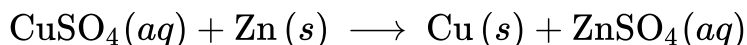
$$\text{Percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

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 7.13

### 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:



What is the percent yield?

### Solution

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

$$1.274 \text{ g CuSO}_4 \times \frac{1 \text{ mol CuSO}_4}{159.62 \text{ g CuSO}_4} \times \frac{1 \text{ mol Cu}}{1 \text{ mol CuSO}_4} \times \frac{63.55 \text{ g Cu}}{1 \text{ mol Cu}} = 0.5072 \text{ g Cu}$$

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

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

$$\text{percent yield} = ( \text{Formula does not parse} ) \times 100$$

### Check Your Learning

What is the percent yield of a reaction that produces 12.5 g of the gas Freon  $\text{CF}_2\text{Cl}_2$  from 32.9 g of  $\text{CCl}_4$  and excess  $\text{HF}$ ?



**Answer:** 48.3%

## How Sciences Interconnect

### 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” (see details on this [website](#)). 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:

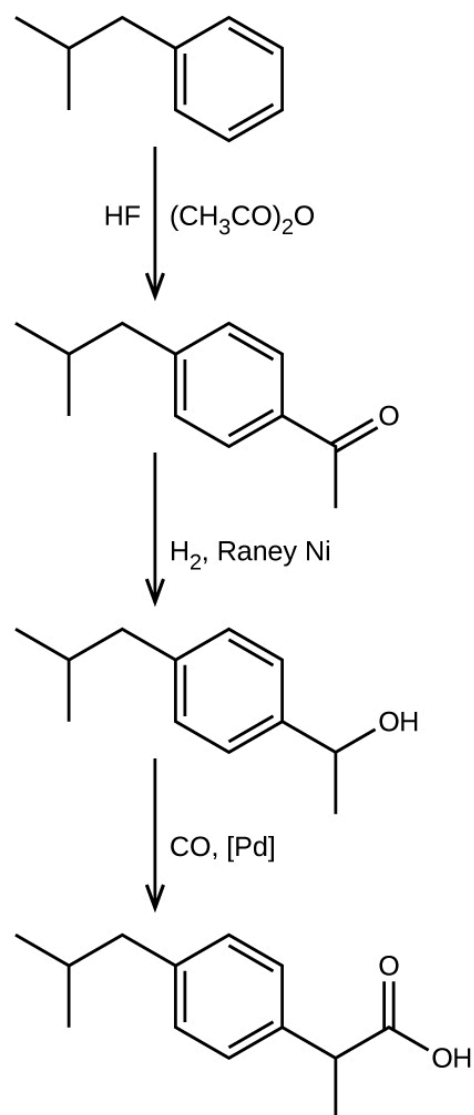
$$\text{atom economy} = \frac{\text{mass of product}}{\text{mass of reactants}} \times 100\%$$

Though the definition of atom economy at first glance appears very similar to that of 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 7.19**). 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.



(a)



(b)

**Figure 7.19** (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. By: Rice University [Openstax CC BY NC SA](https://openstax.org/r/ibuprofen)

# QUANTITATIVE CHEMICAL ANALYSIS (7.5)

OpenStax

## Quantitative Chemical Analysis

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

- Describe the fundamental aspects of titrations and gravimetric analysis
- Perform stoichiometric calculations using typical titration and gravimetric data

In the eighteenth century, the strength (actually the concentration) of vinegar samples was determined by noting the amount of potassium carbonate,  $\text{K}_2\text{CO}_3$ , 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 a reaction with acetic acid,  $\text{CH}_3\text{CO}_2\text{H}$ , the compound primarily responsible for the odor and taste of vinegar. Acetic acid reacts with potassium carbonate according to the following equation:



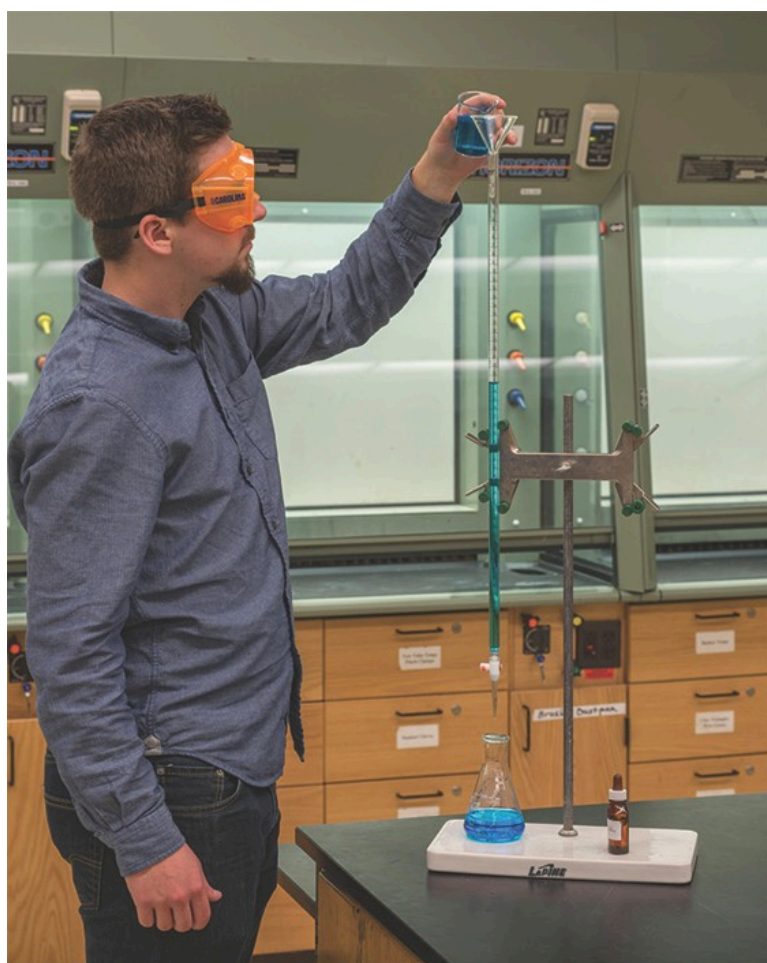
The bubbling was due to the production of  $\text{CO}_2$ .

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 7.20**) 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 the most common. Additional details regarding titration analysis are provided in the chapter on acid-base equilibria.



(a)



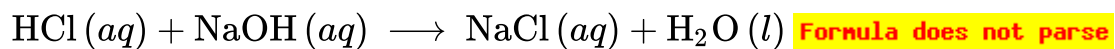
(b)

**Figure 7.20** By: Rice University [Openstax CC BY NC SA](#)

### Example 7.14

#### Titration Analysis

The end point in a titration of a 50.00-mL sample of aqueous HCl was reached by the addition of 35.23 mL of 0.250 M NaOH titrant. The titration reaction is:



Formula does not parse

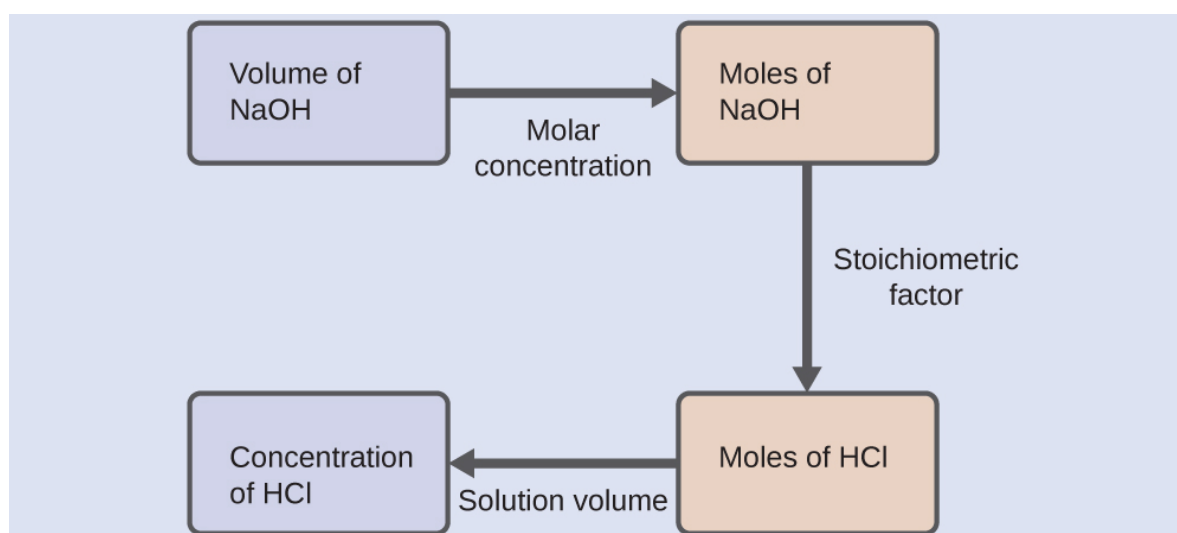


What is the molarity of the HCl?

## 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:



**Figure 7.21** By: Rice University [Openstax CC BY NC SA](#)

The molar amount of HCl is calculated to be:

$$35.23 \text{ mL NaOH} \times \frac{1 \cancel{\text{ L}}}{1000 \cancel{\text{ mL}}} \times \frac{0.250 \cancel{\text{ mol NaOH}}}{1 \cancel{\text{ L}}} \times \frac{1 \text{ mol HCl}}{1 \cancel{\text{ mol NaOH}}} = 8.81 \times 10^{-3} \text{ mol HCl}$$

Using the provided volume of HCl solution and the definition of molarity, the HCl concentration is:

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

$$M = \frac{8.81 \times 10^{-3} \text{ mol HCl}}{50.00 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}}$$

$$M = 0.176 \text{ M}$$

Note: For these types of titration calculations, it is convenient to recognize that solution molarity is also equal to the number of *millimoles* of solute per *milliliter* of solution:

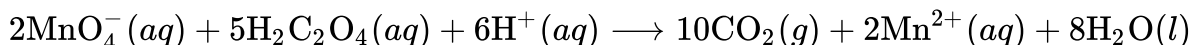
$$M = \frac{\text{mol solute}}{\text{L solution}} \times \frac{\frac{10^3 \text{ mmol}}{\text{mol}}}{\frac{10^3 \text{ mL}}{\text{L}}} = \frac{\text{mmol solute}}{\text{mL solution}}$$

Using this version of the molarity unit will shorten the calculation by eliminating two conversion factors:

$$\frac{35.23 \text{ mL NaOH} \times \frac{0.250 \text{ mmol NaOH}}{\text{mL NaOH}} \times \frac{1 \text{ mmol HCl}}{1 \text{ mmol NaOH}}}{50.00 \text{ mL solution}} = 0.176 \text{ M HCl}$$

### Check Your Learning

A 20.00-mL sample of aqueous oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4$ , was titrated with a 0.09113-M solution of potassium permanganate,  $\text{KMnO}_4$ .



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 7.22**). The mass of the precipitate may then be used, along with relevant stoichiometric relationships, to calculate analyte concentration.

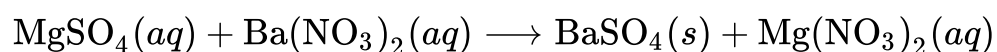


**Figure 7.22** Precipitate may be removed from a reaction mixture by filtration. By: Rice University  
Openstax CC BY NC SA

## Example 7.15

### Gravimetric Analysis

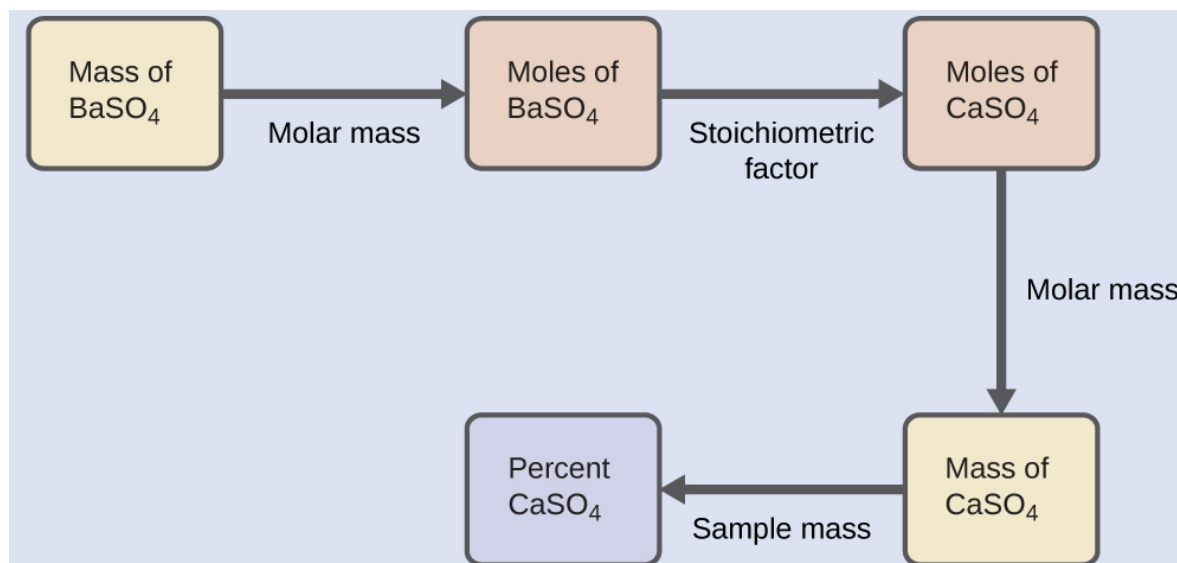
A 0.4550-g solid mixture containing  $\text{MgSO}_4$  is dissolved in water and treated with an excess of  $\text{Ba}(\text{NO}_3)_2$ , resulting in the precipitation of 0.6168 g of  $\text{BaSO}_4$ .



What is the concentration (mass percent) of  $\text{MgSO}_4$  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  $\text{BaSO}_4$  and  $\text{MgSO}_4$  through their stoichiometric factor. Once the mass of  $\text{MgSO}_4$  is computed, it may be used along with the mass of the sample mixture to calculate the requested percentage concentration.



**Figure 7.23** By: Rice University Openstax CC BY NC SA

The mass of  $\text{MgSO}_4$  that would yield the provided precipitate mass is

$$0.6168 \text{ g BaSO}_4 \times \frac{1 \text{ mol } \cancel{\text{BaSO}_4}}{233.43 \text{ g } \cancel{\text{BaSO}_4}} \times \frac{1 \text{ mol } \cancel{\text{MgSO}_4}}{1 \text{ mol } \cancel{\text{BaSO}_4}} \times \frac{120.37 \text{ g } \cancel{\text{MgSO}_4}}{1 \text{ mol } \cancel{\text{MgSO}_4}} = 0.3181 \text{ g MgSO}_4$$

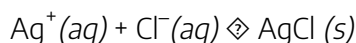
The concentration of  $\text{MgSO}_4$  in the sample mixture is then calculated to be

$$\text{percent MgSO}_4 = \frac{\text{mass MgSO}_4}{\text{mass sample}} \times 100\%$$

$$\frac{0.3181 \text{ g}}{0.4550 \text{ g}} \times 100\% = 69.91\%$$

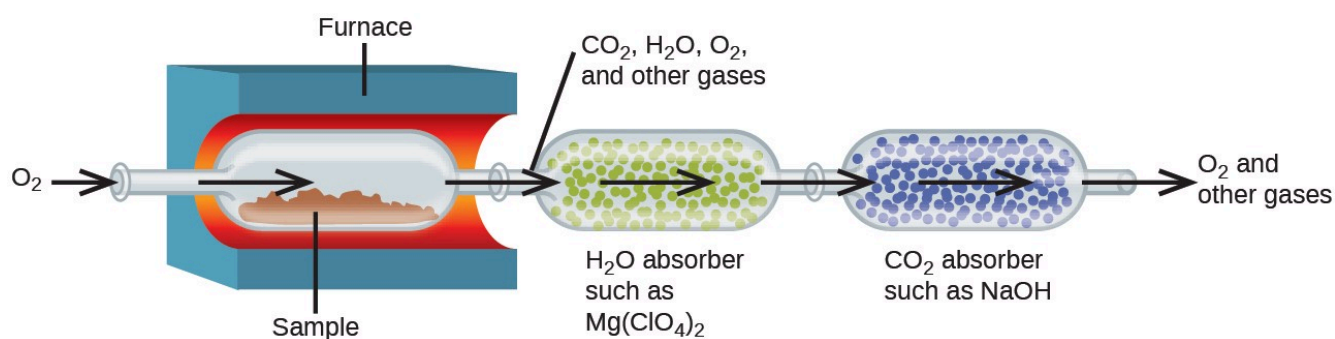
### Check Your Learning

What is the percent of chloride ion in a sample if 1.1324 g of the sample produces 1.0881 g of  $\text{AgCl}$  when treated with excess  $\text{Ag}^+$ ?



**Answer:** 23.76%

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 7.24**). 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 7.24** This schematic diagram illustrates the basic components of a combustion analysis device for determining the carbon and hydrogen content of a sample. By: Rice University [Openstax CC BY NC SA](#)

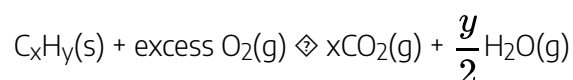
## EXAMPLE 7.16

### 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  $\text{CO}_2$  and 0.00161 g of  $\text{H}_2\text{O}$ . What is the empirical formula of polyethylene?

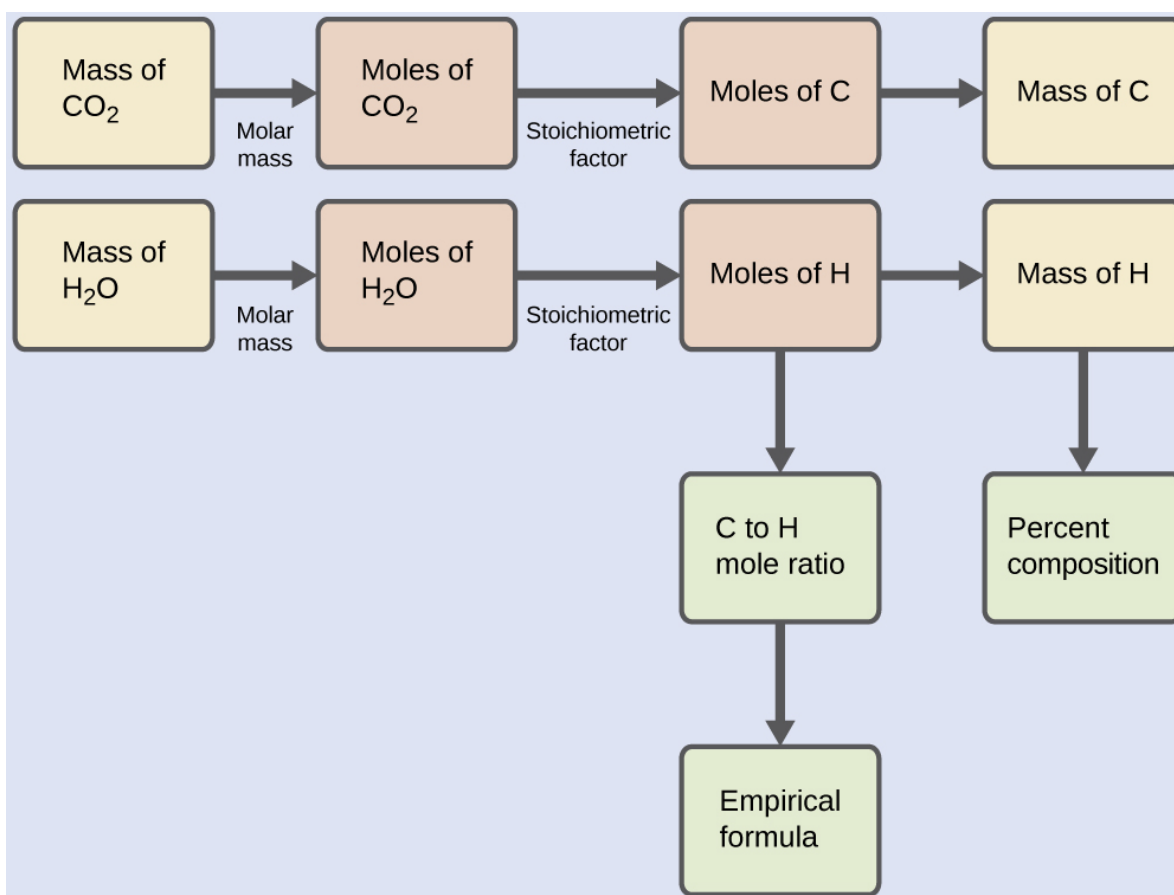
### Solution

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:



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:



**Figure 7.25** By: Rice University [Openstax CC BY NC SA](#)

$$\text{mol } C = 0.00394 \text{ g } CO_2 \times \frac{1 \text{ mol } CO_2}{44.01 \text{ g}} \times \frac{1 \text{ mol } C}{1 \text{ mol } CO_2} = 8.95 \times 10^{-5} \text{ mol } C$$

$$\text{mol } H = 0.00161 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g}} \times \frac{2 \text{ mol } H}{1 \text{ mol } H_2O} = 1.79 \times 10^{-4} \text{ mol } H$$

The empirical formula for the compound is then derived by identifying the smallest whole-number multiples for these molar amounts. The H-to-C molar ratio is

$$\frac{\text{mol } H}{\text{mol } C} = \frac{1.79 \times 10^{-4} \text{ mol } H}{8.95 \times 10^{-5} \text{ mol } C} = \frac{2 \text{ mol } H}{1 \text{ mol } C}$$

and the empirical formula for polyethylene is CH<sub>2</sub>.



### Check Your Learning

A 0.00215-g sample of polystyrene, a polymer composed of carbon and hydrogen, produced 0.00726 g of  $\text{CO}_2$  and 0.00148 g of  $\text{H}_2\text{O}$  in a combustion analysis. What is the empirical formula for polystyrene?

**Answer:** CH



# CHAPTER 8: GASES



**Figure 8.1** The hot air inside these balloons is less dense than the surrounding cool air. This results in a buoyant force that causes the balloons to rise when their guy lines are untied. By: Rice University [Openstax](#) [CC BY NC SA](#)

## Chapter Outline

- Gas Pressure
- Relating Pressure, Volume, Amount, and Temperature: The Ideal Gas Law
- Stoichiometry of Gaseous Substances, Mixtures, and Reactions
- Effusion and Diffusion of Gases
- The Kinetic-Molecular Theory
- Non-Ideal Gas Behavior

### Introduction

We are surrounded by an ocean of gas—the atmosphere—and many of the properties of gases are familiar to us from our daily activities. Heated gases expand, which can make a hot air balloon rise (**Figure 8.1**) or cause a blowout in a bicycle tire left in the sun on a hot day.

Gases have played an important part in the development of chemistry. In the seventeenth and eighteenth centuries, many scientists investigated gas behavior, providing the first mathematical descriptions of the behavior of matter.

In this chapter, we will 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.

# GAS PRESSURE (8.1)

OpenStax

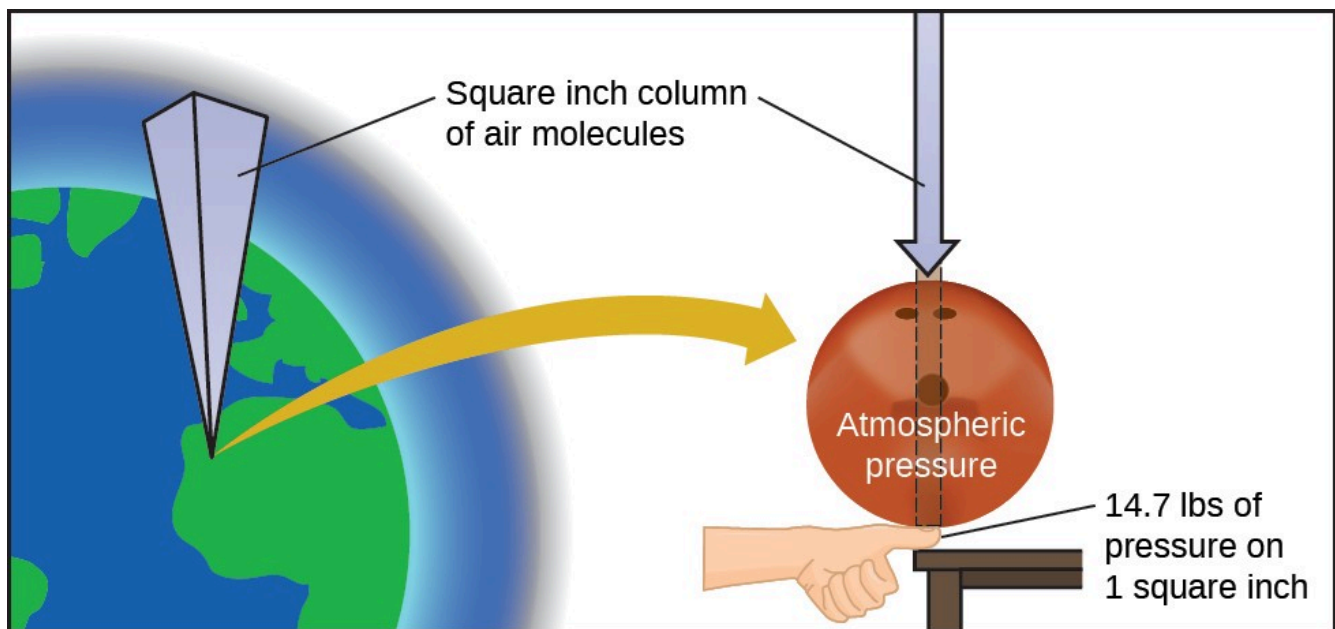
---

## Gas Pressure

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

- 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 8.2**). Although the force of each collision is very small, any surface of an appreciable area experiences a large number of collisions in a short time, which can result in 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 8.2** 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. By: Rice University Openstax CC BY NC SA

### Link to Learning

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. A smaller-scale [demonstration](#) of this phenomenon is briefly explained.

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.

In general, **pressure** is defined as the force exerted on a given area:  $P = \frac{F}{A}$ . Note that pressure is directly proportional to force and inversely proportional to area. Thus, pressure can be increased either by increasing

the amount of force or by decreasing the area over which it is applied; pressure can be decreased by decreasing the force or increasing the area.

Let's apply this concept to determine which would be more likely to fall through thin ice in **Figure 8.3**—the elephant or the figure skater? A large African elephant can weigh 7 tons, supported on four feet, each with a diameter of about 1.5 ft (footprint area of  $250 \text{ in}^2$ ), so the pressure exerted by each foot is about  $14 \text{ lb/in}^2$ :

$$\text{pressure per elephant foot} = 14,000 \text{ lb} \frac{\text{lb}}{\text{elephant}} \times \frac{1 \text{ elephant}}{4 \text{ feet}} \times \frac{1 \text{ foot}}{250 \text{ in}^2} = 14 \text{ lb/in}^2$$

The figure skater weighs about 120 lbs, supported on two skate blades, each with an area of about  $2 \text{ in}^2$ , so the pressure exerted by each blade is about  $30 \text{ lb/in}^2$ :

$$\text{pressure per skate blade} = 120 \frac{\text{lb}}{\text{skater}} \times \frac{1 \text{ skater}}{2 \text{ blades}} \times \frac{1 \text{ blade}}{2 \text{ in}^2} = 30 \text{ lb/in}^2$$

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:

$$\text{pressure per human foot} = 120 \frac{\text{lb}}{\text{skater}} \times \frac{1 \text{ skater}}{2 \text{ feet}} \times \frac{1 \text{ foot}}{30 \text{ in}^2} = 2 \text{ lb/in}^2$$



(a)



(b)

**Figure 8.3** 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. By: Rice University [Openstax CC BY NC SA](#)

The SI unit of pressure is the **pascal (Pa)**, with  $1 \text{ Pa} = 1 \text{ N/m}^2$ , where N is the newton, a unit of force defined as  $1 \text{ kg m/s}^2$ . One pascal is a small pressure; in many cases, it is more convenient to use units of kilopascal ( $1 \text{ kPa} = 1000 \text{ Pa}$ ) or **bar** ( $1 \text{ bar} = 100,000 \text{ Pa}$ ). 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 ( $45^\circ$ ). [Table 8.1](#) provides some information on these and a few other common units for pressure measurements

**Table 8.1 Pressure Units By: Rice University [OpenStax CC BY-NC-SA 4.0](#)**

Unit Name and Abbreviation	Definition or Relation to Other Unit
pascal (Pa)	1 Pa = 1 N/m <sup>2</sup> 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 = 760 torr 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 torr = $\frac{1}{760}$ atm named after Evangelista Torricelli, inventor of the barometer
millimeters of mercury (mm Hg)	1 mm Hg ~1 torr

### Example 8.1

#### 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 8.1](#).

$$(a) 29.2 \text{ in Hg} \times \frac{25.4 \text{ mm}}{1 \text{ in}} \times \frac{1 \text{ torr}}{1 \text{ mm Hg}} = 742 \text{ torr}$$

$$(b) 742 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.976 \text{ atm}$$

$$(c) 742 \text{ torr} \times \frac{101.325 \text{ kPa}}{760 \text{ torr}} = 98.9 \text{ kPa}$$

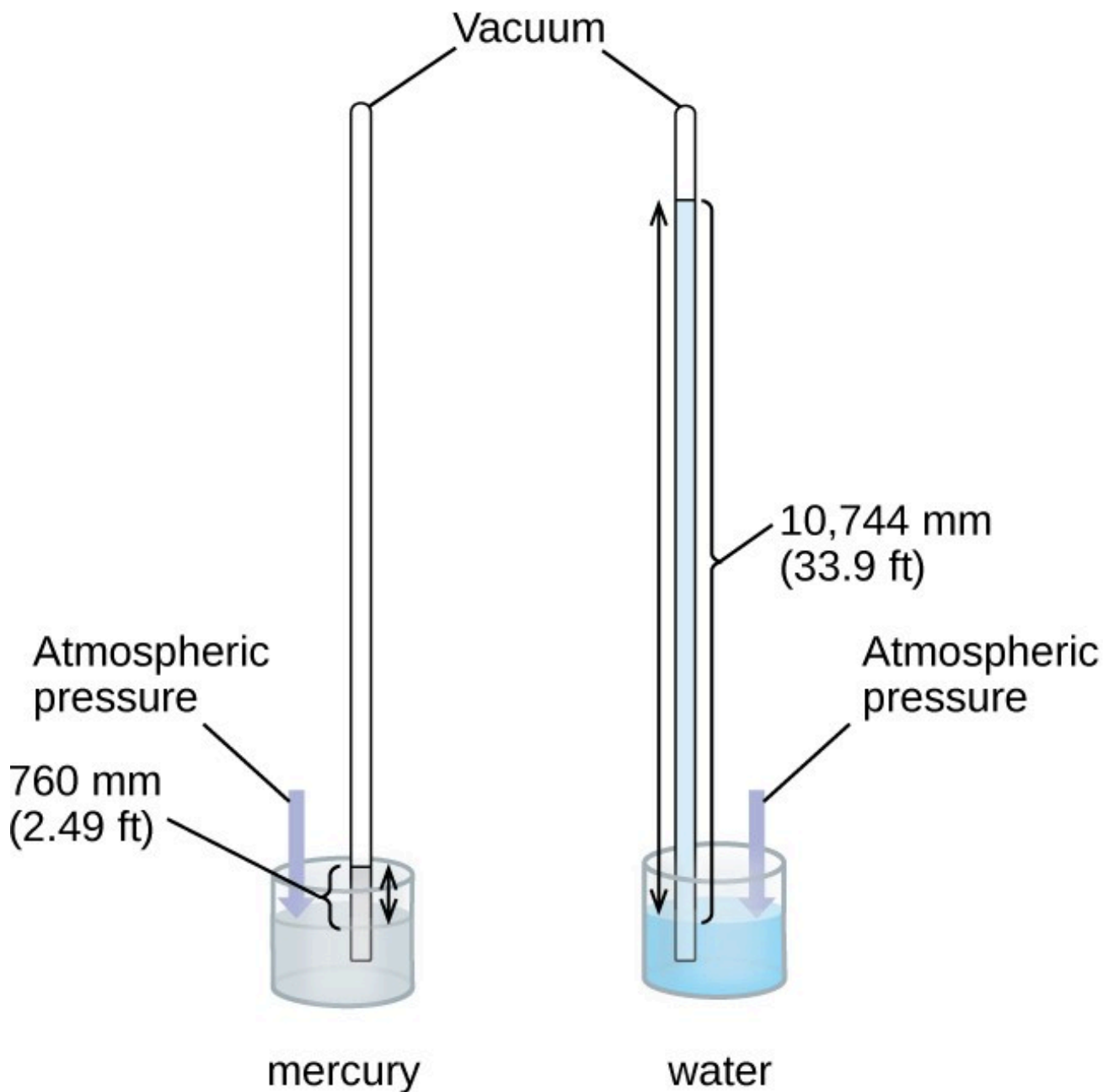
$$(d) 98.9 \text{ kPa} \times \frac{1000 \text{ Pa}}{1 \text{ kPa}} \times \frac{1 \text{ bar}}{100,000 \text{ Pa}} = 989 \text{ mbar}$$

### Check Your Learning

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 8.4**). 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 8.4** 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. By: Rice University  
[Openstax CC BY NC SA](#)

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**,  $p$ :

$$p = h\rho g$$

where  $h$  is the height of the fluid,  $\rho$  is the density of the fluid, and  $g$  is acceleration due to gravity.

## EXAMPLE 8.2

### 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 =  $13.6 \text{ g/cm}^3$ .

### Solution

The hydrostatic pressure is given by  $p = h\rho g$ , with  $h = 760 \text{ mm}$ ,  $\rho = 13.6 \text{ g/cm}^3$ , and  $g = 9.81 \text{ m/s}^2$ . Plugging these values into the equation and doing the necessary unit conversions will give us the value we seek. (Note: We are expecting to find a pressure of  $\sim 101,325 \text{ Pa}$ .)

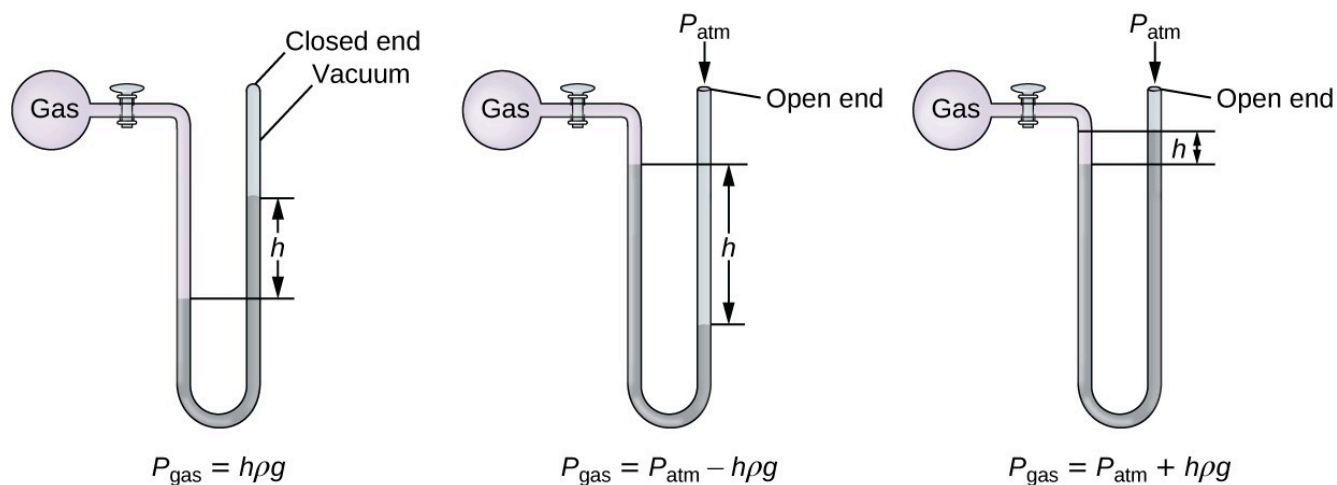
$$\begin{aligned} 101,325 \text{ N/m}^2 &= 101,325 \frac{\text{kg} \cdot \text{m/s}^2}{\text{m}^2} = 101,325 \frac{\text{kg}}{\text{m} \cdot \text{s}^2} \\ p &= \left( 760 \text{ mm} \times \frac{1 \text{ m}}{1000 \text{ mm}} \right) \times \left( \frac{13.6 \text{ g}}{1 \text{ cm}^3} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{(100 \text{ cm})^3}{(1 \text{ m})^3} \right) \times \left( \frac{9.81 \text{ m}}{1 \text{ s}^2} \right) \\ &= (0.760 \text{ m}) (13,600 \text{ kg/m}^3) (9.81 \text{ m/s}^2) = 1.01 \times 10^5 \text{ kg/ms}^2 = 1.01 \times 10^5 \text{ N/m}^2 \\ &= 1.01 \times 10^5 \text{ Pa} \end{aligned}$$

### Check Your Learning

Calculate the height of a column of water at  $25^\circ \text{C}$  that corresponds to normal atmospheric pressure. The density of water at this temperature is  $1.0 \text{ g/cm}^3$ .

**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 8.5**) 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.



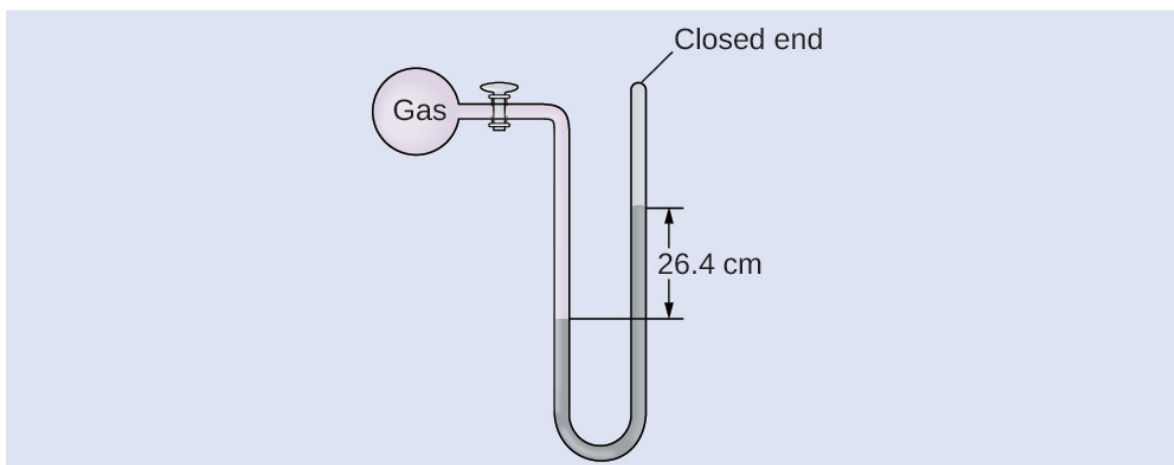
**Figure 8.5** A manometer can be used to measure the pressure of a gas. The (difference in) height between the liquid levels ( $h$ ) is a measure of the pressure. Mercury is usually used because of its large density. By: Rice University [Openstax CC BY NC SA](#)

### EXAMPLE 8.3

#### Calculation of Pressure Using a Closed-End Manometer

The pressure of a sample of gas is measured with a closed-end manometer, as shown to the right. The liquid in the manometer is mercury. Determine the pressure of the gas in:

- (a) torr
- (b) Pa
- (c) bar



**Figure 8.6** By: Rice University [Openstax CC BY NC SA](#)

## Solution

The pressure of the gas is equal to a column of mercury of height 26.4 cm. (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 26.4 cm Hg, or mercury.) We could use the equation  $p = h\rho g$  as in [Example 8.2](#), but it is simpler to just convert between units using [Table 8.1](#).

$$(a) 26.4 \text{ cm Hg} \times \frac{10 \text{ mm Hg}}{1 \text{ cm Hg}} \times \frac{1 \text{ torr}}{1 \text{ mm Hg}} = 264 \text{ torr}$$

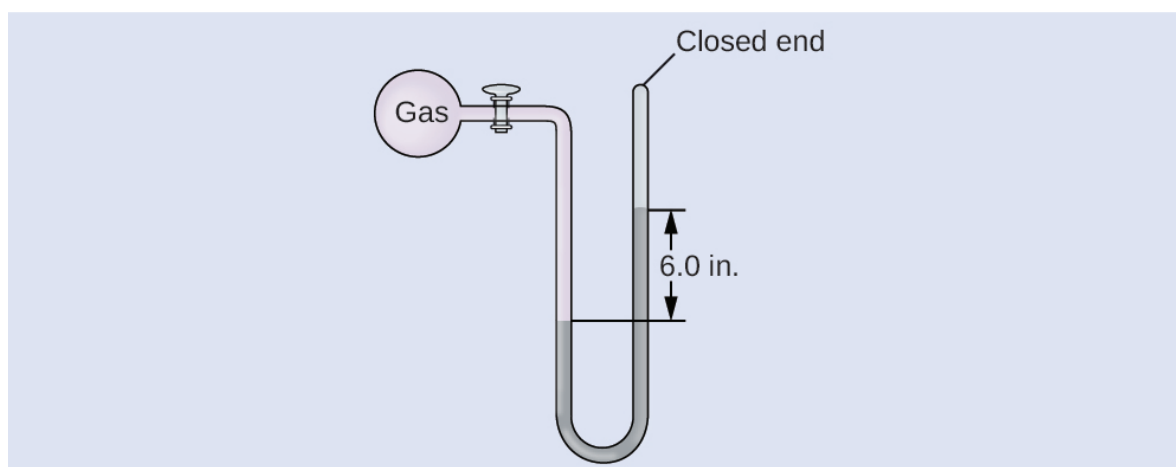
$$(b) 264 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} \times \frac{101,325 \text{ Pa}}{1 \text{ atm}} = 35,200 \text{ Pa}$$

$$(c) 35,200 \text{ Pa} \times \frac{1 \text{ bar}}{100,000 \text{ Pa}} = 0.352 \text{ bar}$$

## Check Your Learning

The pressure of a sample of gas is measured 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



**Figure 8.7** By: Rice University [Openstax CC BY NC SA](#)

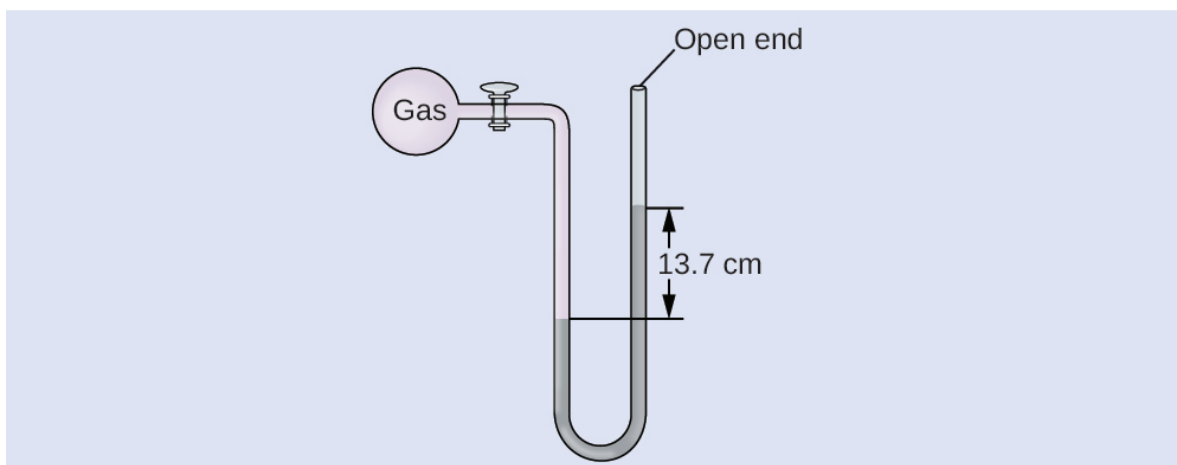
**Answer:** (a) ~150 torr; (b) ~20,000 Pa; (c) ~0.20 bar

## Example 8.4

### 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 to the right. Determine the pressure of the gas in:

- (a) mm Hg
- (b) atm
- (c) kPa



**Figure 8.8** By: Rice University [Openstax CC BY NC SA](#)

### 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

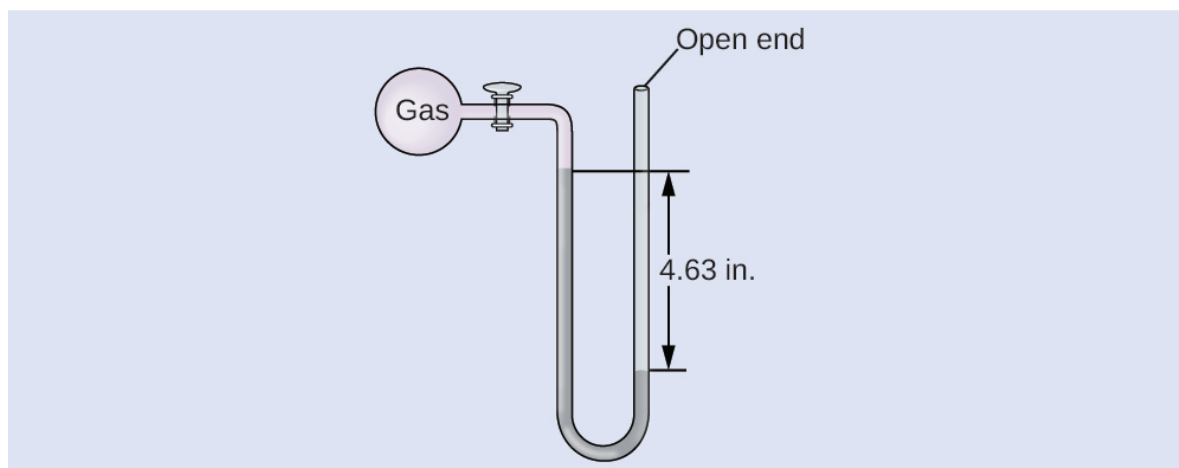
$$(b) 897 \text{ mm Hg} \times \frac{1 \text{ atm}}{760 \text{ mm Hg}} = 1.18 \text{ atm}$$

$$(c) 1.18 \text{ atm} \times \frac{101.325 \text{ kPa}}{1 \text{ atm}} = 1.20 \times 10^2 \text{ kPa}$$

### Check Your Learning

The pressure of a sample of gas is measured at sea level with an open-end Hg manometer, as shown to the right. Determine the pressure of the gas in:

- (a) mm Hg
- (b) atm
- (c) kPa



**Figure 8.9** By: Rice University [Openstax CC BY NC SA](#)

**Answer:** (a) 642 mm Hg; (b) 0.845 atm; (c) 85.6 kPa

## Chemistry in Everyday Life

### 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 8.10**). 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).



(a)



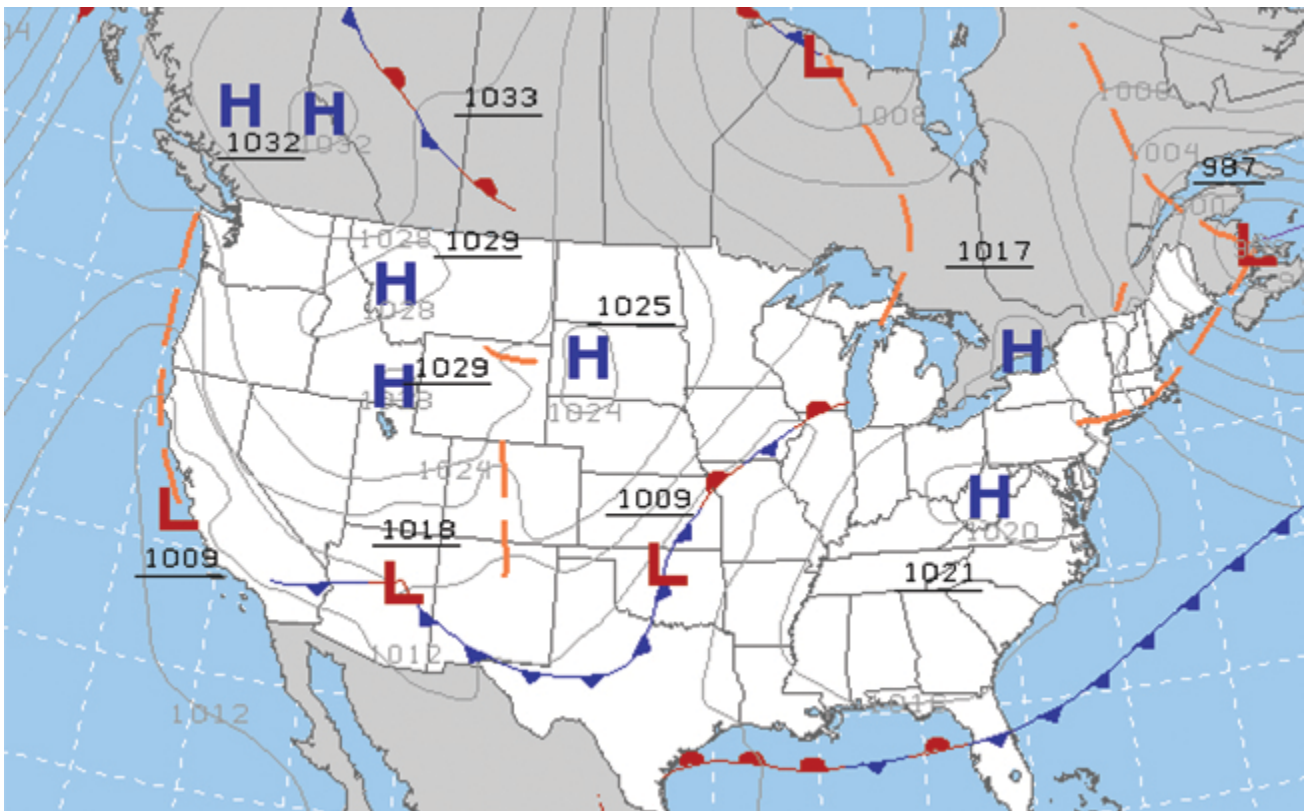
(b)

**Figure 8.10** (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. By: Rice University [Openstax CC BY NC SA](#)

## How Sciences Interconnect

### Meteorology, Climatology, and Atmospheric Science

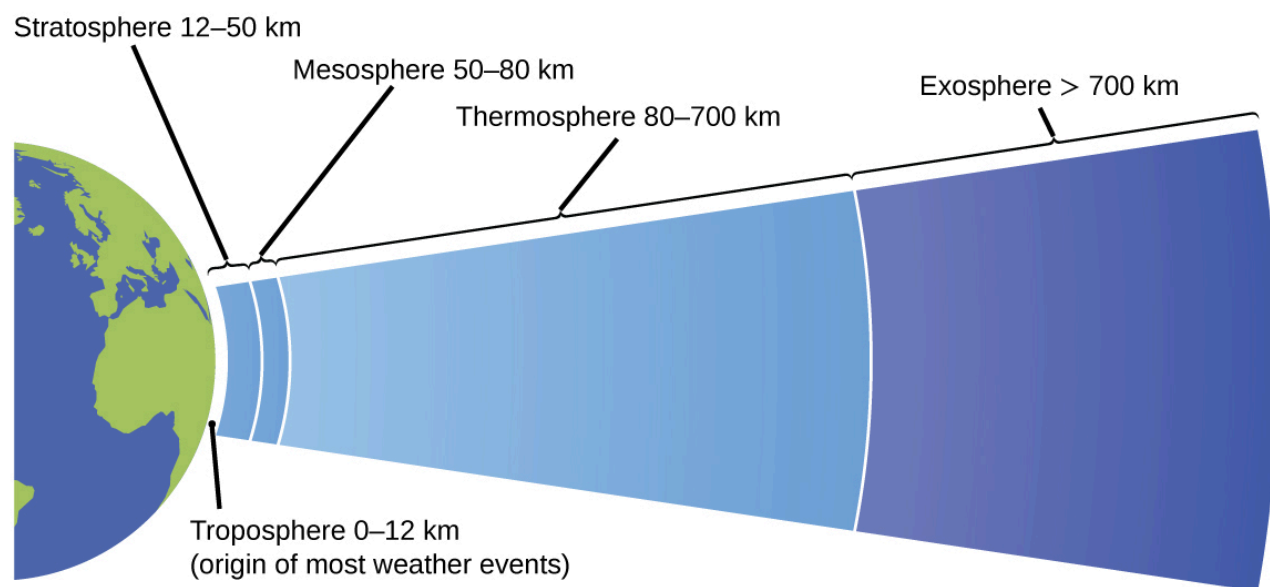
Throughout the ages, people have observed clouds, winds, and precipitation, trying to discern patterns and make predictions: when it is best to plant and harvest, whether it is safe to set out on a sea voyage, and much more. We now face complex weather and atmosphere-related challenges that will have 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 8.11**) 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 8.11** 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. By: Rice University [Openstax CC BY NC SA](#)

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. The 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 8.12**: the exosphere (farthest 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 8.12** Earth's atmosphere has five layers: the troposphere, the stratosphere, the mesosphere, the thermosphere, and the exosphere. By: Rice University [Openstax CC BY NC SA](#)

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.

# RELATING PRESSURE, VOLUME, AMOUNT, AND TEMPERATURE: THE IDEAL GAS LAW (8.2)

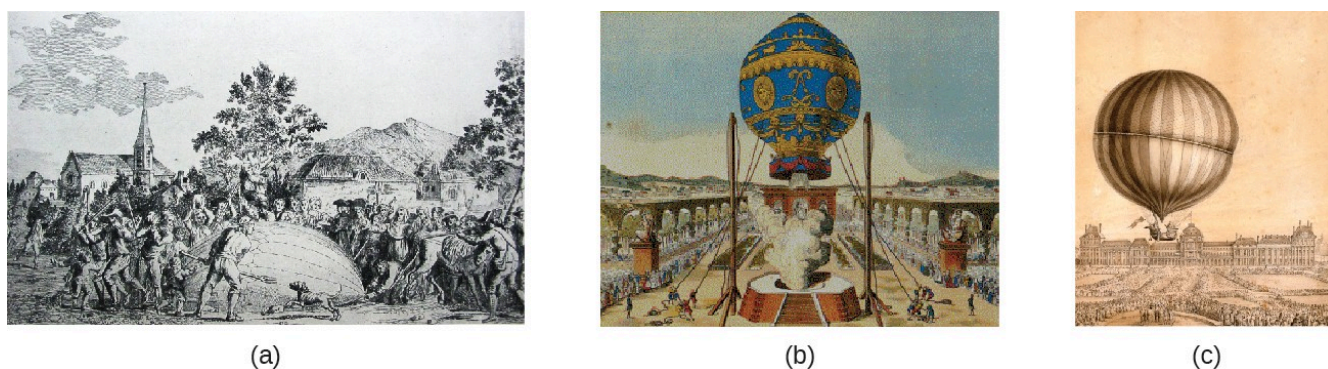
OpenStax

---

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

- 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

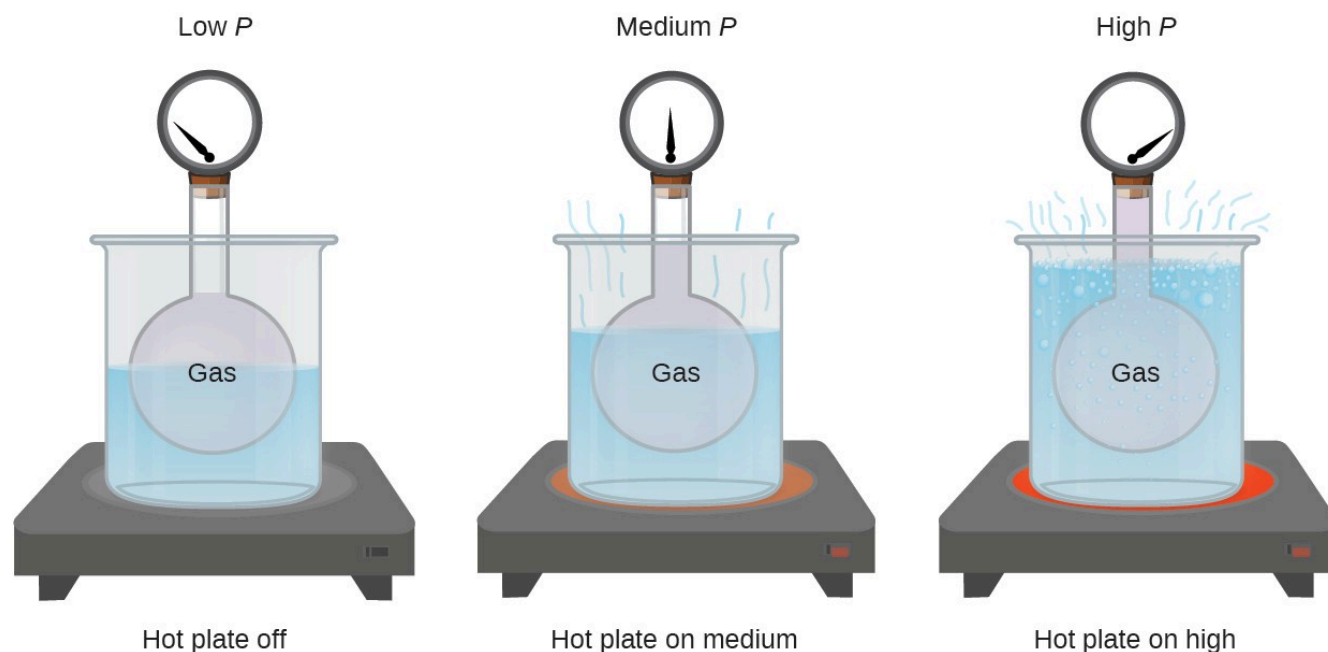
During the seventeenth and especially eighteenth centuries, driven both by a desire to understand nature and a quest to make balloons in which they could fly (**Figure 8.13**), a number of scientists established the relationships between the macroscopic physical properties of gases, that is, pressure, 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 8.13** 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. By: Rice University [Openstax CC BY NC SA](#)

## 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 8.14**), and the pressure increases.



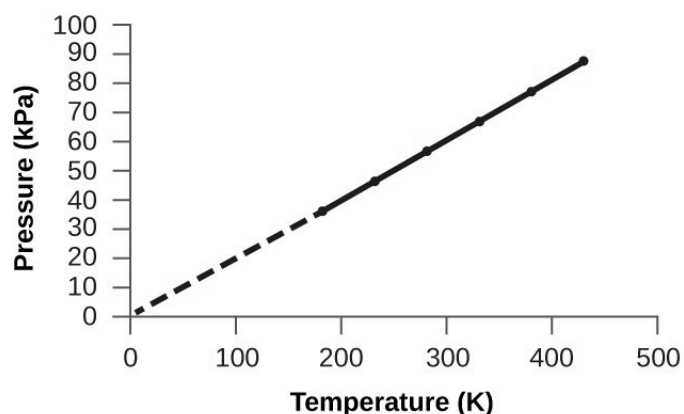
**Figure 8.14** The effect of temperature on gas pressure: When the hot plate is off, the pressure of the gas in the sphere is relatively low. As the gas is heated, the pressure of the gas in the sphere increases. By: Rice University [Openstax CC BY NC SA](#)

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 8.14**. 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)
-100	173	36.0
-50	223	46.4
0	273	56.7
50	323	67.1
100	373	77.5
150	423	88.0



**Figure 8.15** 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  $-273\text{ }^{\circ}\text{C}$ , which is 0 on the kelvin scale and the lowest possible temperature, called absolute zero. By: Rice University [Openstax CC BY NC SA](#)

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  $\propto$  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 8.5

### 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:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ which means that } \frac{360 \text{ kPa}}{297 \text{ K}} = \frac{P_2}{323 \text{ K}}$$

$$\text{Rearranging and solving gives } P_2 = \frac{360 \text{ kPa} \times 323 \cancel{\text{K}}}{297 \cancel{\text{K}}} = 390 \text{ kPa}$$

### Check Your Learning

A sample of nitrogen,  $\text{N}_2$ , 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

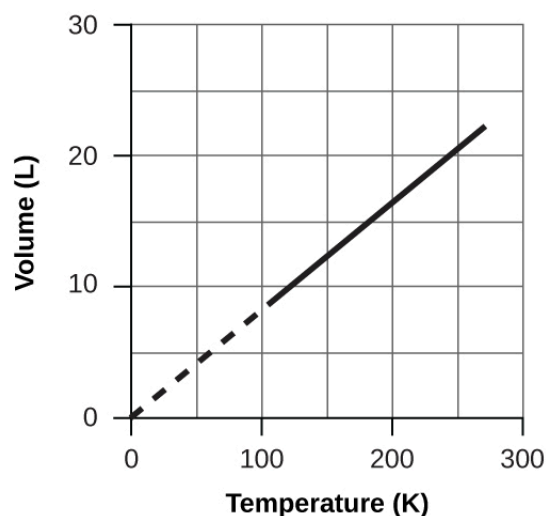
If we fill a balloon with air and seal it, the balloon contains a specific amount of air at atmospheric pressure, let's say 1 atm. If we put the balloon in a refrigerator, the gas inside gets cold, and the balloon shrinks (although both the amount of gas and its pressure remain constant). If we make the balloon very cold, it will shrink a great deal, and it expands again when it warms up.

### Link to Learning

[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 8.16**.

Temperature (°C)	Temperature (K)	Volume (L)
−3	270	22
−23	250	21
−53	220	18
−162	111	9



**Figure 8.16** 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. By: Rice University [Openstax CC BY NC SA](#)

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:

$$V \propto T \text{ or } V = \text{constant} \cdot T \text{ or } V = k \cdot T \text{ or } V_1/T_1 = V_2/T_2$$

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 8.6

### Predicting Change in Volume with Temperature

A sample of carbon dioxide,  $\text{CO}_2$ , 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:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ which means that } \frac{0.300\text{L}}{283\text{K}} = \frac{V_2}{303\text{K}}$$

$$\text{Rearranging and solving gives } V_2 = \frac{0.300 \text{ L} \times 303 \cancel{\text{K}}}{283 \cancel{\text{K}}} = 0.321 \text{ L}$$

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).

### Check Your Learning

A sample of oxygen,  $\text{O}_2$ , 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 8.7

### 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<sup>3</sup> 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<sup>3</sup>. 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:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ which means that } \frac{150.0\text{cm}^3}{273.15\text{K}} = \frac{131.7\text{cm}^3}{T_2}$$

$$\text{rearranging gives } T_2 = \frac{131.7 \cancel{\text{cm}^3} \times 273.15\text{K}}{150.0 \cancel{\text{cm}^3}} = 239.8 \text{ K}$$

Subtracting 273.15 from 239.8 K, we find that the temperature of the boiling ammonia on the Celsius scale is -33.4 °C.

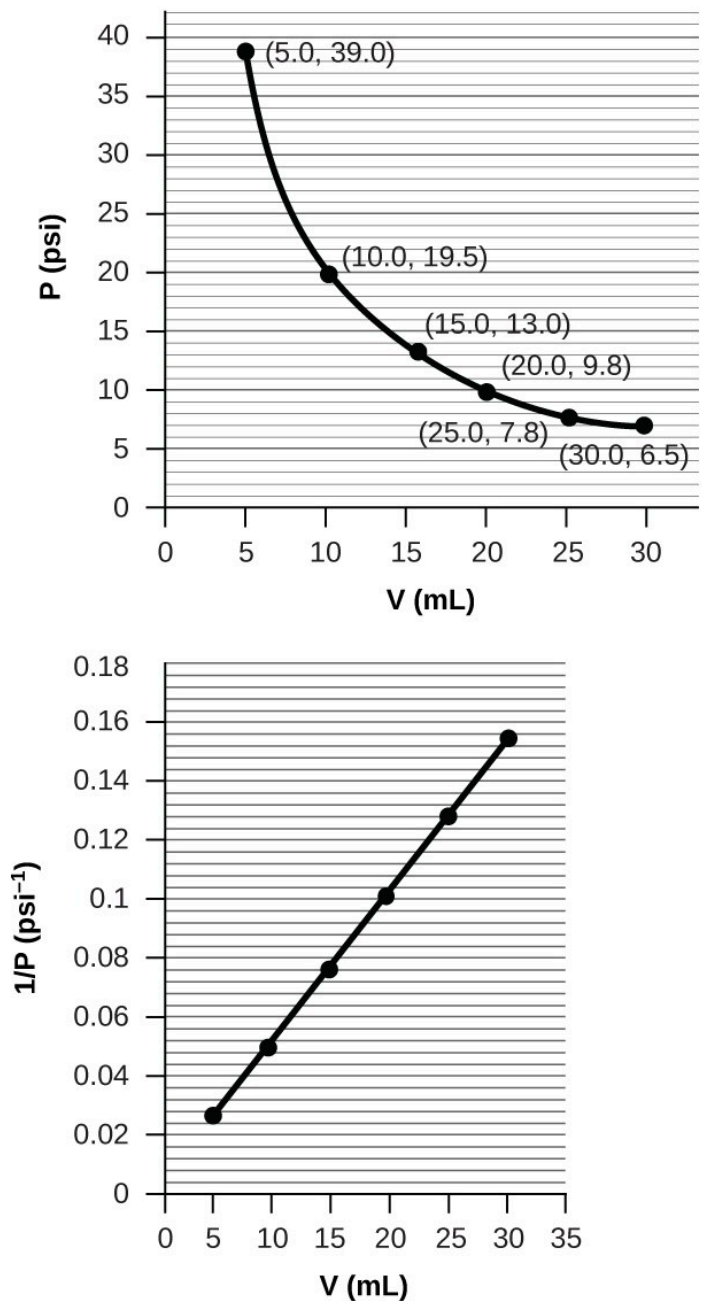
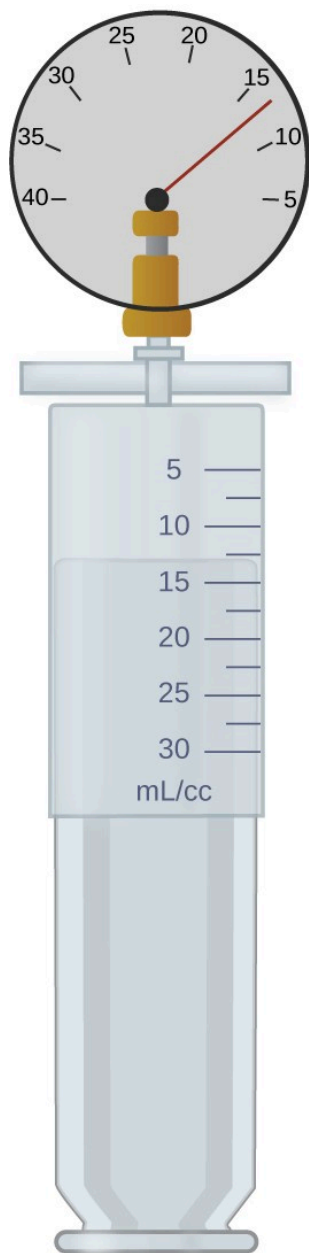
### Check Your Learning

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 the 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 8.17**.



**Figure 8.17** 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. By: Rice University Openstax CC BY NC SA

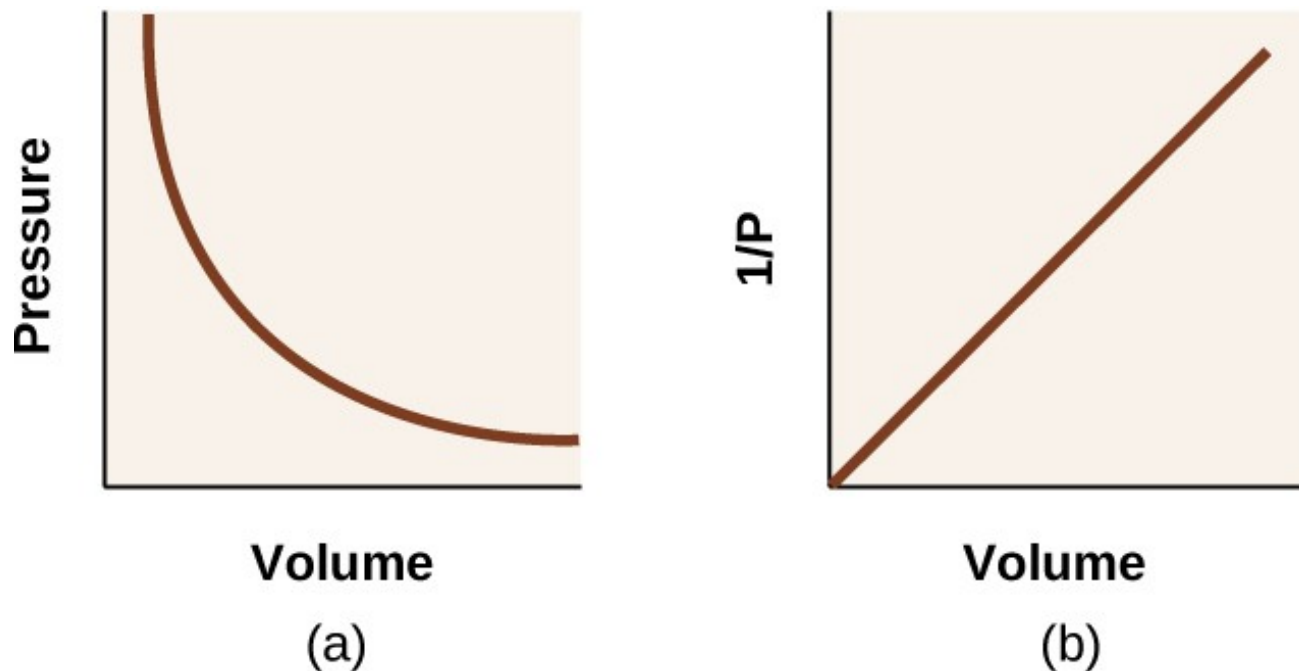
Unlike the  $P$ - $T$  and  $V$ - $T$  relationships, pressure and volume are not directly proportional to each other. Instead,  $P$  and  $V$  exhibit inverse proportionality: Increasing the pressure results in a decrease of the volume of the gas. Mathematically this can be written:

$$P \propto 1/V \text{ or } P = k \cdot 1/V \text{ or } P \cdot V = k \text{ or } P_1 V_1 = P_2 V_2$$

with  $k$  being a constant. Graphically, this relationship is shown by the straight line that results when plotting

the inverse of the pressure ( $\frac{1}{P}$ ) versus the volume ( $V$ ) or the inverse of volume ( $\frac{1}{V}$ ) 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 (see **Figure 8.18**).



**Figure 8.18** The relationship between pressure and volume is inversely proportional. (a) The graph of  $P$  vs.  $V$  is a hyperbola, whereas (b) the graph of  $\frac{1}{P}$  vs.  $V$  is linear. By: Rice University Openstax CC BY NC SA

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 8.8

#### Volume of a Gas Sample

The sample of gas in **Figure 8.17** 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 8.17**  
 (b) the  $\frac{1}{P}$  vs.  $V$  graph in **Figure 8.17**

(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  $\frac{1}{P}$  vs.  $V$  graph gives 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:

$$P_2 = \frac{13.0 \text{ psi} \times 15.0 \text{ mL}}{7.5 \text{ mL}} = 26 \text{ psi}$$

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.

### Check Your Learning

The sample of gas in **Figure 8.17** 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 8.17**  
 (b) the  $\frac{1}{P}$  vs.  $V$  graph in **Figure 8.17**

(c) the Boyle's law equation

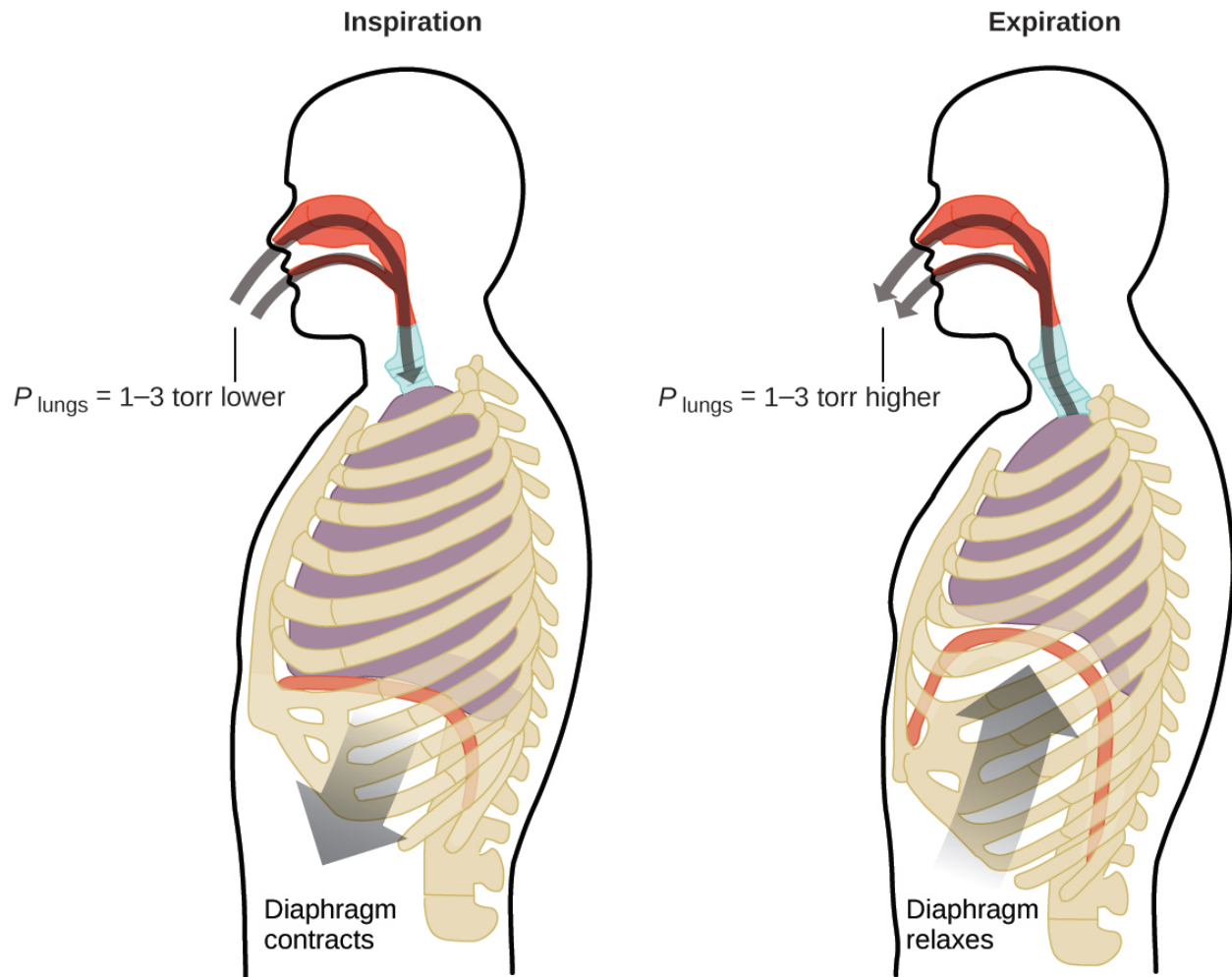
Comment on the likely accuracy of each method.

**Answer:** (a) about 17–18 mL; (b) ~18 mL; (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.

## Chemistry in Everyday Life

### Breathing and Boyle's Law

What do you do about 20 times per minute for your whole life, without a 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 8.19**).



**Figure 8.19** 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. By: Rice University [Openstax CC BY NC SA](#)

## 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:

$$V \propto n \quad \text{or} \quad V = k \times n \quad \text{or} \quad \frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Mathematical relationships can also be determined for the other variable pairs, such as  $P$  versus  $n$  and  $n$  versus  $T$ .



## Link to Learning

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:  $PV = \text{constant}$  at constant  $T$  and  $n$
- Amontons's law:  $\frac{P}{T} = \text{constant}$  at constant  $V$  and  $n$
- Charles's law:  $\frac{V}{T} = \text{constant}$  at constant  $P$  and  $n$
- Avogadro's law:  $\frac{V}{n} = \text{constant}$  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  $0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$  and  $8.314 \text{ kPa L mol}^{-1} \text{ K}^{-1}$ .

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 the use of the ideal gas law to calculate the fifth term as demonstrated in the following example exercises.

## EXAMPLE 8.9

### Using the Ideal Gas Law

Methane,  $\text{CH}_4$ , is being considered for use as an alternative automotive fuel to replace gasoline. One gallon of gasoline could be replaced by 655 g of  $\text{CH}_4$ . What is the volume of this much methane at 25 °C and 745 torr?

### Solution

We must rearrange  $PV = nRT$  to solve for  $V$ :  $V = \frac{nRT}{P}$

If we choose to use  $R = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$ , then the amount must be in moles, temperature must be in kelvin, and pressure must be in atm.

Converting into the “right” units:

$$n = 655 \text{ g CH}_4 \times \frac{1 \text{ mol}}{16.043 \text{ g CH}_4} = 40.8 \text{ mol}$$

$$T = 25 \text{ }^\circ\text{C} + 273 = 298 \text{ K}$$

$$P = 745 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.980 \text{ atm}$$

$$V = \frac{nRT}{P} = \frac{(40.8 \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{0.980 \text{ atm}} = 1.02 \times 10^3 \text{ L}$$

It would require 1020 L (269 gal) of gaseous methane at about 1 atm of pressure to replace 1 gal of gasoline. It requires a large container to hold enough methane at 1 atm to replace several gallons of gasoline.

### Check Your Learning

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 is kept constant under two different sets of conditions, a useful mathematical relationship called the combined gas law is obtained:  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$  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 8.10

#### 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 8.20**). 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 8.20** Scuba divers use compressed air to breathe while underwater. By: Rice University [Openstax](#) CC BY NC SA

### Solution

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:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \rightarrow \frac{(153\text{atm})(13.2\text{L})}{(300\text{K})} = \frac{(3.13\text{atm})(V_2)}{(310\text{K})}$$

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.)

### Check Your Learning

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

## Chemistry in Everyday Life

### The Interdependence between Ocean Depth and Pressure in Scuba Diving

Whether scuba diving at the Great Barrier Reef in Australia (shown in **Figure 8.21**) or in the Caribbean, divers must understand how pressure affects a number of issues related to their comfort and safety.





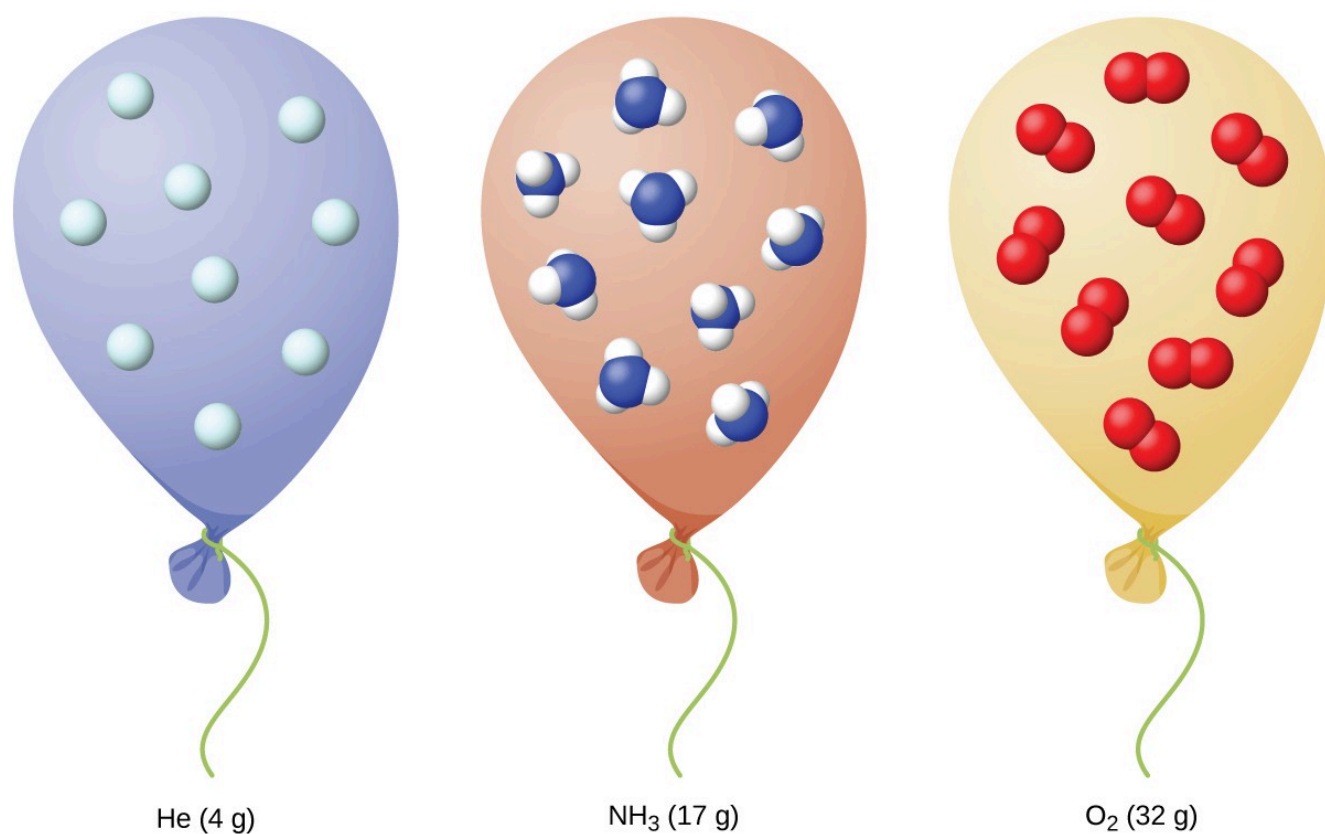
**Figure 8.21** Scuba divers, whether at the Great Barrier Reef or in the Caribbean, must be aware of buoyancy, pressure equalization, and the amount of time they spend underwater to avoid the risks associated with pressurized gases in the body. By: Rice University [Openstax CC BY NC SA](#)

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 and 1 atm (101.325 kPa).<sup>[1]</sup> At STP, one mole of an ideal gas has a volume of about 22.4 L—this is referred to as the **standard molar volume (Figure 8.22)**.



**Figure 8.22** Regardless of its chemical identity, one mole of gas behaving ideally occupies a volume of ~22.4 L at STP. By: Rice University [Openstax](#) [CC BY NC SA](#)

## Footnotes

- 1 The IUPAC definition of standard pressure was changed from 1 atm to 1 bar (100 kPa) in 1982, but the prior definition remains in use by many literature resources and will be used in this text.



# STOICHIOMETRY OF GASEOUS SUBSTANCES, MIXTURES, AND REACTIONS (8.3)

OpenStax

---

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

- 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.”<sup>[2]</sup>

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?” The essential property involved in such use of stoichiometry is the amount of substance, typically measured in moles ( $n$ ). For gases, molar amount can be derived from convenient experimental measurements of pressure, temperature, and volume. Therefore, these measurements are useful in assessing the stoichiometry of pure gases, gas mixtures, and chemical 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.

## Gas Density and Molar Mass

The ideal gas law described previously in this chapter relates the properties of pressure  $P$ , volume  $V$ , temperature  $T$ , and molar amount  $n$ . This law is universal, relating these properties in an identical fashion regardless of the chemical identity of the gas:

$$PV = nRT$$

The density  $d$  of a gas, on the other hand, is determined by its identity. As described in another chapter of this text, the density of a substance is a characteristic property that may be used to identify the substance.

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

Rearranging the ideal gas equation to isolate  $V$  and substituting it into the density equation yields

$$d = \frac{mP}{nRT} = \left(\frac{m}{n}\right) \frac{P}{RT}$$

The ratio  $m/n$  is the definition of molar mass,  $\mathcal{M}$ :

$$\mathcal{M} = \frac{m}{n}$$

The density equation can then be written

$$d = \frac{\mathcal{M}P}{RT}$$

This relation may be used for calculating the densities of gases of known identities at specified values of pressure and temperature as demonstrated in **Example 8.11**.

### EXAMPLE 8.11

#### Measuring Gas Density

What is the density of molecular nitrogen gas at STP?

#### Solution

The molar mass of molecular nitrogen,  $N_2$ , is 28.01 g/mol. Substituting this value along with standard temperature and pressure into the gas density equation yields

$$d = \frac{\mathcal{M}P}{RT} = \frac{(28.01 \text{ g/mol})(1.00 \text{ atm})}{(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(273 \text{ K})} = 1.25 \text{ g/L}$$

### Check Your Learning

What is the density of molecular hydrogen gas at 17.0 °C and a pressure of 760 torr?

**Answer:**  $d = 0.0847 \text{ g/L}$

When the identity of a gas is unknown, measurements of the mass, pressure, volume, and temperature of a sample can be used to calculate the molar mass of the gas (a useful property for identification purposes). Combining the ideal gas equation

$$PV = nRT$$

and the definition of molarity

$$\mathcal{M} = \frac{m}{n}$$

yields the following equation:

$$\mathcal{M} = \frac{mRT}{PV}$$

Determining the molar mass of a gas via this approach is demonstrated in **Example 8.12**.

### Example 8.12

#### Determining the Molecular Formula of a Gas from Its Molar Mass and Empirical Formula

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

First, determine the empirical formula of the gas. 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:

$$85.7 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 7.136 \text{ mol C} \qquad \frac{7.136}{7.136} = 1.00 \text{ mol C}$$

$$14.3 \text{ g H} \times \frac{1 \text{ mol H}}{1.01 \text{ g H}} = 14.158 \text{ mol H} \qquad \frac{14.158}{7.136} = 1.98 \text{ mol H}$$

The empirical formula is  $\text{CH}_2$  [empirical mass (EM) of 14.03 g/empirical unit].

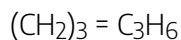
Next, use the provided values for mass, pressure, temperature, and volume to compute the molar mass of the gas:

$$\mathcal{M} = \frac{mRT}{PV} = \frac{(1.56\text{g})(0.0821\text{L atm mol}^{-1}\text{K}^{-1})(323\text{K})}{(0.984\text{atm})(1.00\text{L})} = 42.0\text{g/mol}$$

Comparing the molar mass to the empirical formula mass shows how many empirical formula units make up a molecule:

$$\frac{\mathcal{M}}{EM} = \frac{42.0\text{g/mol}}{14.0\text{g/mol}} = 3$$

The molecular formula is thus derived from the empirical formula by multiplying each of its subscripts by three:



### Check Your Learning

Acetylene, a fuel used in welding torches, is composed of 92.3% C and 7.7% H by mass. Find the empirical formula. If 1.10 g of acetylene occupies a volume of 1.00 L at 1.15 atm and 59.5 °C, what is the molecular formula for acetylene?

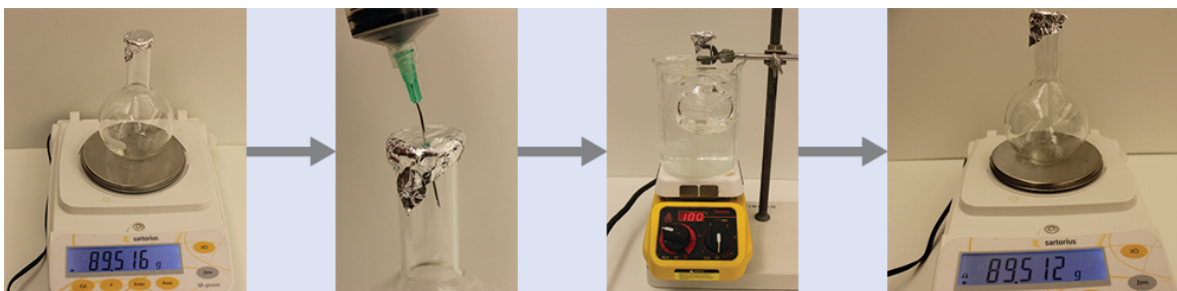
**Answer:** Empirical formula,  $\text{CH}$ ; Molecular formula,  $\text{C}_2\text{H}_2$

## EXAMPLE 8.13

## 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 a 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 (see Figure 8.23)



**Figure 8.23** When the volatile liquid in the flask is heated past its boiling point, it becomes gas and drives air out of the flask. At  $\diamond\diamond\diamond\diamond$ , 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. By: Rice University [Openstax CC BY NC SA](#)

Using this procedure, a sample of chloroform gas weighing 0.494 g is collected in a flask with a volume of  $129 \text{ cm}^3$  at  $99.6^\circ \text{C}$  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

$$\mathcal{M} = \frac{mRT}{PV} = \frac{(0.494\text{g}) \times 0.08206\text{L} \cdot \text{atm/mol K} \times 372.8\text{K}}{0.976\text{atm} \times 0.129\text{L}} = 120\text{g/mol}$$

### Check Your Learning

A sample of phosphorus that weighs  $3.243 \times 10^{-2}$  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?

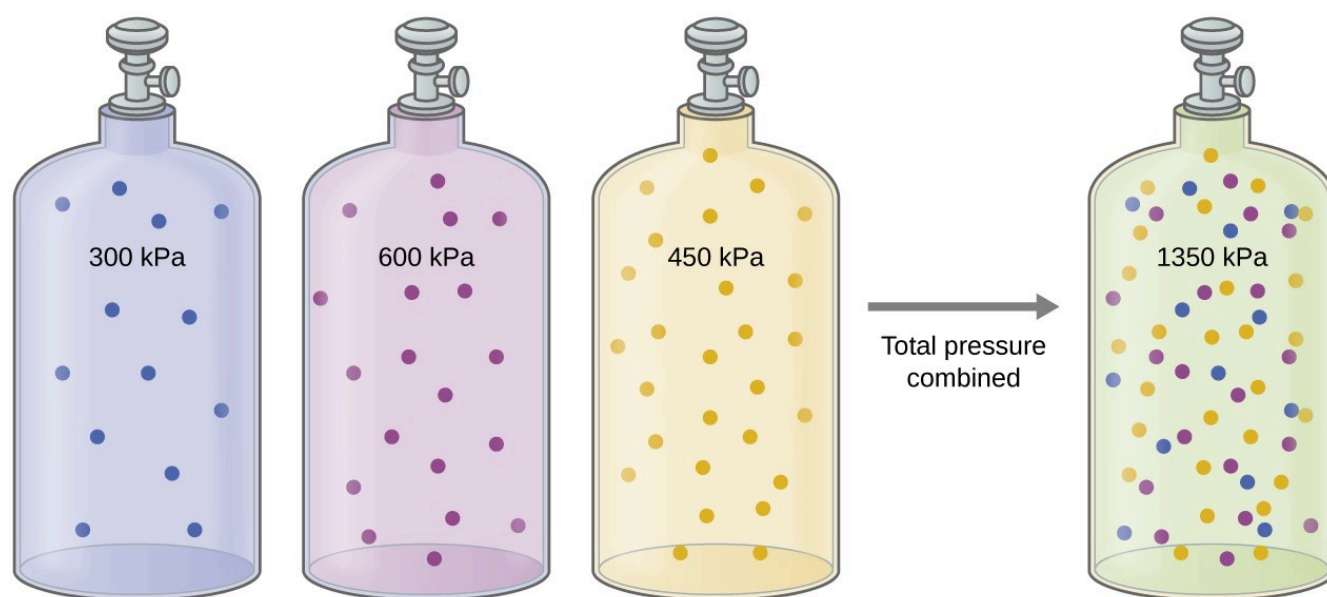
**Answer:** 124 g/mol  $\text{P}_4$

## 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 8.24**). 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*:

$$P_{\text{Total}} = P_A + P_B + P_C + \dots = \sum_i P_i$$

In the equation,  $P_{\text{Total}}$  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 8.24** 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. By: Rice University [Openstax CC BY NC SA](https://openstax.org/r/ocw-openstax)

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:

$$P_A = X_A \times P_{\text{Total}} \quad \text{where} \quad X_A = \frac{n_A}{n_{\text{Total}}}$$

where  $P_A$ ,  $X_A$ , and  $n_A$  are the partial pressure, mole fraction, and number of moles of gas A, respectively, and  $n_{\text{Total}}$  is the number of moles of all components in the mixture.

## EXAMPLE 8.14

### The Pressure of a Mixture of Gases

A 10.0-L vessel contains  $2.50 \times 10^{-3}$  mol of  $\text{H}_2$ ,  $1.00 \times 10^{-3}$  mol of He and  $3.00 \times 10^{-4}$  mol of Ne at 35 °C.

- What are the partial pressures of each of the gases?
- 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  $P = \frac{nRT}{V}$

$$P_{\text{H}_2} = \frac{(2.50 \times 10^{-3} \cancel{\text{mol}})(0.08206 \cancel{\text{L}} \text{ atm } \cancel{\text{mol}^{-1} \text{K}^{-1}})(308 \cancel{\text{K}})}{10.0 \cancel{\text{L}} \text{ atm}} = 6.32 \times 10^{-3}$$

$$P_{\text{He}} = \frac{(1.00 \times 10^{-3} \cancel{\text{mol}})(0.08206 \cancel{\text{L}} \text{ atm } \cancel{\text{mol}^{-1} \text{K}^{-1}})(308 \cancel{\text{K}})}{10.0 \cancel{\text{L}} \text{ } 10^{-3} \text{ atm}} = 2.53 \times 10^{-3}$$

$$P_{\text{Ne}} = \frac{(3.00 \times 10^{-4} \cancel{\text{mol}})(0.08206 \cancel{\text{L}} \text{ atm } \cancel{\text{mol}^{-1} \text{K}^{-1}})(308 \cancel{\text{K}})}{10.0 \cancel{\text{L}} \text{ atm}} = 7.58 \times 10^{-4}$$

The total pressure is given by the sum of the partial pressures:

$$P_{\text{T}} = P_{\text{H}_2} + P_{\text{He}} + P_{\text{Ne}} = (0.00632 + 0.00253 + 0.00076) \text{ atm} = 9.61 \times 10^{-3} \text{ atm}$$

**Check Your Learning**

A 5.73-L flask at 25 °C contains 0.0388 mol of N<sub>2</sub>, 0.147 mol of CO, and 0.0803 mol of H<sub>2</sub>. 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 8.15

## 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  $N_2O$

$$X_{N_2} = \frac{n_{N_2}}{n_{Total}} = \frac{8.41 \text{ mol}}{(2.83 + 8.41) \text{ mol}} = 0.748$$

and

$P_{N_2} = X_{N_2} \times P_{Total} = 0.748 \times 192 \text{ kPa} = 143.6 \text{ kPa}$

## Check Your Learning

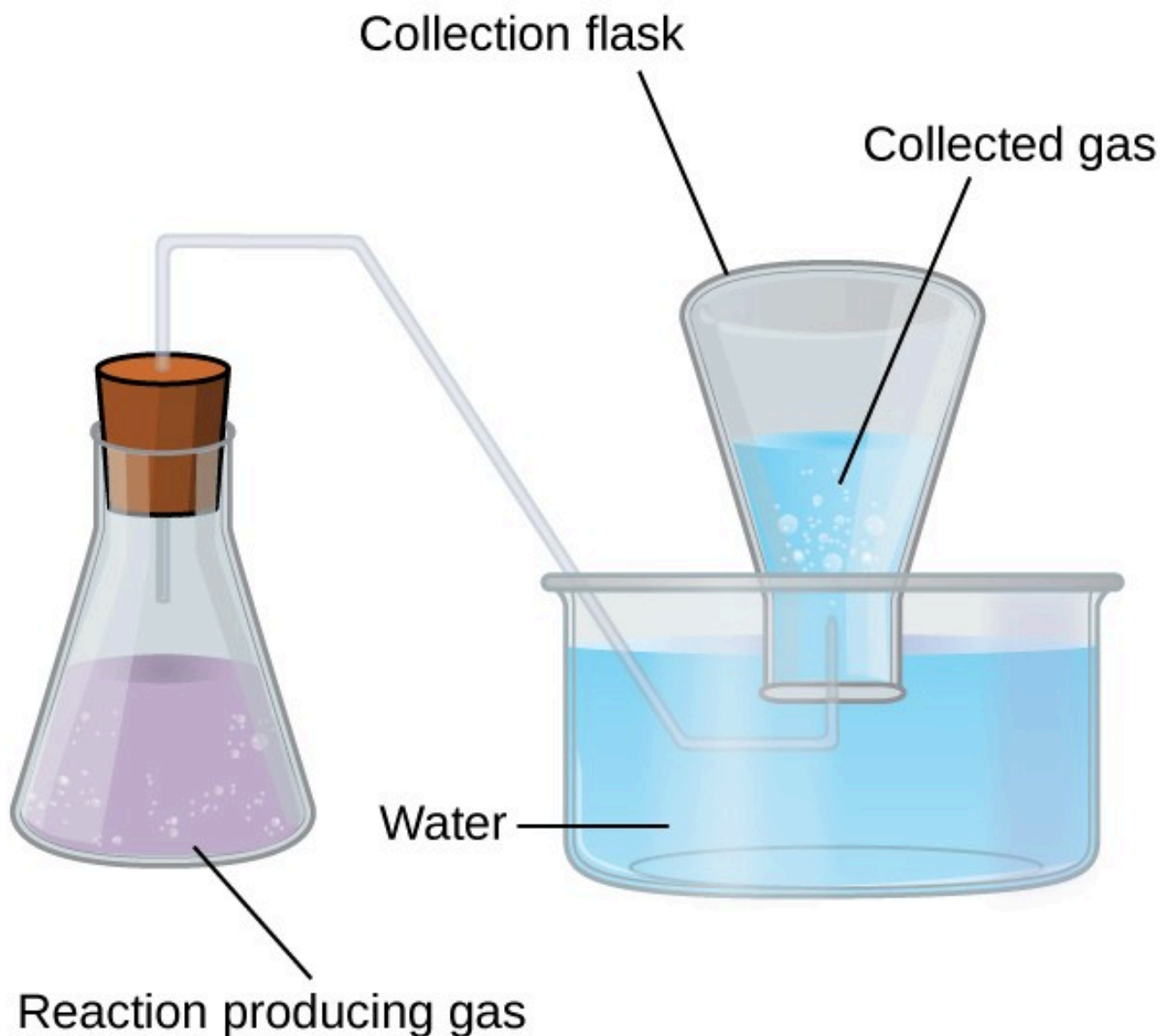
What is the pressure of a mixture of 0.200 g of  $H_2$ , 1.00 g of  $N_2$ , and 0.820 g of Ar in a container with a volume of 2.00 L at 20 °C?

**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

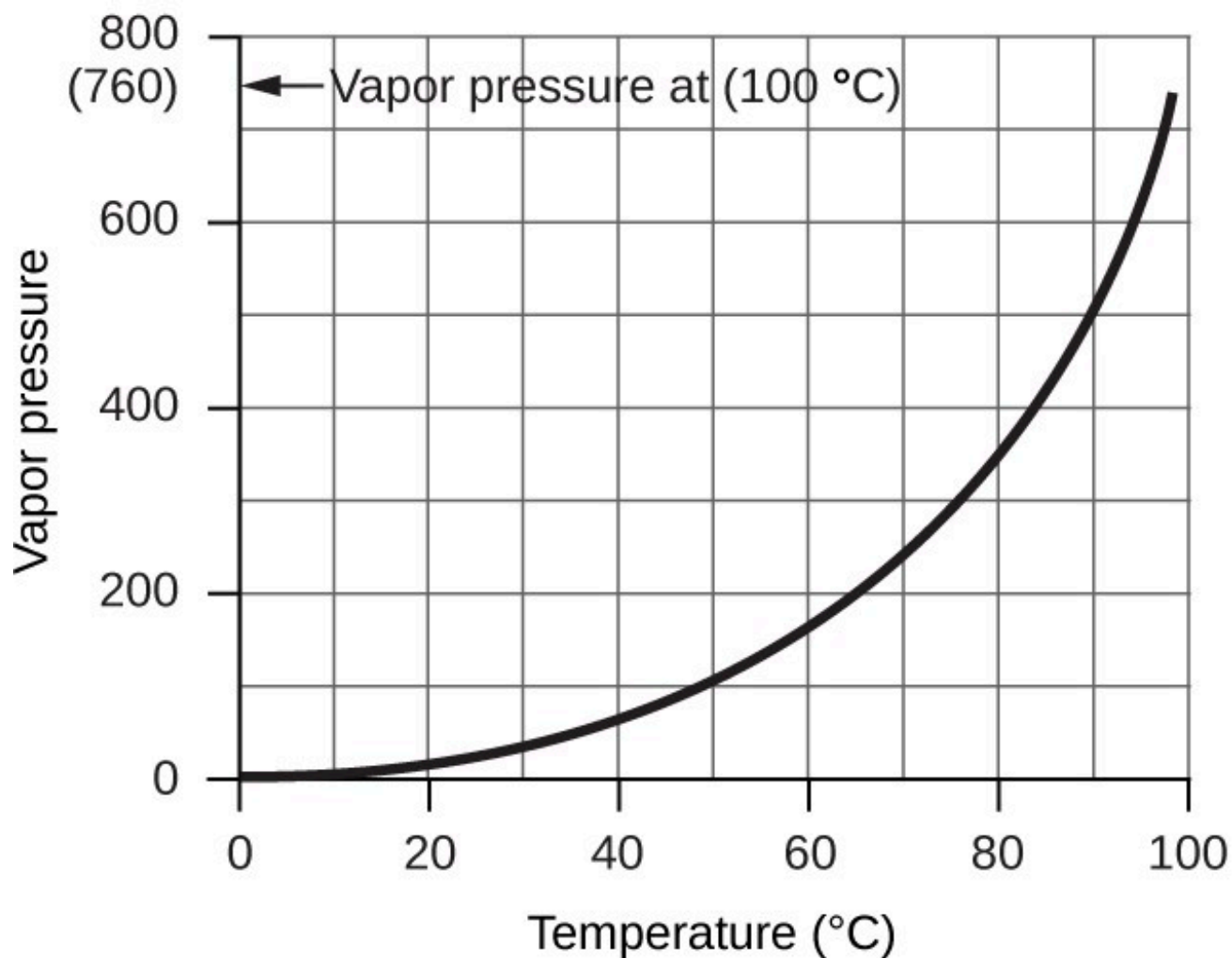
water and inverted into a dish filled with water. The pressure of the gas inside the bottle can be made equal to the air pressure outside by raising or lowering the bottle. When the water level is the same both inside and outside the bottle (**Figure 8.25**), the pressure of the gas is equal to the atmospheric pressure, which can be measured with a barometer.



**Figure 8.25** 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). By: Rice University [Openstax CC BY NC SA](#)

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. 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 8.26**); more detailed information on the temperature dependence of water vapor can be found in [Table 8.2](#), and vapor pressure will be discussed in more detail in the chapter on liquids.



**Figure 8.26** This graph shows the vapor pressure of water at sea level as a function of temperature. By: Rice University [Openstax CC BY NC SA](#)

### Vapor Pressure of Ice and Water in Various Temperatures at Sea Level

**Table 8.2 Vapor Pressure of Ice and Water in Various Temperatures at Sea Level By: Rice University** [OpenStax](#)  
[CC BY-NC-SA 4.0](#)

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	760.0
16	13.6	29	30.0	101	787.6

### EXAMPLE 8.16

#### 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 8.25**, 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:

$$P_{Ar} = 750 \text{ torr} - 25.2 \text{ torr} = 725 \text{ torr}$$

### Check Your Learning

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.

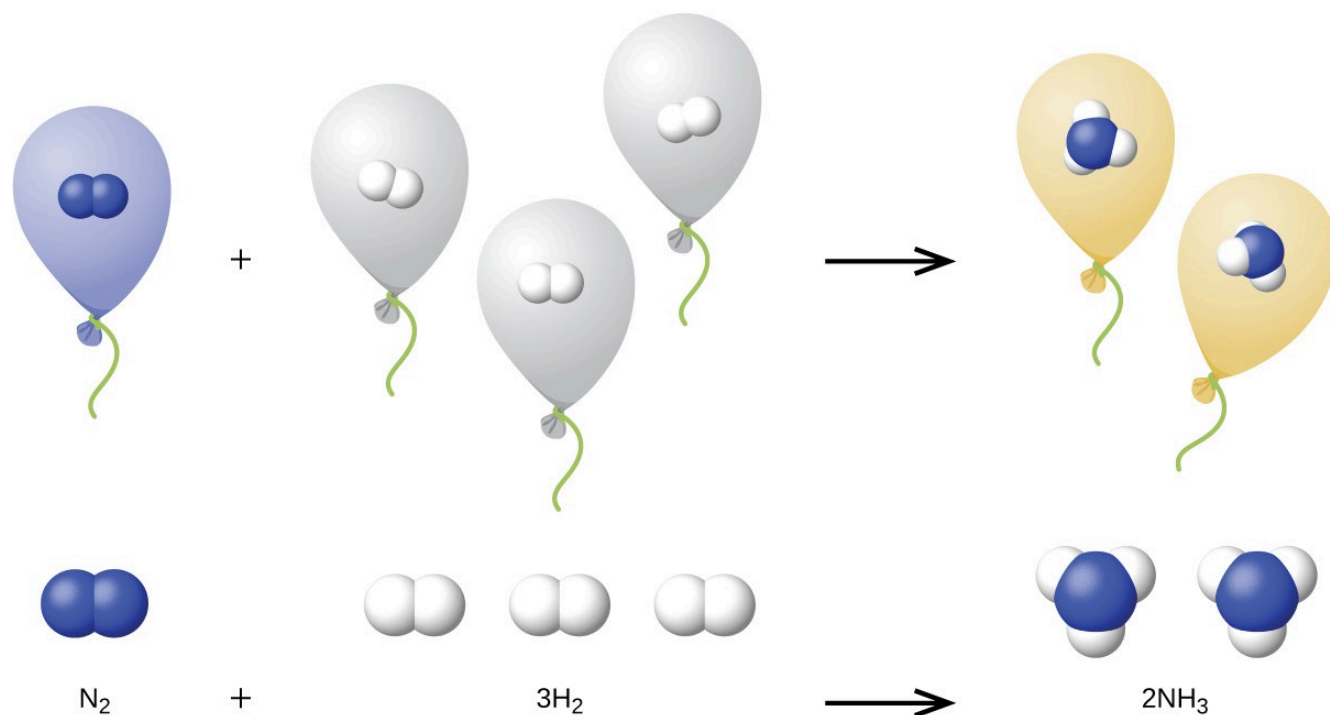
### Avogadro's Law Revisited

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  $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$ , 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 8.27**. According to Avogadro's law, equal volumes of gaseous  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$ , at the same temperature and pressure, contain the same number of molecules. Because one molecule of  $\text{N}_2$  reacts with three molecules of  $\text{H}_2$  to produce two molecules of  $\text{NH}_3$ , the volume of  $\text{H}_2$  required is three times the volume of  $\text{N}_2$ , and the volume of  $\text{NH}_3$  produced is two times the volume of  $\text{N}_2$ .



**Figure 8.27** One volume of  $\text{N}_2$  combines with three volumes of  $\text{H}_2$  to form two volumes of  $\text{NH}_3$ . By: Rice University [Openstax](https://openstax.org) CC BY NC SA

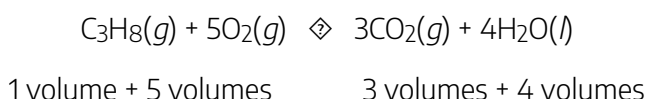
## Example 8.17

### Reaction of Gases

Propane,  $\text{C}_3\text{H}_8(g)$ , is used in gas grills to provide the heat for cooking. What volume of  $\text{O}_2(g)$  measured at  $25^\circ\text{C}$  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  $\text{C}_3\text{H}_8$  and  $\text{O}_2$  will be equal to the ratio of their coefficients in the balanced equation for the reaction:



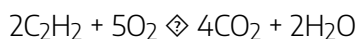
From the equation, we see that one volume of  $\text{C}_3\text{H}_8$  will react with five volumes of  $\text{O}_2$ :

$$2.7 \text{ L C}_3\text{H}_8 \times \frac{5 \text{ L O}_2}{1 \text{ L C}_3\text{H}_8} = 13.5 \text{ L O}_2$$

A volume of 13.5 L of  $\text{O}_2$  will be required to react with 2.7 L of  $\text{C}_3\text{H}_8$ .

### Check Your Learning

An acetylene tank for an oxyacetylene welding torch provides 9340 L of acetylene gas,  $\text{C}_2\text{H}_2$ , at  $0^\circ\text{C}$  and 1 atm. How many tanks of oxygen, each providing  $7.00 \times 10^3$  L of  $\text{O}_2$  at  $0^\circ\text{C}$  and 1 atm, will be required to burn the acetylene?

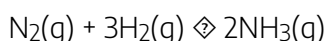


**Answer:** 3.34 tanks ( $2.34 \times 10^4$  L)

## EXAMPLE 8.18

## 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  $\text{H}_2(g)$ , measured under the same conditions, was required to prepare this amount of ammonia by reaction with  $\text{N}_2$ ?



## Solution

Because equal volumes of  $\text{H}_2$  and  $\text{NH}_3$  contain equal numbers of molecules and each three molecules of  $\text{H}_2$  that react produce two molecules of  $\text{NH}_3$ , the ratio of the volumes of  $\text{H}_2$  and  $\text{NH}_3$  will be equal to 3:2. Two volumes of  $\text{NH}_3$ , in this case in units of billion  $\text{ft}^3$ , will be formed from three volumes of  $\text{H}_2$ :

$$683 \text{ billion ft}^3 \text{ NH}_3 \times \frac{3 \text{ billion ft}^3 \text{ H}_2}{2 \text{ billion ft}^3 \text{ NH}_3} = 1.02 \times 10^3 \text{ billion ft}^3 \text{ H}_2$$

The manufacture of 683 billion  $\text{ft}^3$  of  $\text{NH}_3$  required 1020 billion  $\text{ft}^3$  of  $\text{H}_2$ . (At 25 °C and 1 atm, this is the volume of a cube with an edge length of approximately 1.9 miles.)

## Check Your Learning

What volume of  $\text{O}_2(g)$  measured at 25 °C and 760 torr is required to react with 17.0 L of ethylene,  $\text{C}_2\text{H}_4(g)$ , measured under the same conditions of temperature and pressure? The products are  $\text{CO}_2$  and water vapor.

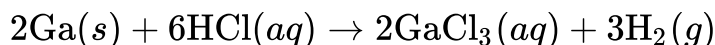
**Answer:** 51.0 L



## EXAMPLE 8.19

## 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?



## Solution

Convert the provided mass of the limiting reactant, Ga, to moles of hydrogen produced:

$$8.88 \text{ g Ga} \times \frac{1 \cancel{\text{mol Ga}}}{69.723 \text{ g Ga}} \times \frac{3 \text{ mol H}_2}{2 \cancel{\text{mol Ga}}} = 0.191 \text{ mol H}_2$$

Convert the provided temperature and pressure values to appropriate units (K and atm, respectively), and then use the molar amount of hydrogen gas and the ideal gas equation to calculate the volume of gas:

$$V = \left( \frac{nRT}{P} \right) = \frac{0.191 \cancel{\text{mol}} \times 0.08206 \text{ L } \cancel{\text{atm mol}^{-1} \text{K}^{-1}} \times 300 \text{ K}}{0.951 \cancel{\text{atm}}} = 4.94 \text{ L}$$

## Check Your Learning

Sulfur dioxide is an intermediate in the preparation of sulfuric acid. What volume of SO<sub>2</sub> at 343 °C and 1.21 atm is produced by burning 1.00 kg of sulfur in excess oxygen?

**Answer:** 1.30 × 10<sup>3</sup> L



An interactive H5P element has been excluded from this version of the text. You can view it online here:

<https://louis.pressbooks.pub/chemistry1/?p=459#h5p-7>



An interactive H5P element has been excluded from this version of the text. You can view it online here:

<https://louis.pressbooks.pub/chemistry1/?p=459#h5p-8>



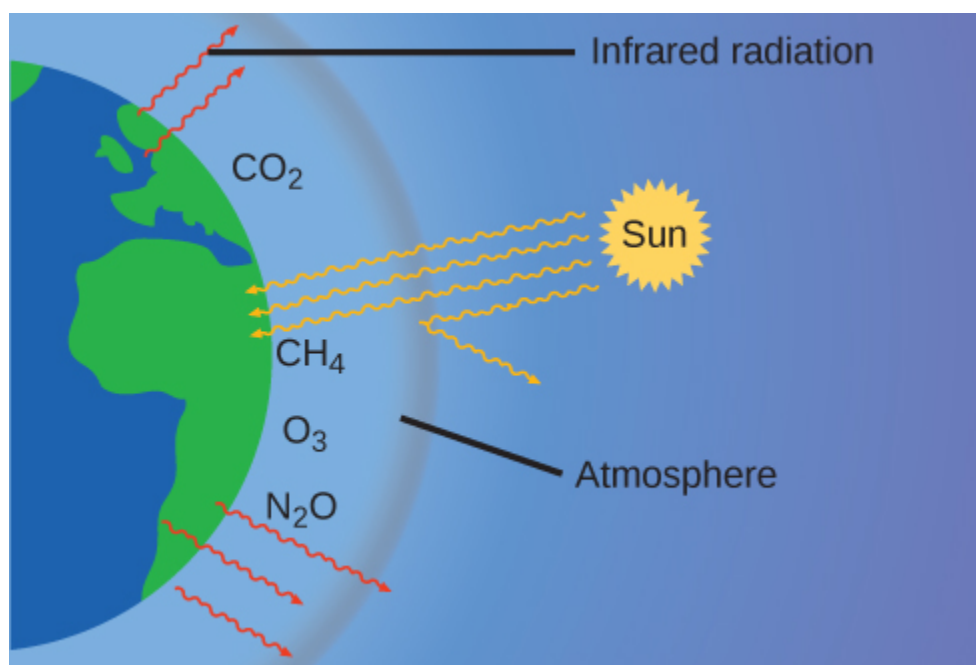
An interactive H5P element has been excluded from this version of the text. You can view it online here:

<https://louis.pressbooks.pub/chemistry1/?p=459#h5p-9>

## How Sciences Interconnect

### Greenhouse Gases and Climate Change

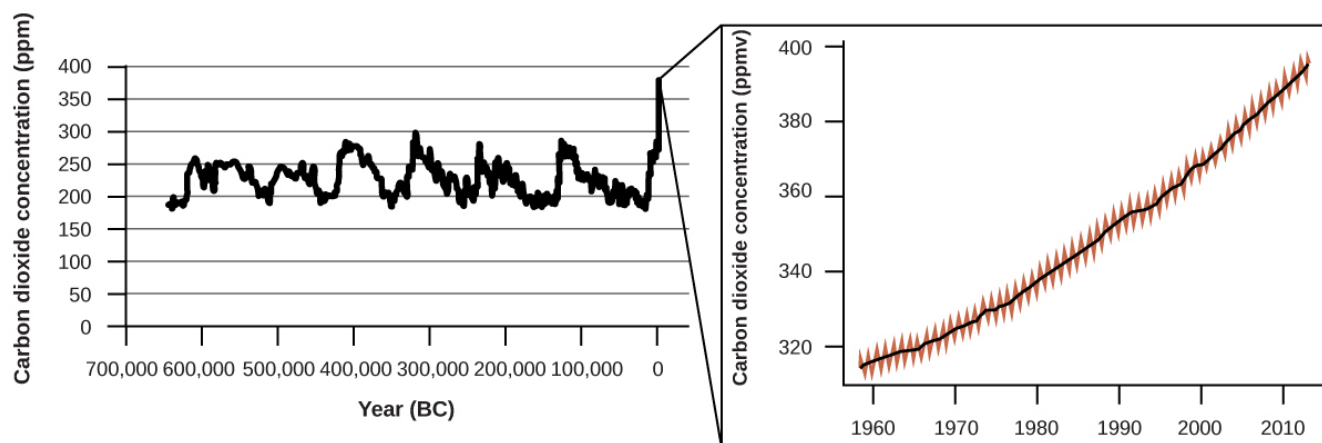
The thin skin of our atmosphere keeps the earth from being an ice planet and makes it habitable. In fact, this is due to less than 0.5% of the air molecules. Of the energy from the sun that reaches the earth, almost  $\frac{1}{3}$  is reflected back into space, with the rest absorbed by the atmosphere 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. Most of this IR radiation, however, is absorbed by certain atmospheric gases, effectively trapping heat within the atmosphere in a phenomenon known as the *greenhouse effect*. This effect maintains global temperatures within the range needed to sustain life on earth. Without our atmosphere, the earth's average temperature would be lower by more than 30 °C (nearly 60 °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 8.28**).



**Figure 8.28** 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. By: Rice University [Openstax CC BY NC SA](#)

There is strong evidence from multiple sources that higher atmospheric levels of CO<sub>2</sub> are caused by human activity, with fossil fuel burning accounting for about  $\frac{3}{4}$  of the recent increase in CO<sub>2</sub>. Reliable data from ice cores reveals that CO<sub>2</sub> concentration in the atmosphere has been at its 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<sub>2</sub> concentration has increased from preindustrial levels of ~280 ppm to more than 400 ppm today (**Figure 8.29**).

#### Carbon Dioxide in the Atmosphere



**Figure 8.29** CO<sub>2</sub> levels over the past 700,000 years were typically from 200–300 ppm, with a steep, unprecedented increase over the past 50 years. By: Rice University [Openstax CC BY NC SA](#)

## Link to Learning

[Click here](#) to see a 2-minute video explaining greenhouse gases and global warming.

## Portrait of a Chemist

### Susan Solomon

Atmospheric and climate scientist Susan Solomon (**Figure 8.30**) is the author of one of the *New York Times* books of the year (*The Coldest March*, 2001), one of *Time* magazine's 100 most influential people in the world (2008), and a working group leader of the Intergovernmental Panel on Climate Change (IPCC), which was the recipient of the 2007 Nobel Peace Prize. She helped determine and explain the cause of the formation of the ozone hole over Antarctica and has authored many important papers on climate change. She has been awarded the top scientific honors in the US and France (the National Medal of Science and the Grande Medaille, respectively) and is a member of the National Academy of Sciences, the Royal Society, the French Academy of Sciences, and the European Academy of Sciences. Formerly a professor at the University of Colorado, she is now at MIT and continues to work at NOAA. For more information, [watch this video](#) about Susan Solomon.



**Figure 8.30**

Susan Solomon's research focuses on climate change and has been instrumental in determining the cause of the ozone hole over Antarctica. By: Rice University Openstax CC BY NC SA

## Footnotes

- <sup>2</sup>“Quotations by Joseph-Louis Lagrange,” last modified February 2006, accessed February 10, 2015, <http://www-history.mcs.st-andrews.ac.uk/Quotations/Lagrange.html>

# EFFUSION AND DIFFUSION OF GASES (8.4)

OpenStax

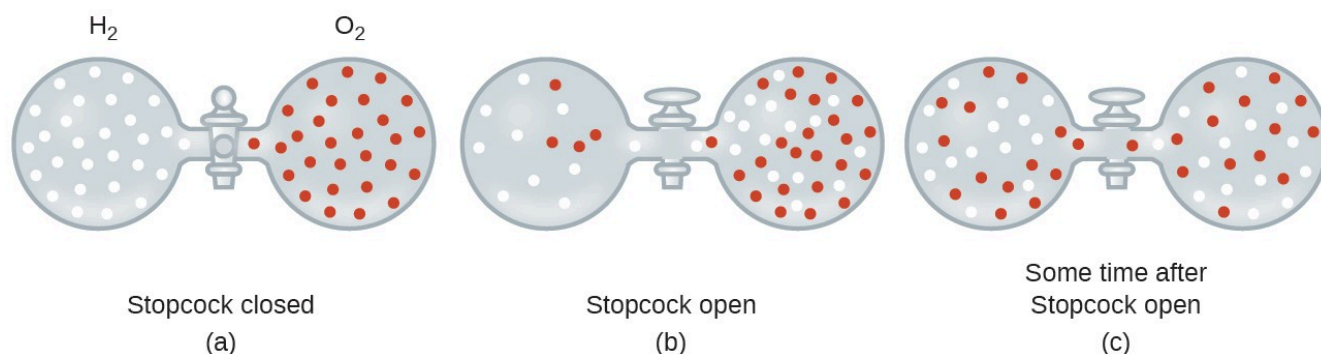
---

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

- Define and explain effusion and diffusion
- State Graham's law and use it to compute relevant gas properties

If you have ever been in a room when a piping hot pizza was delivered, you have been made aware of the fact that gaseous molecules can quickly spread throughout a room, as evidenced by the pleasant aroma that soon reaches your nose. Although gaseous molecules travel at tremendous speeds (hundreds of meters per second), they collide with other gaseous molecules and travel in many different directions before reaching the desired target. At room temperature, a gaseous molecule will experience billions of collisions per second. The **mean free path** is the average distance a molecule travels between collisions. The mean free path increases with decreasing pressure; in general, the mean free path for a gaseous molecule will be hundreds of times the diameter of the molecule.

In general, we know that when a sample of gas is introduced to one part of a closed container, its molecules very quickly disperse throughout the container; this process by which molecules disperse in space in response to differences in concentration is called **diffusion** (shown in **Figure 8.31**). The gaseous atoms or molecules are, of course, unaware of any concentration gradient; they simply move randomly—regions of higher concentration have more particles than regions of lower concentrations, and so a net movement of species from high to low concentration areas takes place. In a closed environment, diffusion will ultimately result in equal concentrations of gas throughout, as depicted in **Figure 8.31**. The gaseous atoms and molecules continue to move, but since their concentrations are the same in both bulbs, the rates of transfer between the bulbs are equal (no *net* transfer of molecules occurs).



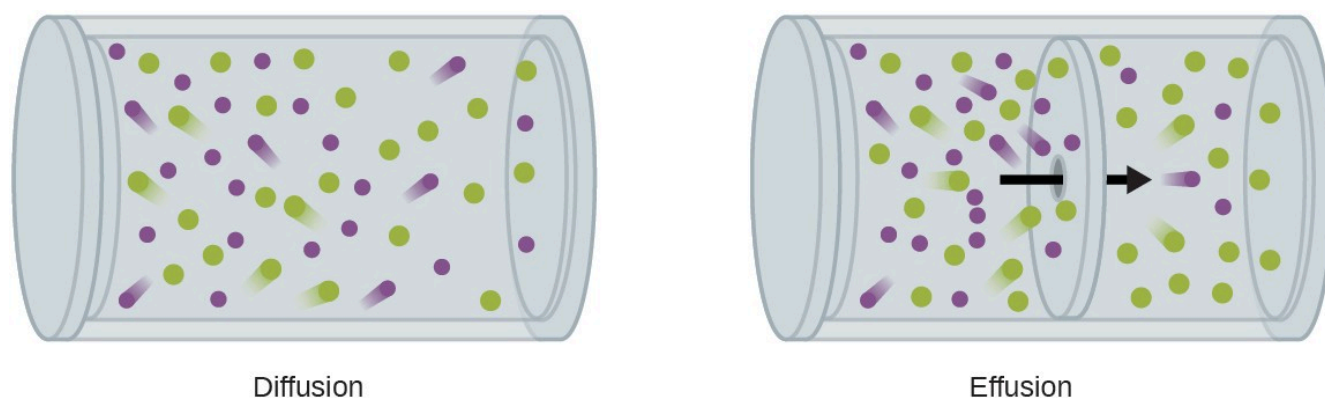
**Figure 8.31** (a) Two gases,  $\text{H}_2$  and  $\text{O}_2$ , are initially separated. (b) When the stopcock is opened, they mix together. The lighter gas,  $\text{H}_2$ , passes through the opening faster than  $\text{O}_2$ , so just after the stopcock is opened, more  $\text{H}_2$  molecules move to the  $\text{O}_2$  side than  $\text{O}_2$  molecules move to the  $\text{H}_2$  side. (c) After a short time, both the slower-moving  $\text{O}_2$  molecules and the faster-moving  $\text{H}_2$  molecules have distributed themselves evenly on both sides of the vessel. By: Rice University [Openstax CC BY NC SA](#)

We are often interested in the **rate of diffusion**, the amount of gas passing through some area per unit of time:

$$\text{rate of diffusion} = \frac{\text{amount of gas passing through an area}}{\text{unit of time}}$$

The diffusion rate depends on several factors: the concentration gradient (the increase or decrease in concentration from one point to another), the amount of surface area available for diffusion, and the distance the gas particles must travel. Note also that the time required for diffusion to occur is inversely proportional to the rate of diffusion, as shown in the rate of diffusion equation.

A process involving the movement of gaseous species similar to diffusion is **effusion**, the escape of gas molecules through a tiny hole such as a pinhole in a balloon into a vacuum (**Figure 8.32**). Although diffusion and effusion rates both depend on the molar mass of the gas involved, their rates are not equal; however, the ratios of their rates are the same.



**Figure 8.32** Diffusion involves the unrestricted dispersal of molecules throughout space due to their random motion. When this process is restricted to the passage of molecules through very small openings in a physical barrier, the process is called effusion. By: Rice University [Openstax CC BY NC SA](#)

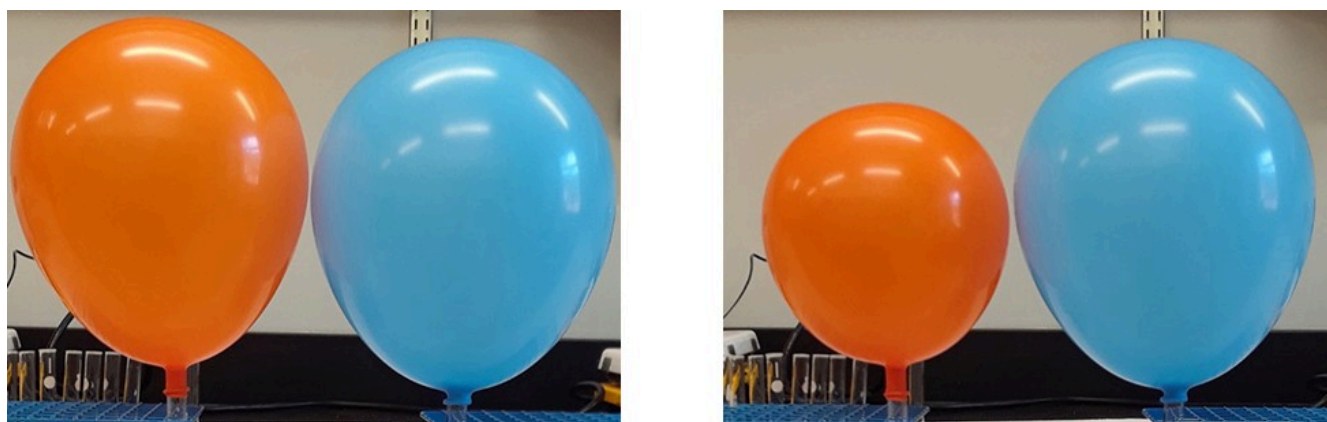
If a mixture of gases is placed in a container with porous walls, the gases effuse through the small openings in

the walls. The lighter gases pass through the small openings more rapidly (at a higher rate) than the heavier ones (**Figure 8.33**). In 1832, Thomas Graham studied the rates of effusion of different gases and formulated **Graham's law of effusion**: *The rate of effusion of a gas is inversely proportional to the square root of the mass of its particles*:

$$\text{rate of effusion} \propto \frac{1}{\sqrt{\mathcal{M}}}$$

This means that if two gases A and B are at the same temperature and pressure, the ratio of their effusion rates is inversely proportional to the ratio of the square roots of the masses of their particles:

$$\frac{\text{rate of effusion of A}}{\text{rate of effusion of B}} = \frac{\sqrt{\mathcal{M}_B}}{\sqrt{\mathcal{M}_A}}$$



**Figure 8.33** The left photograph shows two balloons inflated with different gases, helium (orange) and argon (blue). The right-side photograph shows the balloons approximately 12 hours after being filled, at which time the helium balloon has become noticeably more deflated than the argon balloon, due to the greater effusion rate of the lighter helium gas. By: Rice University [Openstax CC BY NC SA](#)

## EXAMPLE 8.20

### Applying Graham's Law to Rates of Effusion

Calculate the ratio of the rate of effusion of hydrogen to the rate of effusion of oxygen.

#### Solution

From Graham's law, we have:



$$\frac{\text{rate of effusion of hydrogen}}{\text{rate of effusion of oxygen}} = \frac{\sqrt{\cancel{32 \text{ g mol}^{-1}}}}{\sqrt{\cancel{2 \text{ g mol}^{-1}}}} = \frac{\sqrt{16}}{\sqrt{1}} = \frac{4}{1}$$

Hydrogen effuses four times as rapidly as oxygen.

### Check Your Learning

At a particular pressure and temperature, nitrogen gas effuses at the rate of 79 mL/s. Under the same conditions, at what rate will sulfur dioxide effuse?

**Answer:** 52 mL/s

## EXAMPLE 8.21

### Effusion Time Calculations

It takes 243 s for  $4.46 \times 10^{-5}$  mol Xe to effuse through a tiny hole. Under the same conditions, how long will it take  $4.46 \times 10^{-5}$  mol Ne to effuse?

### Solution

It is important to resist the temptation to use the times directly and to remember how rate relates to time as well as how it relates to mass. Recall the definition of rate of effusion:

$$\text{rate of effusion} = \frac{\text{amount of gas transferred}}{\text{time}}$$

and combine it with Graham's law:

$$\frac{\text{rate of effusion of gas Xe}}{\text{rate of effusion of gas Ne}} = \frac{\sqrt{\mathcal{M}_{\text{Ne}}}}{\sqrt{\mathcal{M}_{\text{Xe}}}}$$

to get:

$$\frac{\frac{\text{amount of Xe transferred}}{\text{time for Xe}}}{\frac{\text{amount of Ne transferred}}{\text{time for Ne}}} = \frac{\sqrt{\mathcal{M}_{\text{Ne}}}}{\sqrt{\mathcal{M}_{\text{Xe}}}}$$

Noting that *amount of A = amount of B* and solving for *time for Ne*:

$$\frac{\frac{\cancel{\text{amount of Xe}}}{\text{time for Xe}}}{\frac{\cancel{\text{amount of Ne}}}{\text{time for Ne}}} = \frac{\text{time for Ne}}{\text{time for Xe}} = \frac{\sqrt{\mathcal{M}_{\text{Ne}}}}{\sqrt{\mathcal{M}_{\text{Xe}}}} = \frac{\sqrt{\mathcal{M}_{\text{Ne}}}}{\sqrt{\mathcal{M}_{\text{Xe}}}}$$

and substitute values:

$$\frac{\text{time for Ne}}{243\text{s}} = \sqrt{\frac{20.2 \cancel{\text{ g mol}}}{131.3 \cancel{\text{ g mol}}}} = 0.392$$

Finally, solve for the desired quantity:

$$\text{time for Ne} = 0.392 \times 243 \text{ s} = 95.3 \text{ s}$$

Note that this answer is reasonable: Since Ne is lighter than Xe, the effusion rate for Ne will be larger than that for Xe, which means the time of effusion for Ne will be smaller than that for Xe.

### Check Your Learning

A party balloon filled with helium deflates to  $\frac{2}{3}$  of its original volume in 8.0 hours. How long will it take an identical balloon filled with the same number of moles of air ( $\mathcal{M} = 28.2 \text{ g/mol}$ ) to deflate to  $\frac{1}{2}$  of its original volume?

**Answer:** 32 h

## EXAMPLE 8.22

## Determining Molar Mass Using Graham's Law

An unknown gas effuses 1.66 times more rapidly than CO<sub>2</sub>. What is the molar mass of the unknown gas? Can you make a reasonable guess as to its identity?

## Solution

From Graham's law, we have:

$$\frac{\text{rate of effusion of Unknown}}{\text{rate of effusion of CO}_2} = \frac{\sqrt{\mathcal{M}_{\text{CO}_2}}}{\sqrt{\mathcal{M}_{\text{Unknown}}}}$$

Plug in known data:

$$\frac{1.66}{1} = \frac{\sqrt{44.0\text{g/mol}}}{\sqrt{\mathcal{M}_{\text{Unknown}}}}$$

Solve:

$$\mathcal{M}_{\text{Unknown}} = \frac{44.0\text{g/mol}}{(1.66)^2} = 16.0\text{g/mol}$$

The gas could well be CH<sub>4</sub>, the only gas with this molar mass.

## Check Your Learning

Hydrogen gas effuses through a porous container 8.97 times faster than an unknown gas. Estimate the molar mass of the unknown gas.

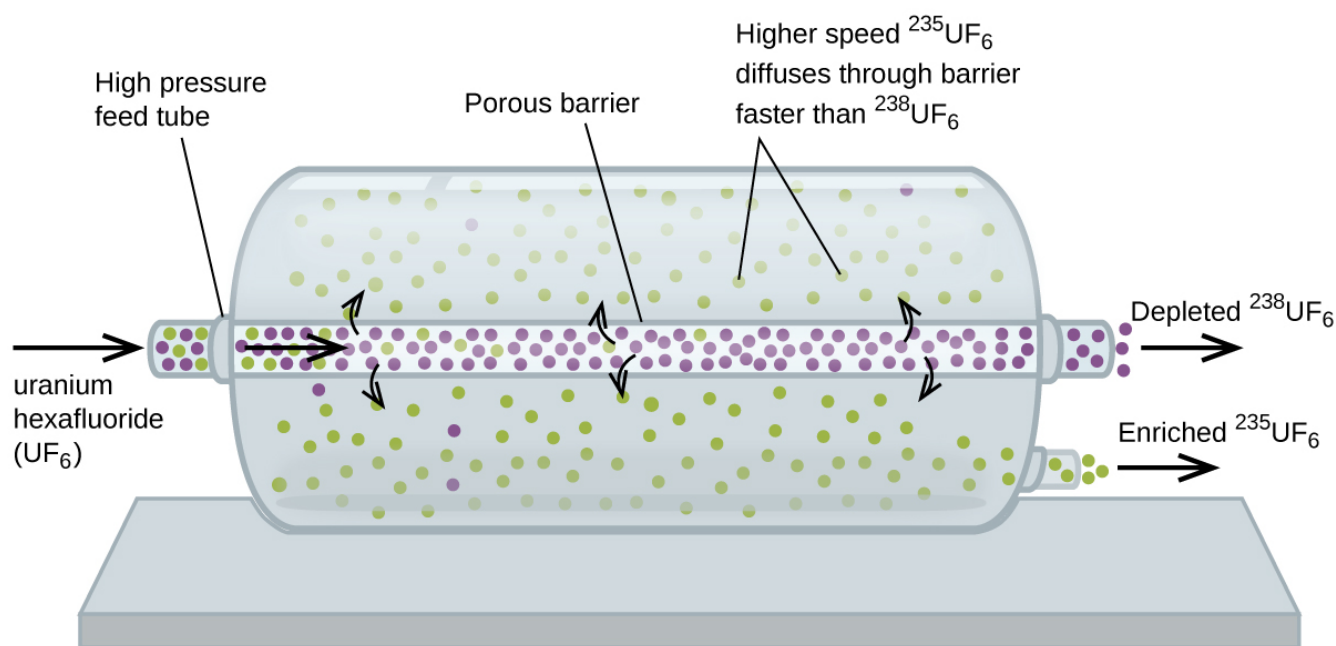
**Answer:** 163 g/mol

## How Sciences Interconnect

## Use of Diffusion for Nuclear Energy Applications: Uranium Enrichment

Gaseous diffusion has been used to produce enriched uranium for use in nuclear power plants and weapons. Naturally occurring uranium contains only 0.72% of <sup>235</sup>U, the kind of uranium that is “fissile,” that is, capable

of sustaining a nuclear fission chain reaction. Nuclear reactors require fuel that is 2–5%  $^{235}\text{U}$ , and nuclear bombs need even higher concentrations. One way to enrich uranium to the desired levels is to take advantage of Graham's law. In a gaseous diffusion enrichment plant, uranium hexafluoride ( $\text{UF}_6$ , the only uranium compound that is volatile enough to work) is slowly pumped through large cylindrical vessels called diffusers, which contain porous barriers with microscopic openings. The process is one of diffusion because the other side of the barrier is not evacuated. The  $^{235}\text{UF}_6$  molecules have a higher average speed and diffuse through the barrier a little faster than the heavier  $^{238}\text{UF}_6$  molecules. The gas that has passed through the barrier is slightly enriched in  $^{235}\text{UF}_6$ , and the residual gas is slightly depleted. The small difference in molecular weights between  $^{235}\text{UF}_6$  and  $^{238}\text{UF}_6$  only about 0.4% enrichment, is achieved in one diffuser (**Figure 8.34**). But by connecting many diffusers in a sequence of stages (called a cascade), the desired level of enrichment can be attained.



**Figure 8.34** In a diffuser, gaseous  $\text{UF}_6$  is pumped through a porous barrier, which partially separates  $^{235}\text{UF}_6$  from  $^{238}\text{UF}_6$ . The  $\text{UF}_6$  must pass through many large diffuser units to achieve sufficient enrichment in  $^{235}\text{U}$ . By: Rice University [Openstax CC BY NC SA](#)

The large-scale separation of gaseous  $^{235}\text{UF}_6$  from  $^{238}\text{UF}_6$  was first done during World War II, at the atomic energy installation in Oak Ridge, Tennessee, as part of the Manhattan Project (the development of the first atomic bomb). Although the theory is simple, this required surmounting many daunting technical challenges to make it work in practice. The barrier must have tiny, uniform holes (about  $10^{-6}$  cm in diameter) and be porous enough to produce high flow rates. All materials (the barrier, tubing, surface coatings, lubricants, and gaskets) need to be able to contain, but not react with, the highly reactive and corrosive  $\text{UF}_6$ . Because gaseous diffusion plants require very large amounts of energy (to compress the gas to the high pressures required and drive it through the diffuser cascade, to remove the heat produced during compression, and so on), it is now

being replaced by gas centrifuge technology, which requires far less energy. A current hot political issue is how to deny this technology to Iran, to prevent it from producing enough enriched uranium for them to use to make nuclear weapons.

# THE KINETIC-MOLECULAR THEORY (8.5)

OpenStax

---

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

- 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.)

- Gases are composed of molecules that are in continuous motion, traveling in straight lines and changing direction only when they collide with other molecules or with the walls of a container.
- The molecules composing the gas are negligibly small compared to the distances between them.
- The pressure exerted by a gas in a container results from collisions between the gas molecules and the container walls.
- 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).
- The average kinetic energy of the gas molecules is proportional to the kelvin temperature of the gas.

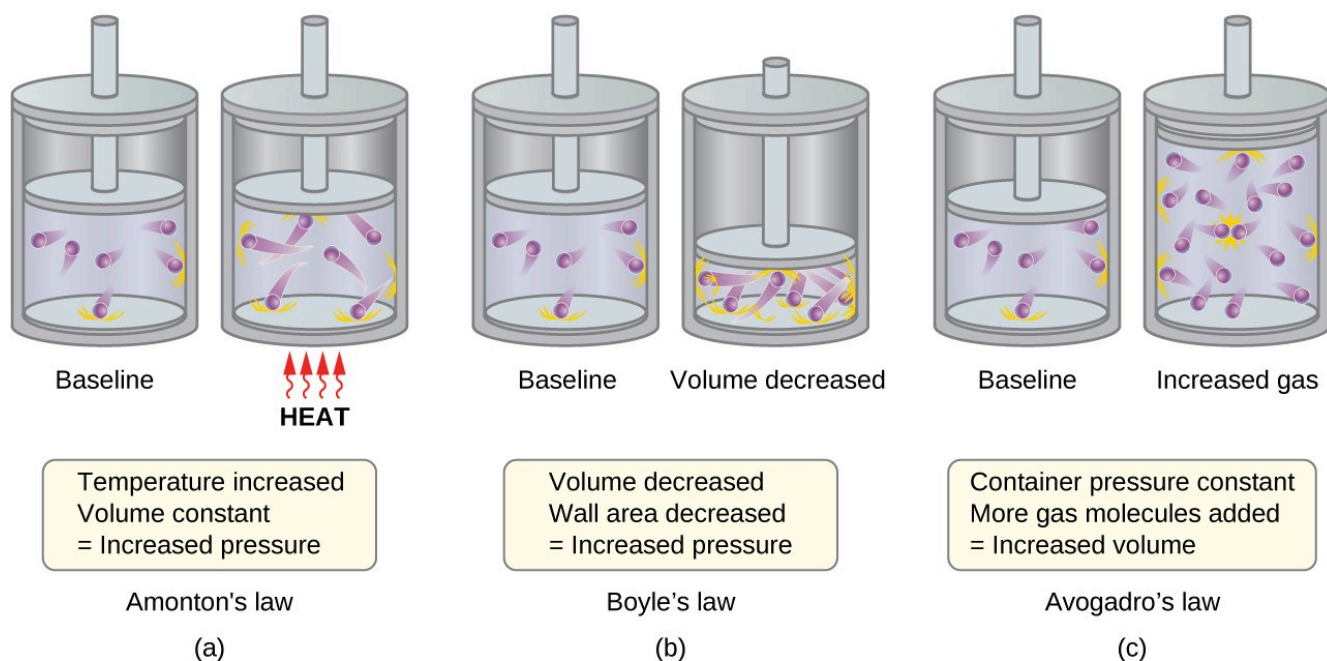
The test of the KMT and its postulates is its ability to explain and describe the behavior of a gas. The various gas laws can be derived from the assumptions of the KMT, which have led chemists to believe that the assumptions of the theory accurately represent the properties of gas molecules. We will 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 8.35**).
- *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 8.35**).
- *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 8.35**).
- *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.



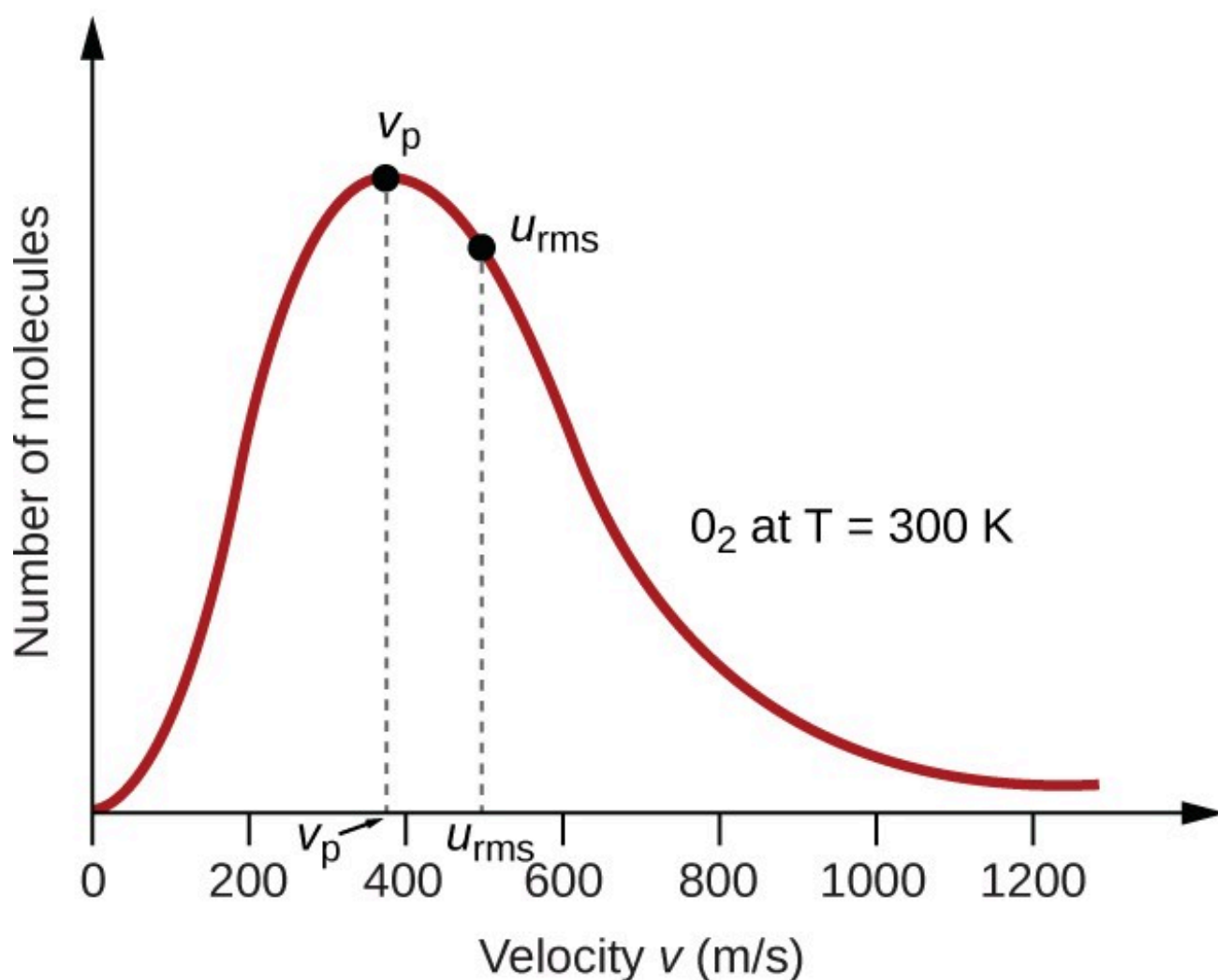
**Figure 8.35** (a) When gas temperature increases, gas pressure increases due to increased force and frequency of molecular collisions. (b) When volume decreases, gas pressure increases due to increased frequency of molecular collisions. (c) When the amount of gas increases at a constant pressure, volume increases to yield a constant number of collisions per unit wall area per unit time. By: Rice University Openstax CC BY NC SA

## 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 the 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 8.36**).





**Figure 8.36** 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. By: Rice University [Openstax CC BY NC SA](#)

The kinetic energy (KE) of a particle of mass ( $m$ ) and speed ( $u$ ) is given by:

$$KE = \frac{1}{2} mu^2$$

Expressing mass in kilograms and speed in meters per second will yield energy values in units of joules ( $J = \text{kg m}^2 \text{s}^{-2}$ ). 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:

$$u_{rms} = \sqrt{u^2} = \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + u_4^2 + \dots}{n}}$$

The average kinetic energy for a mole of particles,  $\text{KE}_{\text{avg}}$ , is then equal to:

$$\text{KE}_{\text{avg}} = \frac{1}{2} M u_{\text{rms}}^2$$

where  $M$  is the molar mass expressed in units of kg/mol. The  $\text{KE}_{\text{avg}}$  of a mole of gas molecules is also directly proportional to the temperature of the gas and may be described by the equation:

$$\text{KE}_{\text{avg}} = \frac{3}{2} RT$$

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  $8.314 \text{ J/mol}\cdot\text{K}$  ( $8.314 \text{ kg m}^2 \text{ s}^{-2} \text{ mol}^{-1} \text{ K}^{-1}$ ). These two separate equations for  $\text{KE}_{\text{avg}}$  may be combined and rearranged to yield a relation between molecular speed and temperature:

$$\begin{aligned} \frac{1}{2} M u_{\text{rms}}^2 &= \frac{3}{2} RT \\ u_{\text{rms}} &= \sqrt{\frac{3RT}{M}} \end{aligned}$$

## EXAMPLE 8.23

### Calculation of $u_{\text{rms}}$

Calculate the root-mean-square velocity for a nitrogen molecule at  $30^\circ\text{C}$ .

### Solution

Convert the temperature into Kelvin:

$$30^\circ\text{C} + 273 = 303 \text{ K}$$

Determine the molar mass of nitrogen in kilograms:

$$\frac{28.0 \cancel{\text{g}}}{1 \text{ mol}} \times \frac{1 \text{ kg}}{1000 \cancel{\text{g}}} = 0.028 \text{ kg/mol}$$

Replace the variables and constants in the root-mean-square velocity equation, replacing Joules with the equivalent  $\text{kg m}^2 \text{ s}^{-2}$ :

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

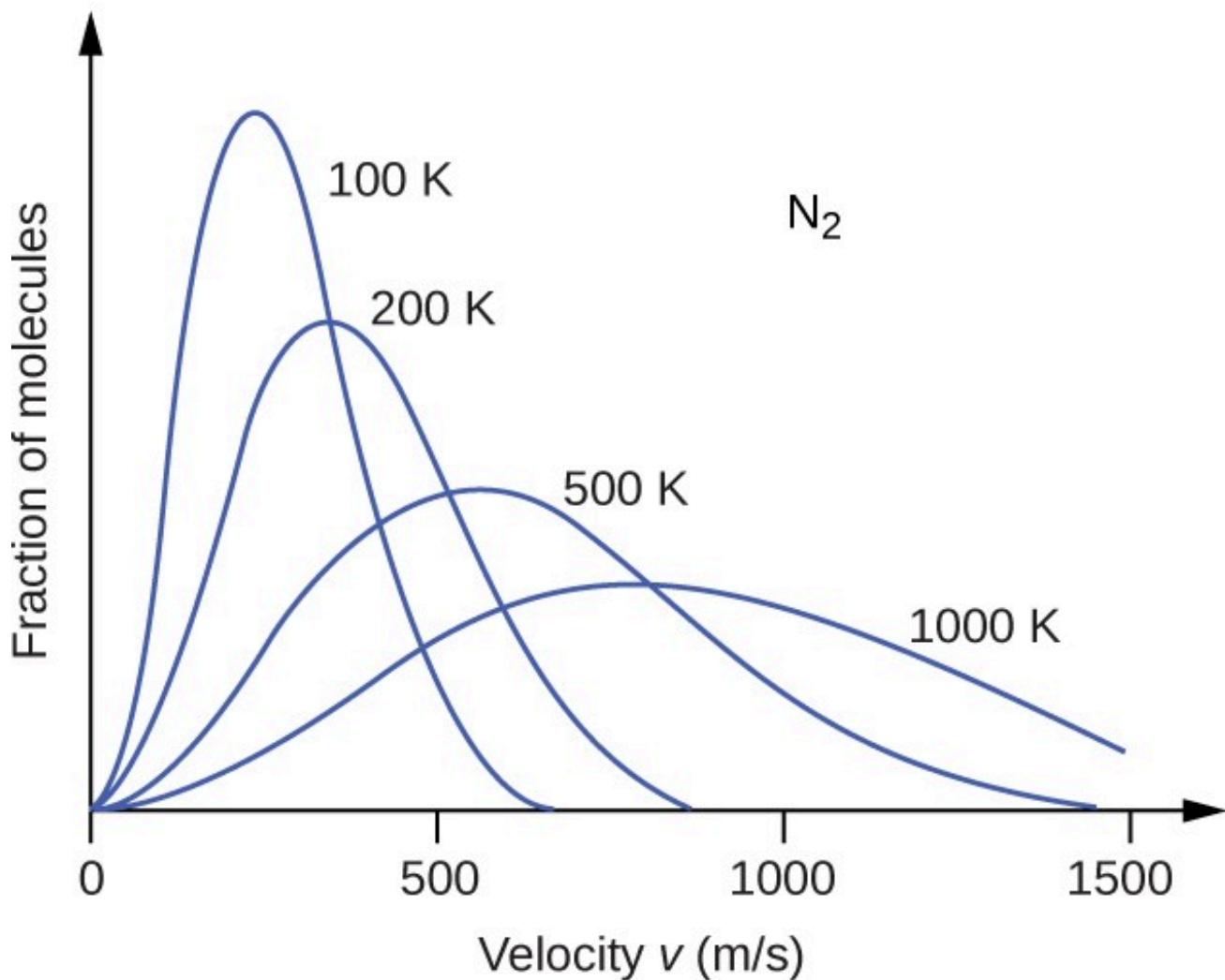
$$u_{\text{rms}} = \sqrt{\frac{3(8.314\text{J/molK})(303\text{K})}{(0.028\text{kg/mol})}} = \sqrt{2.70 \times 10^5 \text{m}^2\text{s}^{-2}} = 519\text{m/s}$$

### Check Your Learning

Calculate the root-mean-square velocity for a mole of oxygen molecules at  $-23^\circ\text{C}$ .

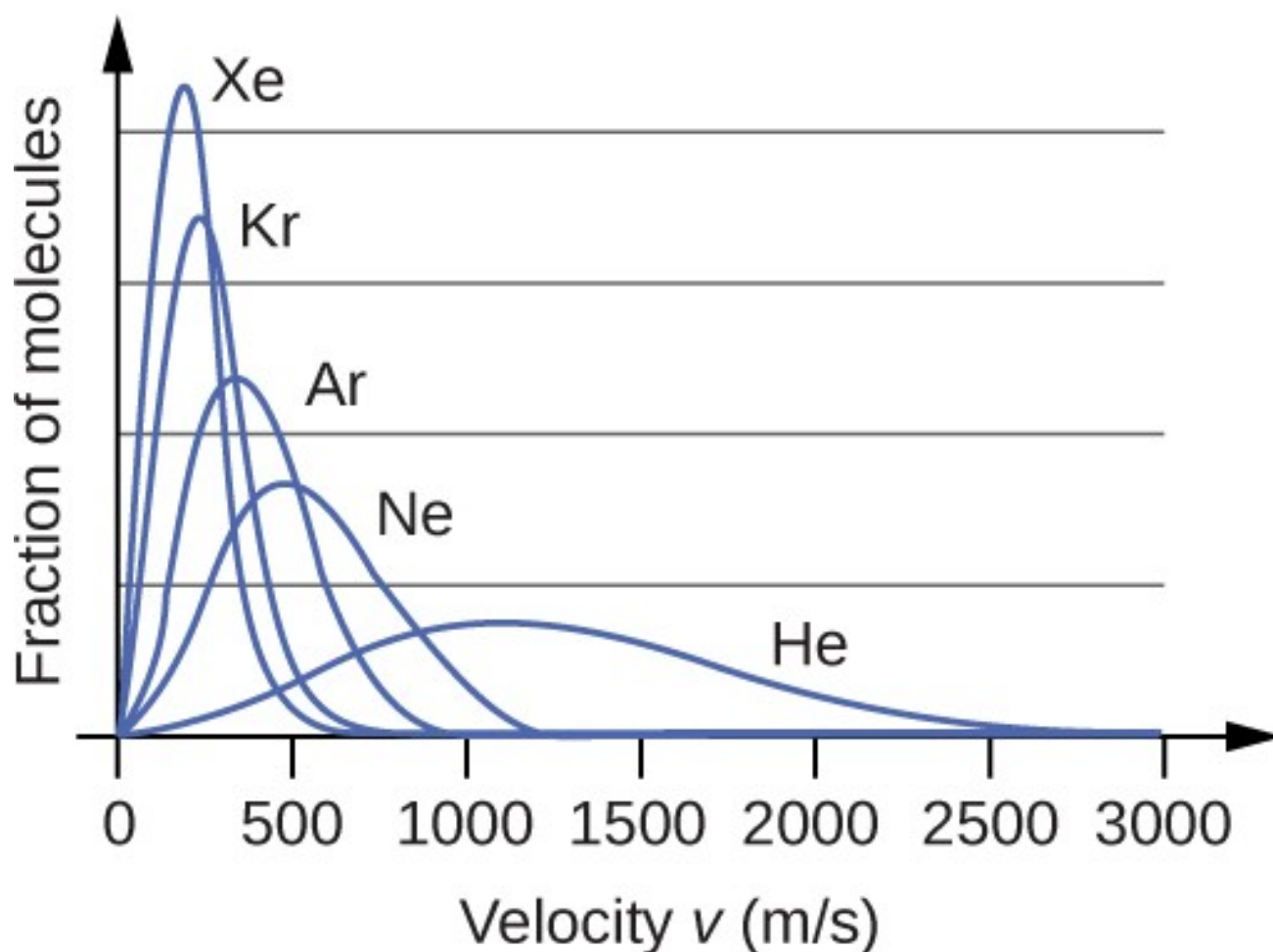
**Answer:** 441 m/s

If the temperature of a gas increases, its  $\text{KE}_{\text{avg}}$  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,  $\text{KE}_{\text{avg}}$  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 8.37**.



**Figure 8.37** 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. By: Rice University [Openstax CC BY NC SA](#)

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 8.38**.



**Figure 8.38** Molecular velocity is directly related to molecular mass. At a given temperature, lighter molecules move faster on average than heavier molecules. By: Rice University [Openstax CC BY NC SA](#)

### Link to Learning

[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:

$$\begin{aligned} u_{\text{rms}} &= \sqrt{\frac{3RT}{M}} \\ M &= \frac{3RT}{u_{\text{rms}}^2} = \frac{3RT}{\bar{u}^2} \\ \frac{\text{effusion rate A}}{\text{effusion rate B}} &= \frac{u_{\text{rms A}}}{u_{\text{rms B}}} = \frac{\sqrt{\frac{3RT}{M_A}}}{\sqrt{\frac{3RT}{M_B}}} = \sqrt{\frac{M_B}{M_A}} \end{aligned}$$

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.

# NON-IDEAL GAS BEHAVIOR (8.6)

OpenStax

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

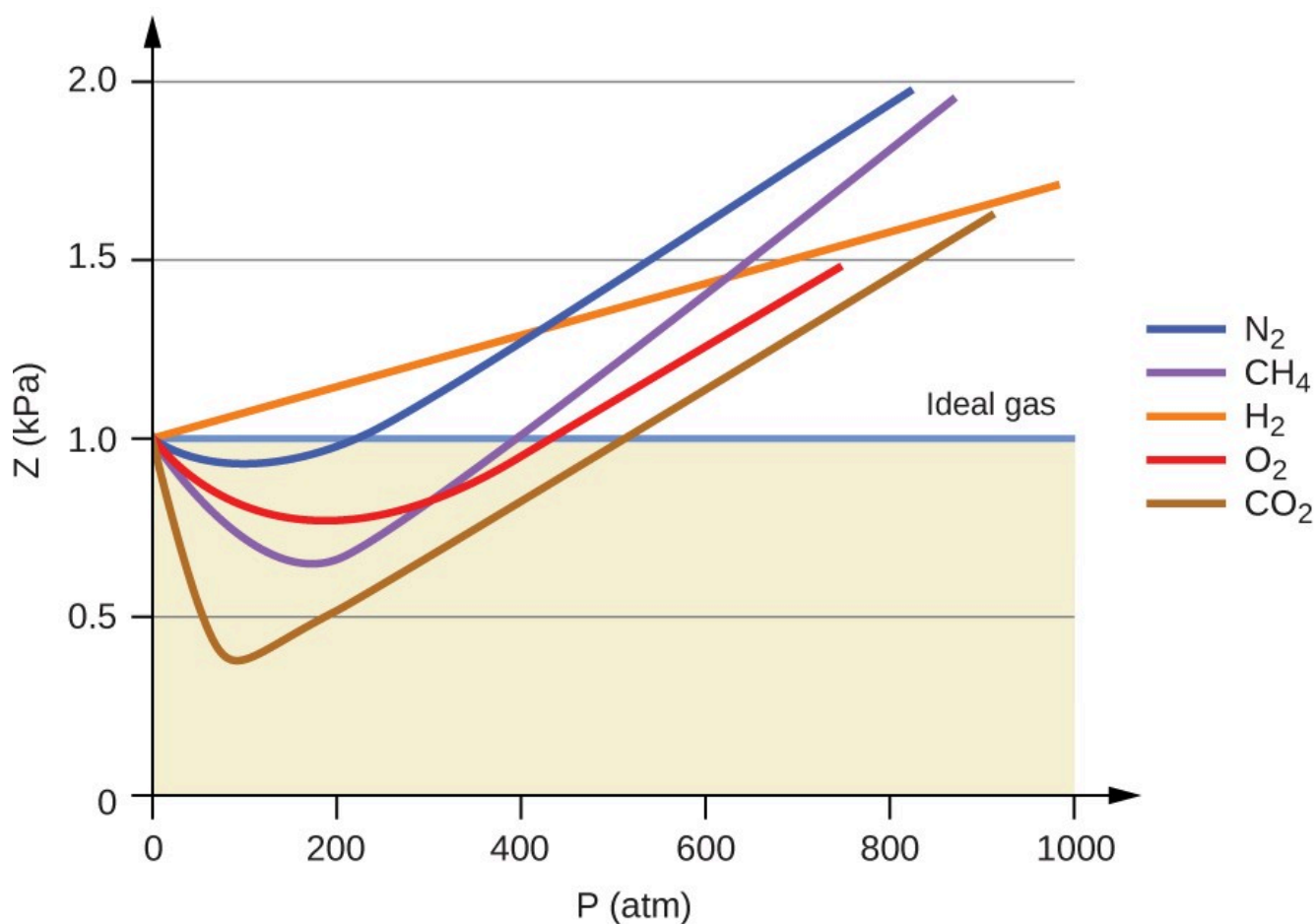
- Describe the physical factors that lead to deviations from ideal gas behavior
- Explain how these factors are represented in the van der Waals equation
- Define compressibility ( $Z$ ) and describe how its variation with pressure reflects non-ideal behavior
- Quantify non-ideal behavior by comparing computations of gas properties using the ideal gas law and the van der Waals equation

Thus far, the ideal gas law,  $PV = nRT$ , has been applied to a variety of different types of problems, ranging from reaction stoichiometry and empirical and molecular formula problems to determining the density and molar mass of a gas. As mentioned in the previous modules of this chapter, however, the behavior of a gas is often non-ideal, meaning that the observed relationships between its pressure, volume, and temperature are not accurately described by the gas laws. In this section, the reasons for these deviations from ideal gas behavior are considered.

One way in which the accuracy of  $PV = nRT$  can be judged is by comparing the actual volume of 1 mole of gas (its molar volume,  $V_m$ ) to the molar volume of an ideal gas at the same temperature and pressure. This ratio is called the **compressibility factor ( $Z$ )** with:

$$Z = \frac{\text{molar volume of gas at same } T \text{ and } P}{\text{molar volume of ideal gas at same } T \text{ and } P} = \left( \frac{PV_m}{RT} \right)_{\text{measured}}$$

Ideal gas behavior is therefore indicated when this ratio is equal to 1, and any deviation from 1 is an indication of non-ideal behavior. **Figure 8.39** shows plots of  $Z$  over a large pressure range for several common gases.



**Figure 8.39** A graph of the compressibility factor ( $Z$ ) vs. pressure shows that gases can exhibit significant deviations from the behavior predicted by the ideal gas law. By: Rice University [Openstax CC BY NC SA](#)

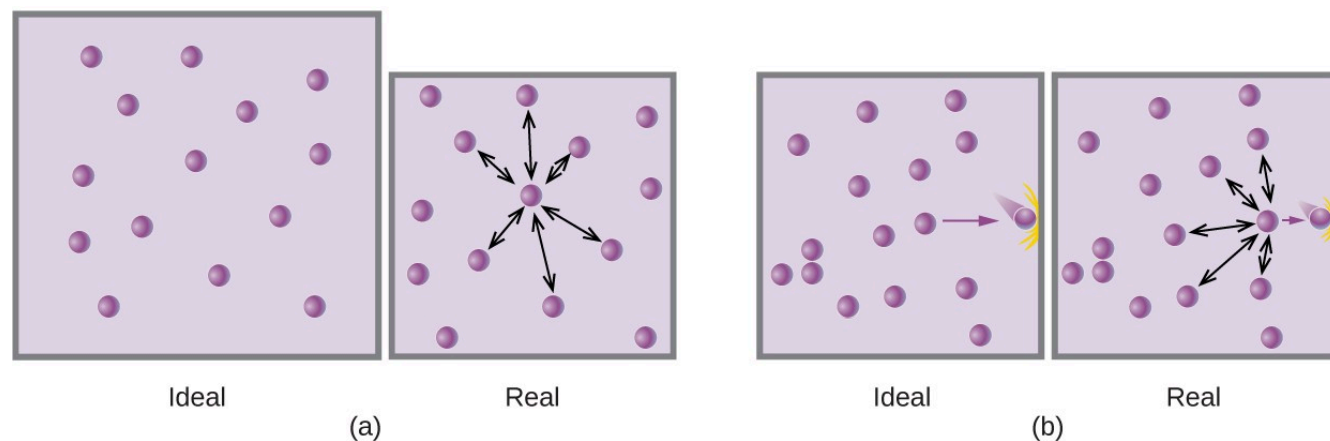
As is apparent from **Figure 8.39**, the ideal gas law does not describe gas behavior well at relatively high pressures. To determine why this is, consider the differences between real gas properties and what is expected of a hypothetical ideal gas.

Particles of a hypothetical ideal gas have no significant volume and do not attract or repel each other. In general, real gases approximate this behavior at relatively low pressures and high temperatures. However, at high pressures, the molecules of a gas are crowded closer together, and the amount of empty space between the molecules is reduced. At these higher pressures, the volume of the gas molecules themselves becomes appreciable relative to the total volume occupied by the gas. The gas therefore becomes less compressible at these high pressures, and although its volume continues to decrease with increasing pressure, this decrease is not *proportional* as predicted by Boyle's law.

At relatively low pressures, gas molecules have practically no attraction for one another because they are (on average) so far apart, and they behave almost like particles of an ideal gas. At higher pressures, however, the force of attraction is also no longer insignificant. This force pulls the molecules a little closer together, slightly decreasing the pressure (if the volume is constant) or decreasing the volume (at constant pressure) (**Figure**



**8.40).** This change is more pronounced at low temperatures because the molecules have lower KE relative to the attractive forces, and so they are less effective in overcoming these attractions after colliding with one another.



**Figure 8.40** (a) Attractions between gas molecules serve to decrease the gas volume at constant pressure compared to an ideal gas whose molecules experience no attractive forces. (b) These attractive forces will decrease the force of collisions between the molecules and container walls, therefore reducing the pressure exerted at constant volume compared to an ideal gas. By: Rice University [Openstax CC BY NC SA](#)

There are several different equations that better approximate gas behavior than the ideal gas law does. The first, and simplest, of these was developed by the Dutch scientist Johannes van der Waals in 1879. The **van der Waals equation** improves upon the ideal gas law by adding two terms: one to account for the volume of the gas molecules and another for the attractive forces between them.

$$PV = nRT \longrightarrow \left( P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

Correction for molecular attraction
Correction for volume of molecules

**Figure 8.41** By: Rice University [Openstax CC BY NC SA](#)

The constant  $a$  corresponds to the strength of the attraction between molecules of a particular gas, and the constant  $b$  corresponds to the size of the molecules of a particular gas. The “correction” to the pressure term in the ideal gas law is  $\frac{n^2 a}{V^2}$ , and the “correction” to the volume is  $nb$ . Note that when  $V$  is relatively large and  $n$  is relatively small, both of these correction terms become negligible, and the van der Waals equation reduces to the ideal gas law,  $PV=nRT$ . Such a condition corresponds to a gas in which a relatively low number of

molecules is occupying a relatively large volume, that is, a gas at a relatively low pressure. Experimental values for the van der Waals constants of some common gases are given in **Table 8.3**.

**Table 8.3 Values of van der Waals Constants for Some Common Gases** By: Rice University [OpenStax CC BY-NC-SA 4.0](#)

Gas		$a$ ( $\text{L}^2 \text{ atm/mol}^2$ )	$b$ ( $\text{L/mol}$ )
$\text{N}_2$	1.39	0.0391	
$\text{O}_2$	1.36	0.0318	
$\text{CO}_2$	3.59	0.0427	
$\text{H}_2\text{O}$	5.46	0.0305	
He	0.0342	0.0237	
$\text{CCl}_4$	20.4	0.1383	

At low pressures, the correction for intermolecular attraction,  $a$ , is more important than the one for molecular volume,  $b$ . At high pressures and small volumes, the correction for the volume of the molecules becomes important because the molecules themselves are incompressible and constitute an appreciable fraction of the total volume. At some intermediate pressure, the two corrections have opposing influences, and the gas appears to follow the relationship given by  $PV = nRT$  over a small range of pressures. This behavior is reflected by the “dips” in several of the compressibility curves shown in **Figure 8.35**. The attractive force between molecules initially makes the gas more compressible than an ideal gas, as pressure is raised ( $Z$  decreases with increasing  $P$ ). At very high pressures, the gas becomes less compressible ( $Z$  increases with  $P$ ), as the gas molecules begin to occupy an increasingly significant fraction of the total gas volume.

Strictly speaking, the ideal gas equation functions well when intermolecular attractions between gas molecules are negligible and the gas molecules themselves do not occupy an appreciable part of the whole volume. These criteria are satisfied under conditions of *low pressure and high temperature*. Under such conditions, the gas is said to behave ideally, and deviations from the gas laws are small enough that they may be disregarded—this is, however, very often not the case.

## EXAMPLE 8.24

## Comparison of Ideal Gas Law and van der Waals Equation

A 4.25-L flask contains 3.46 mol CO<sub>2</sub> at 229 °C. Calculate the pressure of this sample of CO<sub>2</sub>:

- (a) From the ideal gas law.
- (b) From the van der Waals equation.
- (c) Explain the reason(s) for the difference.

## Solution

- (a) From the ideal gas law:

$$P = \frac{nRT}{V} = \frac{3.46 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 502 \text{ K}}{4.25 \text{ L}} = 33.5 \text{ atm}$$

- (b) From the van der Waals equation:

$$\left(P + \frac{n^2 a}{V^2}\right) \times (V - nb) = nRT \longrightarrow P = \frac{nRT}{(V - nb)} - \frac{n^2 a}{V^2}$$

$$P = \frac{3.46 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 502 \text{ K}}{(4.25 \text{ L} - 3.46 \text{ mol} \times 0.0427 \text{ L mol}^{-1})} - \frac{(3.46 \text{ mol})^2 \times 3.59 \text{ L}^2 \text{ atm mol}^{-2}}{(4.25 \text{ L})^2}$$

This finally yields  $P = 32.4 \text{ atm}$ .

- (c) This is not very different from the value from the ideal gas law because the pressure is not very high, and the temperature is not very low. The value is somewhat different because CO<sub>2</sub> molecules do have some volume and attractions between molecules, and the ideal gas law assumes they do not have volume or attractions.

## Check your Learning

A 560-mL flask contains 21.3 g N<sub>2</sub> at 145 °C. Calculate the pressure of N<sub>2</sub>:

- (a) From the ideal gas law.
- (b) From the van der Waals equation.
- (c) Explain the reason(s) for the difference.

**Answer:** (a) 46.562 atm; (b) 46.594 atm; (c) The van der Waals equation takes into account the volume of the gas molecules themselves as well as intermolecular attractions.

# CHAPTER 9: THERMOCHEMISTRY



**Figure 9.1** Sliding a match head along a rough surface initiates a combustion reaction that produces energy in the form of heat and light. By: Rice University [Openstax CC BY NC SA](#)

## Chapter Outline

- Energy Basics
- Calorimetry
- Enthalpy
- Strengths of Ionic and Covalent Bonds

### Introduction

Chemical reactions, such as those that occur when you light a match, involve changes in energy as well as matter. Societies at all levels of development could not function without the energy released by chemical reactions. In 2012, about 85% of US energy consumption came from the combustion of petroleum products, coal, wood, and garbage. We use this energy to produce electricity (38%); to transport food, raw materials, manufactured goods, and people (27%); for industrial production (21%); and to heat and power our homes

and businesses (10%).<sup>1</sup> While these combustion reactions help us meet our essential energy needs, they are also recognized by the majority of the scientific community as a major contributor to global climate change.

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.

The chemical bond is simply another form of energy, and its strength is indicated in exactly the same units as any other process involving energy. That is, in joules (or kilojoules)—or when taken on a molar basis, in J/mol or kJ/mol. All of the principles involving energy we have examined up to now apply to bond energies exactly as they do to all other forms of energy: That is, energy may change form or be absorbed or released, but it cannot be created or destroyed. The energy of a chemical bond is indicated by the bond enthalpy, taken by convention to be the energy required to break a chemical bond. The same energy is released when a chemical bond is formed. Given that a chemical reaction involves breaking some bonds and making others, the enthalpy change for a chemical reaction can be estimated by analyzing the bonds broken and formed during the reaction. While this procedure gives an estimate of the overall enthalpy, it should be noted that a far more precise method involves using enthalpies of formation; the fact that there can be significant differences between, for example, an O–H bond in water and that in acetic acid accounts for the discrepancy in calculating  $\Delta H$  using bond enthalpies versus the use of enthalpies of formation.

---

1. US Energy Information Administration, Primary Energy Consumption by Source and Sector, 2012, [http://www.eia.gov/totalenergy/data/monthly/pdf/flow/css\\_2012\\_energy.pdf](http://www.eia.gov/totalenergy/data/monthly/pdf/flow/css_2012_energy.pdf). Data derived from US Energy Information Administration, Monthly Energy Review (January 2014).

# ENERGY BASICS (9.1)

OpenStax

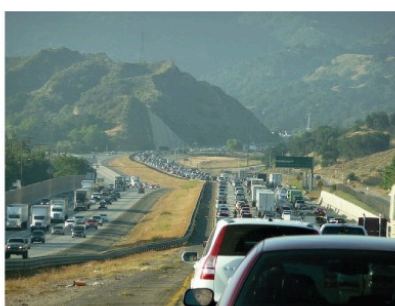
By the end of this section, you will be able to:

- 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

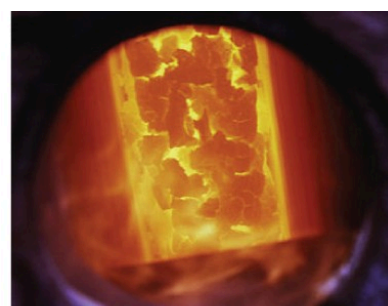
Chemical changes and their accompanying changes in energy are important parts of our everyday world (**Figure 9.2**). The macronutrients in food (proteins, fats, and carbohydrates) undergo metabolic reactions that provide the energy to keep our bodies functioning. We burn a variety of fuels (gasoline, natural gas, coal) to produce energy for transportation, heating, and the generation of electricity. Industrial chemical reactions use enormous amounts of energy to produce raw materials (such as iron and aluminum). Energy is then used to manufacture those raw materials into useful products, such as cars, skyscrapers, and bridges.



(a)



(b)



(c)

**Figure 9.2** The energy involved in chemical changes is important to our daily lives: (a) A cheeseburger for lunch provides the energy you need to get through the rest of the day; (b) the combustion of gasoline provides the energy that moves your car (and you) between home, work, and school; and (c) coke, a processed form of coal, provides the energy needed to convert iron ore into iron, which is essential for making many of the products we use daily. By: Rice University [Openstax](#) CC BY NC SA

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 get their energy by eating plants. Burning coal and petroleum also releases stored solar energy: These fuels are fossilized plant and animal matter.

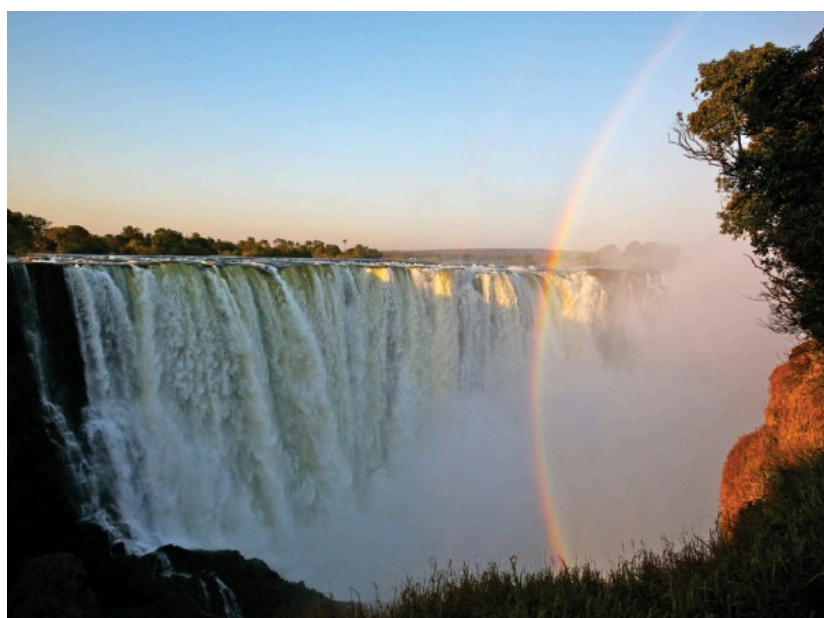
This chapter will introduce the basic ideas of an important area of science concerned with the amount of heat absorbed or released during chemical and physical changes—an area called **thermochemistry**. The concepts introduced in this chapter are widely used in almost all scientific and technical fields. 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 already in 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 9.3**). A battery has potential energy because the chemicals within it can produce electricity that can do work.





(a)



(b)

**Figure 9.3** (a) Water at a higher 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. By: Rice University [Openstax CC BY NC SA](#)

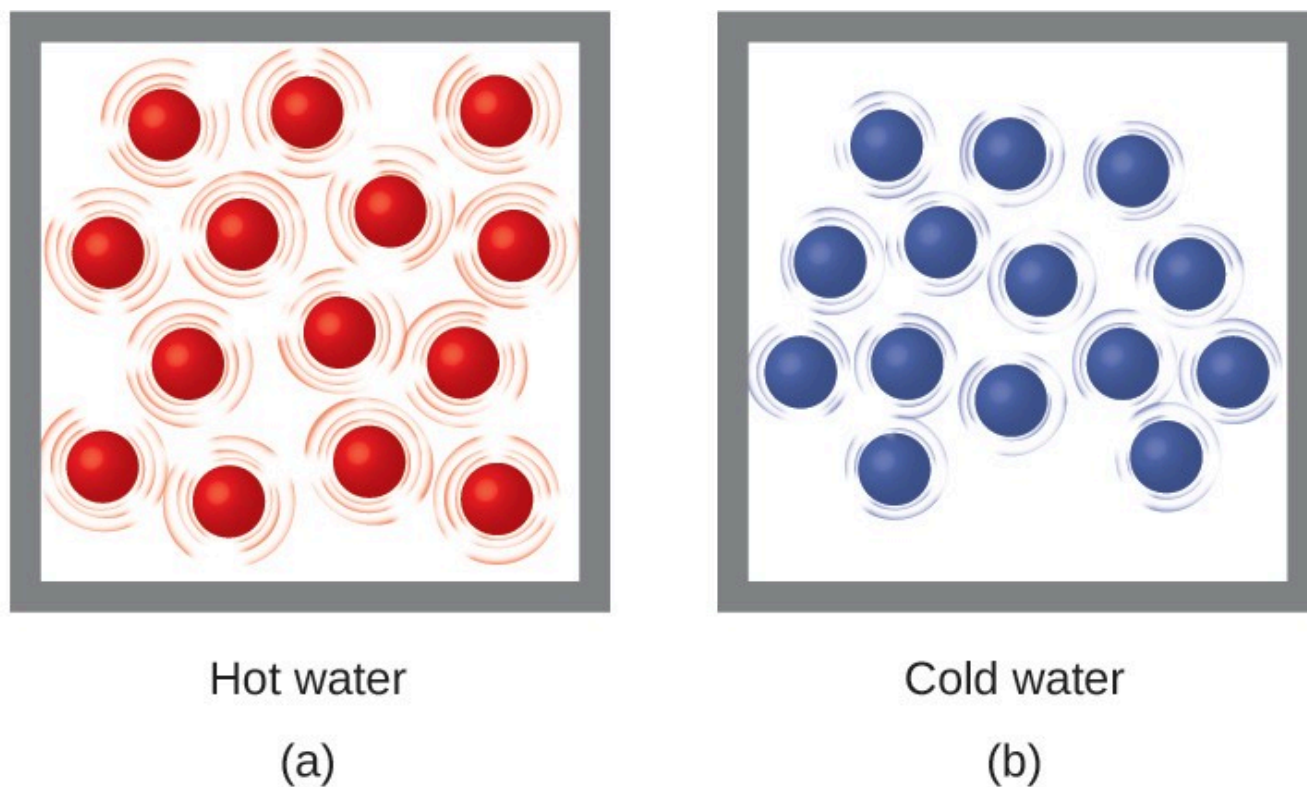
Energy can be converted from one form into another, but all of the energy present before a change occurs always exists in some form after the change is completed. This observation is expressed in the law of conservation of energy: During a chemical or physical change, energy can be neither created nor 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.

## 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 average KE, and we say that the object is “cold” (**Figure 9.4**). Assuming that no chemical reaction or phase change (such as melting or vaporizing) occurs, increasing the amount of thermal energy in a sample of matter will cause its temperature to increase. And assuming that no chemical reaction or phase change (such as condensation or freezing) occurs, decreasing the amount of thermal energy in a sample of matter will cause its temperature to decrease.

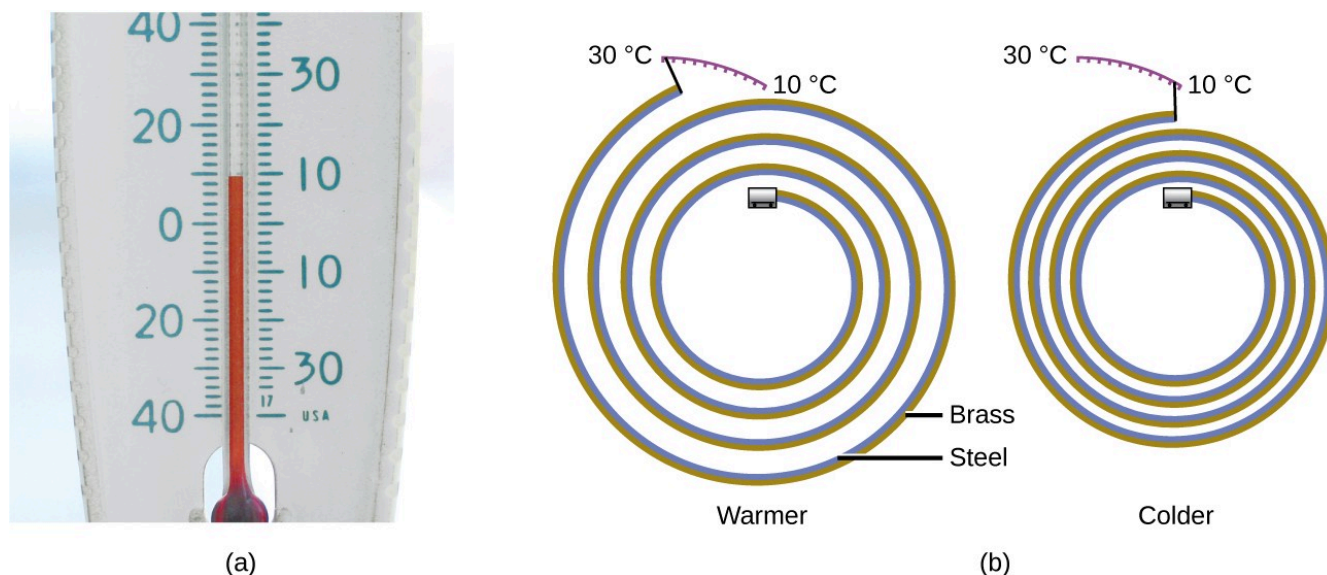


**Figure 9.4** (a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water. By: Rice University [Openstax CC BY NC SA](#)

### Link to Learning

[Click on this interactive simulation](#) to view the effects of temperature on molecular motion.

Most substances expand as their temperature increases and contract as their temperature decreases. This property can be used to measure temperature changes, as shown in **Figure 9.5**. The operation of many thermometers depends on the expansion and contraction of substances in response to temperature changes.



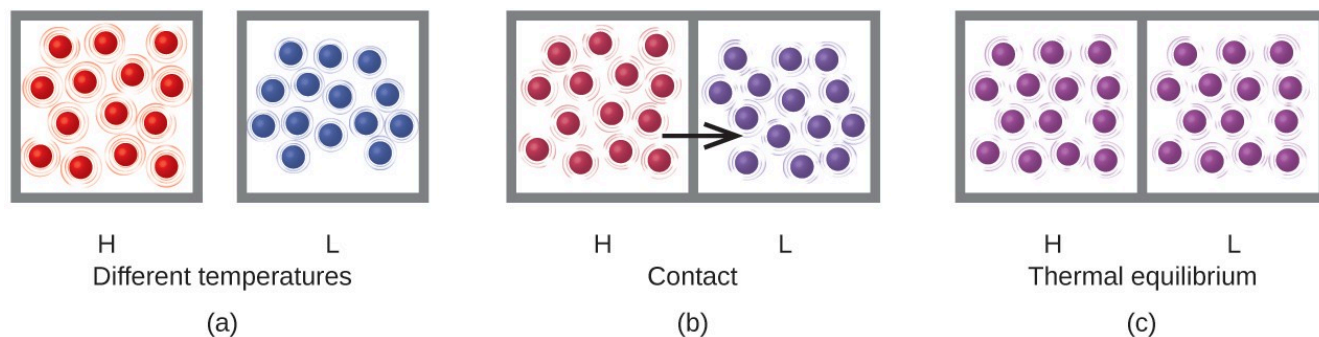
**Figure 9.5** (a) In an alcohol or mercury thermometer, the liquid (dyed red for visibility) expands when heated and contracts when cooled, much more so than the glass tube that contains the liquid. (b) In a bimetallic thermometer, two different metals (such as brass and steel) form a two-layered strip. When heated or cooled, one of the metals (brass) expands or contracts more than the other metal (steel), causing the strip to coil or uncoil. Both types of thermometers have a calibrated scale that indicates the temperature. By: Rice University [Openstax CC BY NC SA](#)

### Link to Learning

The following [demonstration](#) allows one to view the effects of heating and cooling a coiled bimetallic strip.

**Heat ( $q$ )** is the transfer of thermal energy between two bodies at different temperatures. Heat flow (a redundant term but one commonly used) increases the thermal energy of one body and decreases the thermal energy of the other. Suppose we initially have a high-temperature (and high thermal energy) substance (H) and a low-temperature (and low thermal energy) substance (L). The atoms and molecules in H have a higher average KE than those in L. If we place substance H in contact with substance L, the thermal energy will flow spontaneously from substance H to substance L. The temperature of substance H will decrease, as will the

average KE of its molecules; the temperature of substance L will increase, along with the average KE of its molecules. Heat flow will continue until the two substances are at the same temperature (**Figure 9.6**).



**Figure 9.6** (a) Substances H and L are initially at different temperatures, and their atoms have different average kinetic energies. (b) When they contact each other, collisions between the molecules result in the transfer of kinetic (thermal) energy from the hotter to the cooler matter. (c) The two objects reach “thermal equilibrium” when both substances are at the same temperature and their molecules have the same average kinetic energy. By: Rice University [Openstax CC BY NC SA](#)

### Link to Learning

Click on the [PhET simulation](#) to explore energy forms and changes. Visit the Energy Systems tab to create combinations of energy sources, transformation methods, and outputs. Click on Energy Symbols to visualize the transfer of energy.

Matter undergoing chemical reactions and physical changes can release or absorb heat. A change that releases heat is called an **exothermic process**. For example, the combustion reaction that occurs when using an oxyacetylene torch is an exothermic process—this process also releases energy in the form of light as evidenced by the torch’s flame (**Figure 9.7**). A reaction or change that absorbs heat is an **endothermic process**. A cold pack used to treat muscle strains provides an example of an endothermic process. When the substances in the cold pack (water and a salt like ammonium nitrate) are brought together, the resulting process absorbs heat, leading to the sensation of cold.





(a)



(b)

**Figure 9.7** (a) An oxyacetylene torch produces heat by the combustion of acetylene in oxygen. The energy released by this exothermic reaction heats and then melts the metal being cut. The sparks are tiny bits of the molten metal flying away. (b) A cold pack uses an endothermic process to create the sensation of cold. By: Rice University [Openstax CC BY NC SA](https://openstax.org/r/CC-BY-NC-SA)

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  $1 \text{ kg m}^2/\text{s}^2$ , 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 ( $\Delta T$ ) of 1 degree Celsius (or equivalently, 1 kelvin):

$$C = \frac{q}{\Delta T}$$

Heat capacity is determined by both the type and amount of substance that absorbs or releases heat. It is therefore an extensive property—its value is proportional to the amount of the substance.

For example, consider the heat capacities of two cast iron frying pans. The heat capacity of the large pan is five times greater than that of the small pan because, although both are made of the same material, the mass of the large pan is five times greater than the mass of the small pan. More mass means more atoms are present in the larger pan, so it takes more energy to make all of those atoms vibrate faster. The heat capacity of the small

cast iron frying pan is found by observing that it takes 18,150 J of energy to raise the temperature of the pan by 50.0 °C:

$$C_{\text{small pan}} = \frac{18,140 \text{ J}}{50.0 \text{ }^{\circ}\text{C}} = 363 \text{ J/}^{\circ}\text{C}$$

The larger cast iron frying pan, while made of the same substance, requires 90,700 J of energy to raise its temperature by 50.0 °C. The larger pan has a (proportionally) larger heat capacity because the larger amount of material requires a (proportionally) larger amount of energy to yield the same temperature change:

$$C_{\text{large pan}} = \frac{90,700 \text{ J}}{50.0 \text{ }^{\circ}\text{C}} = 1814 \text{ J/}^{\circ}\text{C}$$

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):

$$c = \frac{q}{m\Delta T}$$

Specific heat capacity depends only on the kind of substance absorbing or releasing heat. It is an intensive property—the type, but not the amount, of the substance is all that matters. For example, the small cast iron frying pan has a mass of 808 g. The specific heat of iron (the material used to make the pan) is therefore:

$$c_{\text{iron}} = \frac{18,140 \text{ J}}{(808 \text{ g})(50.0 \text{ }^{\circ}\text{C})} = 0.449 \text{ J/g }^{\circ}\text{C}$$

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:

$$c_{\text{iron}} = \frac{90,700 \text{ J}}{(4040 \text{ g})(50.0 \text{ }^{\circ}\text{C})} = 0.449 \text{ J/g }^{\circ}\text{C}$$

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 9.8**).



**Figure 9.8** Because of 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. By: Rice University [Openstax CC BY NC SA](#)

Water has a relatively high specific heat (about  $4.2 \text{ J/g } ^\circ\text{C}$  for the liquid and  $2.09 \text{ J/g } ^\circ\text{C}$  for the solid); most metals have much lower specific heats (usually less than  $1 \text{ J/g } ^\circ\text{C}$ ). 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 9.1**.

**Table 9.1 Specific Heats of Common Substances at 25 °C and 1 bar By: Rice University [OpenStax CC BY-NC-SA 4.0](#)**

Substance	Symbol ( <i>state</i> )	Specific Heat (J/g °C)
helium	He( <i>g</i> )	5.193
water	H <sub>2</sub> O( <i>l</i> )	4.184
ethanol	C <sub>2</sub> H <sub>6</sub> O( <i>l</i> )	2.376
ice	H <sub>2</sub> O( <i>s</i> )	2.093 (at −10 °C)
water vapor	H <sub>2</sub> O( <i>g</i> )	1.864
nitrogen	N <sub>2</sub> ( <i>g</i> )	1.040
air	–	1.007
oxygen	O <sub>2</sub> ( <i>g</i> )	0.918
aluminum	Al( <i>s</i> )	0.897
carbon dioxide	CO <sub>2</sub> ( <i>g</i> )	0.853
argon	Ar( <i>g</i> )	0.522
iron	Fe( <i>s</i> )	0.449
copper	Cu( <i>s</i> )	0.385
lead	Pb( <i>s</i> )	0.130
gold	Au( <i>s</i> )	0.129
silicon	Si( <i>s</i> )	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  $\Delta T$  (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 9.1

### Measuring Heat

A flask containing  $8.0 \times 10^2$  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,  $8.0 \times 10^2$  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  $8.0 \times 10^2$  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:

$$\begin{aligned} q &= c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}}) \\ &= (4.184 \text{ J/g } ^\circ\text{C}) \times (8.0 \times 10^2 \text{ g}) \times (85 - 21) ^\circ\text{C} \\ &= (4.184 \text{ J/g } ^\circ\text{C}) \times (8.0 \times 10^2 \text{ g}) \times (64) ^\circ\text{C} \\ &= 210,000 \text{ J } (= 2.1 \times 10^5 \text{ kJ}) \end{aligned}$$

Because the temperature increased, the water-absorbed heat and  $q$  is positive.

### Check Your Learning

How much heat, in joules, must be added to a 502 g iron skillet to increase its temperature from 25 °C to 250 °C? The specific heat of iron is 0.449 J/g °C.

**Answer:**  $5.12 \times 10^6$  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.



An interactive H5P element has been excluded from this version of the text. You can view it online here:

<https://louis.pressbooks.pub/chemistry1/?p=492#h5p-2>

## Example 9.2

### 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:

$$6640 \text{ J} = c \times (348 \text{ g}) \times (43.6 - 22.4) ^\circ\text{C}$$

Solving:

$$c = \frac{6640 \text{ J}}{(348 \text{ g}) \times (21.2 ^\circ\text{C})} = 0.900 \text{ J/g}^\circ\text{C}$$

Comparing this value with the values in Table 9.1, this value matches the specific heat of aluminum, which suggests that the unknown metal may be aluminum.

### Check Your Learning

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:**  $c = 0.451 \text{ J/g}^\circ\text{C}$ ; the metal is likely to be iron

## Chemistry in Everyday Life

### Solar Thermal Energy Power Plants

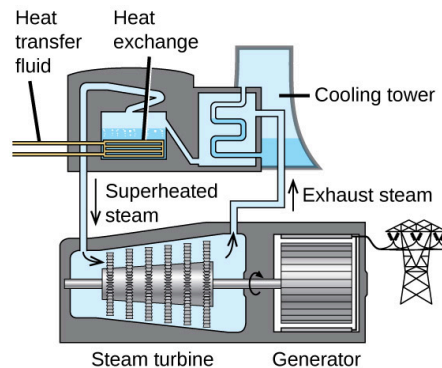
The sunlight that reaches the earth contains thousands of times more energy than we presently capture. Solar thermal systems provide one possible solution to the problem of converting energy from the sun into energy we can use. Large-scale solar thermal plants have different design specifics, but all 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 9.9**). 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.



(a)



(b)

**Figure 9.9** This solar thermal plant uses parabolic trough mirrors to concentrate sunlight. By: Rice University  
[Openstax CC BY NC SA](#)

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 9.10**). 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 9.10** (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. By: Rice University [Openstax CC BY NC SA](#)

# CALORIMETRY (9.2)

OpenStax

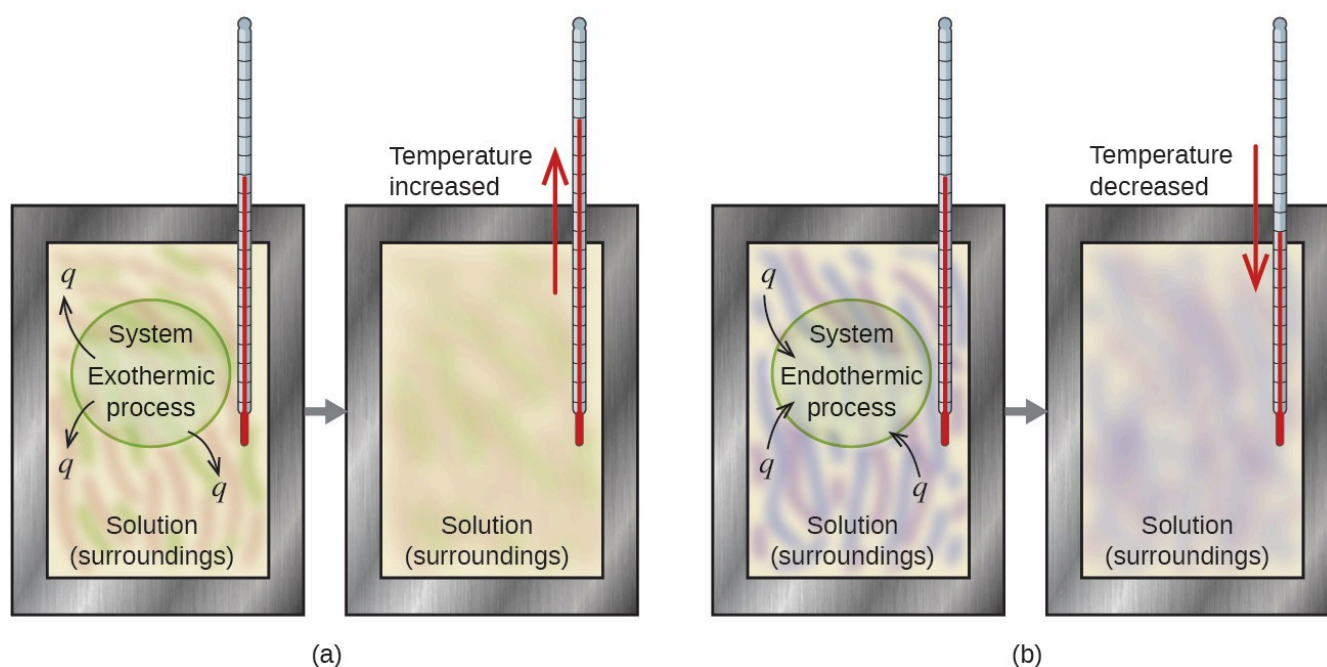
---

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

- Explain the technique of calorimetry
- Calculate and interpret heat and related properties using typical calorimetry data

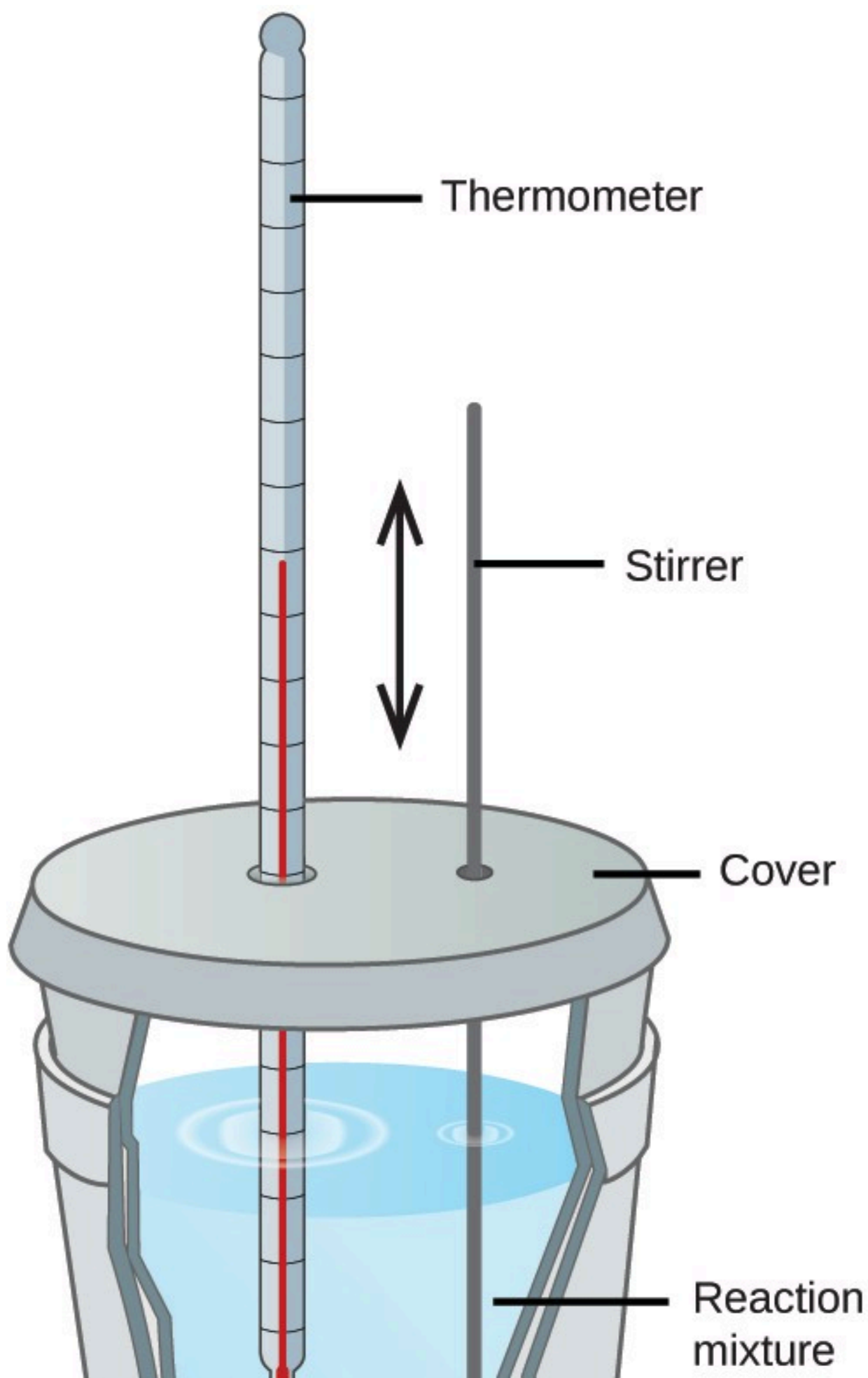
One technique we can use to measure the amount of heat involved in a chemical or physical process is known as **calorimetry**. Calorimetry is used to measure amounts of heat transferred to or from a substance. To do so, the heat is exchanged with a calibrated object (calorimeter). The temperature change measured by the calorimeter is used to derive the amount of heat transferred by the process under study. The measurement of heat transfer using this approach requires the definition of a **system** (the substance or substances undergoing the chemical or physical change) and its **surroundings** (all other matter, including components of the measurement apparatus, that serve to either provide heat to the system or absorb heat from the system).

A **calorimeter** is a device used to measure the amount of heat involved in a chemical or physical process. For example, when an exothermic reaction occurs in solution in a calorimeter, the heat produced by the reaction is absorbed by the solution, which increases its temperature. When an endothermic reaction occurs, the heat required is absorbed from the thermal energy of the solution, which decreases its temperature (**Figure 9.11**). The temperature change, along with the specific heat and mass of the solution, can then be used to calculate the amount of heat involved in either case.



**Figure 9.11** In a calorimetric determination, either (a) an exothermic process occurs and heat,  $q$ , is negative, indicating that thermal energy is transferred from the system to its surroundings, or (b) an endothermic process occurs and heat,  $q$ , is positive, indicating that thermal energy is transferred from the surroundings to the system. By: Rice University [Openstax CC BY NC SA](#)

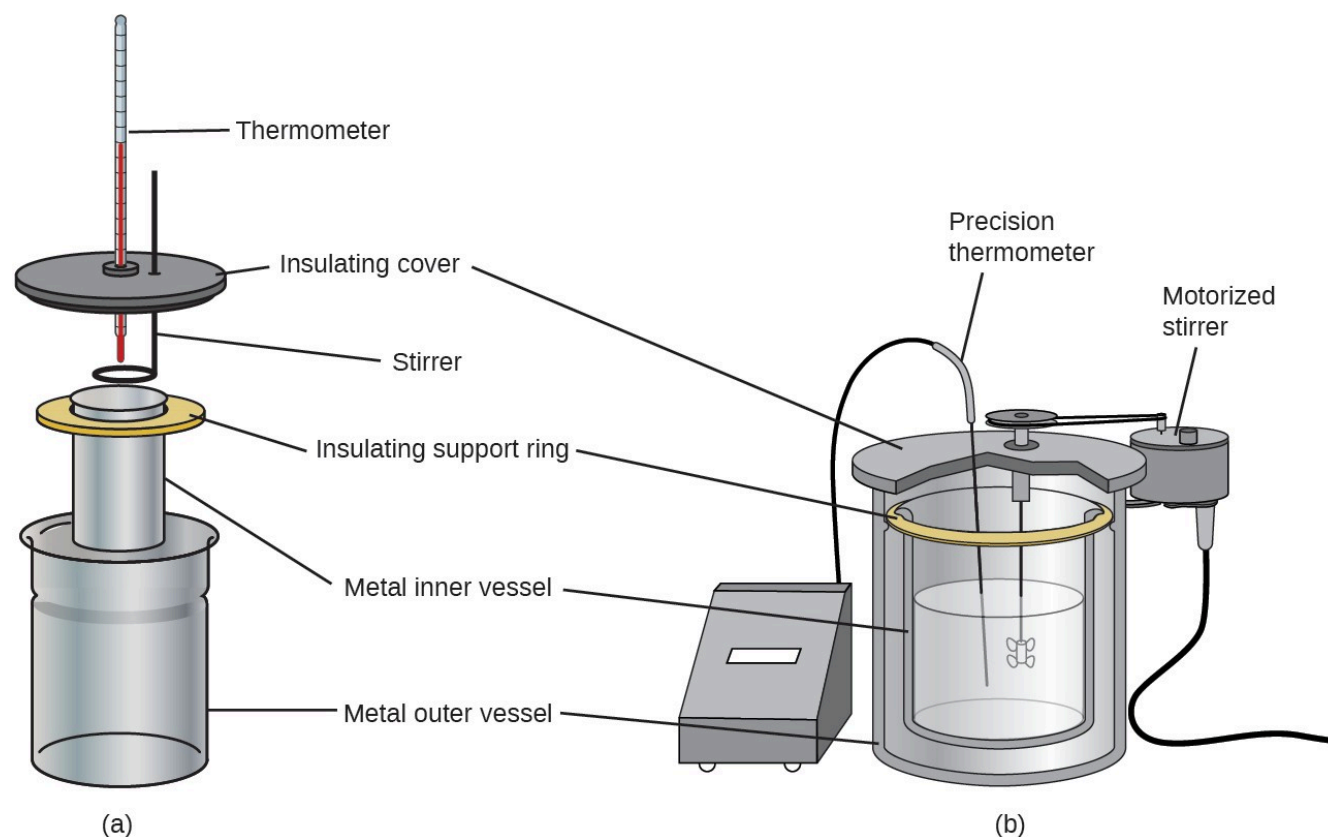
Scientists use well-insulated calorimeters that all but prevent the transfer of heat between the calorimeter and its environment, which effectively limits the “surroundings” to the nonsystem components of the calorimeter (and the calorimeter itself). This enables the accurate determination of the heat involved in chemical processes, the energy content of foods, and so on. General chemistry students often use simple calorimeters constructed from polystyrene cups (**Figure 9.12**). These easy-to-use “coffee cup” calorimeters allow more heat exchange with the outside environment and therefore produce less accurate energy values.





**Figure 9.12** A simple calorimeter can be constructed from two polystyrene cups. A thermometer and stirrer extend through the cover into the reaction mixture. By: Rice University [Openstax CC BY NC SA](#)

Commercial solution calorimeters are also available. Relatively inexpensive calorimeters often consist of two thin-walled cups that are nested in a way that minimizes thermal contact during use, along with an insulated cover, handheld stirrer, and simple thermometer. More expensive calorimeters used for industry and research typically have a well-insulated, fully enclosed reaction vessel, motorized stirring mechanism, and a more accurate temperature sensor (**Figure 9.13**).



**Figure 9.13** Commercial solution calorimeters range from (a) simple, inexpensive models for student use to (b) expensive, more accurate models for industry and research. By: Rice University [Openstax CC BY NC SA](#)

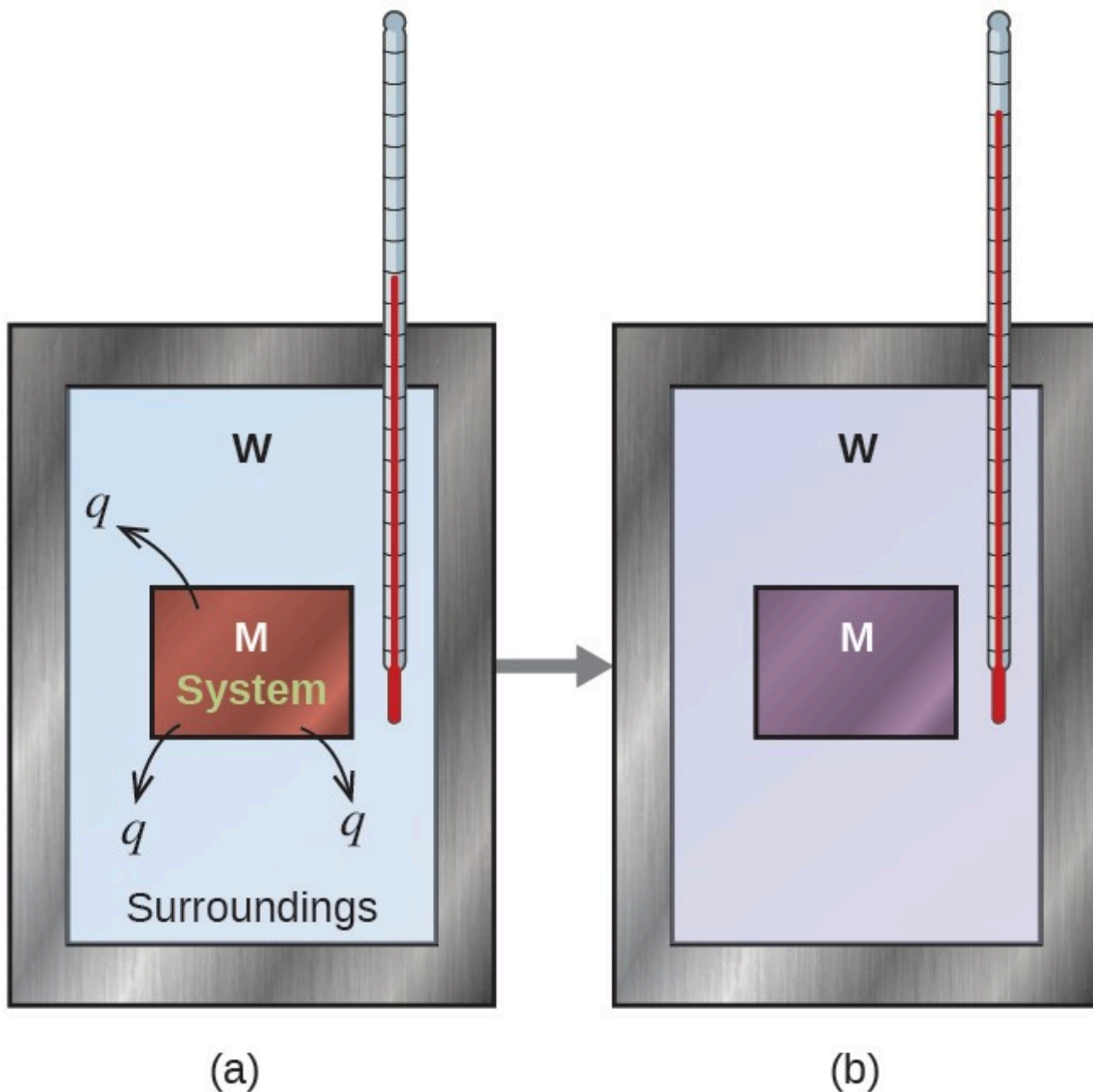
Before discussing the calorimetry of chemical reactions, consider a simpler example that illustrates the core idea behind calorimetry. Suppose we initially have a high-temperature substance, such as a hot piece of metal (M), and a low-temperature substance, such as cool water (W). If we place the metal in the water, heat will flow from M to W. The temperature of M will decrease, and the temperature of W will increase, until the two substances have the same temperature—that is, when they reach thermal equilibrium (**Figure 9.14**). If this occurs in a calorimeter, ideally all of this heat transfer occurs between the two substances, with no heat gained or lost by either its external environment. Under these ideal circumstances, the net heat change is zero:

$$q_{\text{substance M}} + q_{\text{substance W}} = 0$$

This relationship can be rearranged to show that the heat gained by substance M is equal to the heat lost by substance W:

$$q_{\text{substance M}} = -q_{\text{substance W}}$$

The magnitude of the heat (change) is therefore the same for both substances, and the negative sign merely shows that  $q_{\text{substance M}}$  and  $q_{\text{substance W}}$  are opposite in direction of heat flow (gain or loss) but does not indicate the arithmetic sign of either  $q$  value (that is determined by whether the matter in question gains or loses heat, per definition). In the specific situation described,  $q_{\text{substance M}}$  is a negative value, and  $q_{\text{substance W}}$  is positive, since heat is transferred from M to W.



**Figure 9.14** In a simple calorimetry process, (a) heat,  $q$ , is transferred from the hot metal, M, to the cool water, W, until (b) both are at the same temperature. By: Rice University [Openstax CC BY NC SA](#)

## EXAMPLE 9.3

## Heat Transfer between Substances at Different Temperatures

A 360.0-g piece of rebar (a steel rod used for reinforcing concrete) is dropped into 425 mL of water at 24.0 °C. The final temperature of the water was measured as 42.7 °C. Calculate the initial temperature of the piece of rebar. Assume the specific heat of steel is approximately the same as that for iron (Table 9.1) and that all heat transfer occurs between the rebar and the water (there is no heat exchange with the surroundings).

## Solution

The temperature of the water increases from 24.0 °C to 42.7 °C, so the water absorbs heat. That heat came from the piece of rebar, which initially was at a higher temperature. Assuming that all heat transfer was between the rebar and the water, with no heat “lost” to the outside environment, then *heat given off by rebar* = *-heat taken in by water*, or:

$q_{\text{rebar}} = -q_{\text{water}}$  Since we know how heat is related to other measurable quantities, we have:

$(c \times m \times \Delta T)_{\text{rebar}} = -(c \times m \times \Delta T)_{\text{water}}$  Letting f = final and i = initial, in expanded form, this becomes:

$$c_{\text{rebar}} \times m_{\text{rebar}} \times (T_{\text{f, rebar}} - T_{\text{i, rebar}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{\text{f, water}} - T_{\text{i, water}})$$

The density of water is approximately 1.0 g/mL, so 425 mL has a mass of about 425 g (two significant figures). The specific heat of water is approximately 4.184 J/g °C, so we use that for the specific heat of the solution. Substituting these values gives:

$$(0.449 \text{ J/g } ^\circ\text{C})(360.0 \text{ g})(42.7 ^\circ\text{C} - T_{\text{i, rebar}}) = -(4.184 \text{ J/g } ^\circ\text{C})(425 \text{ g})(42.7 ^\circ\text{C} - 24.0 ^\circ\text{C})$$

$$T_{\text{i, rebar}} = \frac{(4.184 \text{ J/g } ^\circ\text{C})(425 \text{ g})(42.7 ^\circ\text{C} - 24.0 ^\circ\text{C})}{(0.449 \text{ J/g } ^\circ\text{C})(360.0 \text{ g})} + 42.7 ^\circ\text{C}$$

Solving this gives  $T_{\text{i, rebar}} = 248 ^\circ\text{C}$ , so the initial temperature of the rebar was 248 °C.

## Check Your Learning

A 248-g piece of copper is dropped into 390 mL of water at 22.6 °C. The final temperature of the water was measured as 39.9 °C. Calculate the initial temperature of the piece of copper. Assume that all heat transfer occurs between the copper and the water.

**Answer:** The initial temperature of the copper was 335.6 °C.

This method can also be used to determine other quantities, such as the specific heat of an unknown metal.

## EXAMPLE 9.4

### Identifying a Metal by Measuring Specific Heat

A 59.7-g piece of metal that had been submerged in boiling water was quickly transferred into 60.0 mL of water initially at 22.0 °C. The final temperature is 28.5 °C. Use these data to determine the specific heat of the metal. Use this result to identify the metal.

#### Solution

Assuming perfect heat transfer, *heat given off by metal* = *-heat taken in by water*, or:

$q_{\text{metal}} = -q_{\text{water}}$  In expanded form, this is:

$$c_{\text{metal}} \times m_{\text{metal}} \times (T_{\text{f,metal}} - T_{\text{i, metal}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{\text{f,water}} - T_{\text{i,water}})$$

Noting that since the metal was submerged in boiling water, its initial temperature was 100.0 °C and that for water, 60.0 mL = 60.0 g, we have:

$$(c_{\text{metal}})(59.7 \text{ g})(28.5 \text{ °C} - 100.0 \text{ °C}) = -(4.18 \text{ J/g °C})(60.0 \text{ g})(28.5 \text{ °C} - 22.0 \text{ °C})$$

Solving this:

$$c_{\text{metal}} = \frac{-(4.184 \text{ J/g °C})(60.0 \text{ g})(6.5 \text{ °C})}{(59.7 \text{ g})(-71.5 \text{ °C})} = 0.38 \text{ J/g °C}$$

Comparing this with values in Table 9.1, our experimental specific heat is closest to the value for copper (0.39 J/g °C), so we identify the metal as copper.

### Check Your Learning

A 92.9-g piece of a silver/gray metal is heated to 178.0 °C and then quickly transferred into 75.0

mL of water initially at 24.0 °C. After 5 minutes, both the metal and the water have reached the same temperature: 29.7 °C. Determine the specific heat and the identity of the metal. (Note: You should find that the specific heat is close to that of two different metals. Explain how you can confidently determine the identity of the metal.)

**Answer:**  $c_{\text{metal}} = 0.13 \text{ J/g } ^\circ\text{C}$

This specific heat is close to that of either gold or lead. It would be difficult to determine which metal this was based solely on the numerical values. However, the observation that the metal is silver/gray in addition to the value for the specific heat indicates that the metal is lead.

When we use calorimetry to determine the heat involved in a chemical reaction, the same principles we have been discussing apply. The amount of heat absorbed by the calorimeter is often small enough that we can neglect it (though not for highly accurate measurements, as discussed later), and the calorimeter minimizes energy exchange with the outside environment. Because energy is neither created nor destroyed during a chemical reaction, the heat produced or consumed in the reaction (the “system”),  $q_{\text{reaction}}$ , plus the heat absorbed or lost by the solution (the “surroundings”),  $q_{\text{solution}}$ , must add up to zero:

$$q_{\text{reaction}} + q_{\text{solution}} = 0$$

This means that the amount of heat produced or consumed in the reaction equals the amount of heat absorbed or lost by the solution:

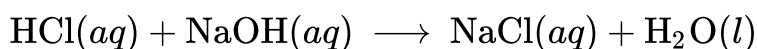
$$q_{\text{reaction}} = -q_{\text{solution}}$$

This concept lies at the heart of all calorimetry problems and calculations.

## EXAMPLE 9.5

### Heat Produced by an Exothermic Reaction

When 50.0 mL of 1.00 M  $\text{HCl}(aq)$  and 50.0 mL of 1.00 M  $\text{NaOH}(aq)$ , both at 22.0 °C, are added to a coffee cup calorimeter, the temperature of the mixture reaches a maximum of 28.9 °C. What is the approximate amount of heat produced by this reaction?



## Solution

To visualize what is going on, imagine that you could combine the two solutions so quickly that no reaction took place while they mixed; then after mixing, the reaction took place. At the instant of mixing, you have 100.0 mL of a mixture of HCl and NaOH at 22.0 °C. The HCl and NaOH then react until the solution temperature reaches 28.9 °C.

The heat given off by the reaction is equal to that taken in by the solution. Therefore:

$$q_{\text{reaction}} = -q_{\text{solution}}$$

(It is important to remember that this relationship only holds if the calorimeter does not absorb any heat from the reaction, and there is no heat exchange between the calorimeter and the outside environment.)

Next, we know that the heat absorbed by the solution depends on its specific heat, mass, and temperature change:

$q_{\text{solution}} = (c \times m \times \Delta T)_{\text{solution}}$  To proceed with this calculation, we need to make a few more reasonable assumptions or approximations. Since the solution is aqueous, we can proceed as if it were water in terms of its specific heat and mass values. The density of water is approximately 1.0 g/mL, so 100.0 mL has a mass of about  $1.0 \times 10^2$  g (two significant figures). The specific heat of water is approximately 4.184 J/g °C, so we use that for the specific heat of the solution. Substituting these values gives:

$$q_{\text{solution}} = (4.184 \text{ J/g } ^\circ\text{C})(1.0 \times 10^2 \text{ g})(28.9 ^\circ\text{C} - 22.0 ^\circ\text{C}) = 2.9 \times 10^3 \text{ J}$$

Finally, since we are trying to find the heat of the reaction, we have:

$$q_{\text{reaction}} = -q_{\text{solution}} = -2.9 \times 10^3 \text{ J}$$

The negative sign indicates that the reaction is exothermic. It produces 2.9 kJ of heat.

## Check Your Learning

When 100 mL of 0.200 M NaCl(aq) and 100 mL of 0.200 M AgNO<sub>3</sub>(aq), both at 21.9 °C, are mixed in a coffee cup calorimeter, the temperature increases to 23.5 °C as solid AgCl forms. How much heat is produced by this precipitation reaction? What assumptions did you make to determine your value?

**Answer:**  $1.34 \times 10^3$  J; assume no heat is absorbed by the calorimeter, no heat is exchanged

between the calorimeter and its surroundings, and that the specific heat and mass of the solution are the same as those for water.

## Chemistry in Everyday Life

### Thermochemistry of Hand Warmers

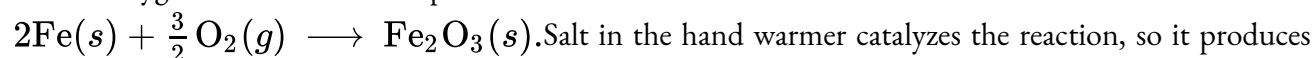
When working or playing outdoors on a cold day, you might use a hand warmer to warm your hands (**Figure 9.15**). A common reusable hand warmer contains a supersaturated solution of  $\text{NaC}_2\text{H}_3\text{O}_2$  (sodium acetate) and a metal disc. Bending the disk creates nucleation sites around which the metastable  $\text{NaC}_2\text{H}_3\text{O}_2$  quickly crystallizes (a later chapter on solutions will investigate saturation and supersaturation in more detail).

The process  $\text{NaC}_2\text{H}_3\text{O}_2(aq) \longrightarrow \text{NaC}_2\text{H}_3\text{O}_2(s)$  is exothermic, and the heat produced by this process is absorbed by your hands, thereby warming them (at least for a while). If the hand warmer is reheated, the  $\text{NaC}_2\text{H}_3\text{O}_2$  redissolves and can be reused.



**Figure 9.15** Chemical hand warmers produce heat that warms your hand on a cold day. In this one, you can see the metal disc that initiates the exothermic precipitation reaction. By: Rice University [Openstax](#) [CC BY NC SA](#)

Another common hand warmer produces heat when it is ripped open, exposing iron and water in the hand warmer to oxygen in the air. One simplified version of this exothermic reaction is



Salt in the hand warmer catalyzes the reaction, so it produces heat more rapidly; cellulose, vermiculite, and activated carbon help distribute the heat evenly. Other types of hand warmers use lighter fluid (a platinum catalyst helps lighter fluid oxidize exothermically), charcoal (charcoal oxidizes in a special case), or electrical units that produce heat by passing an electrical current from a battery through resistive wires.

## Link to Learning

[This link](#) shows the precipitation reaction that occurs when the disk in a chemical hand warmer is flexed.

## EXAMPLE 9.6

### Heat Flow in an Instant Ice Pack

When solid ammonium nitrate dissolves in water, the solution becomes cold. This is the basis for an “instant ice pack” (**Figure 9.16**). When 3.21 g of solid  $\text{NH}_4\text{NO}_3$  dissolves in 50.0 g of water at 24.9 °C in a calorimeter, the temperature decreases to 20.3 °C.

Calculate the value of  $q$  for this reaction and explain the meaning of its arithmetic sign. State any assumptions that you made.





**Figure 9.16** An instant cold pack consists of a bag containing solid ammonium nitrate and a second bag of water. When the bag of water is broken, the pack becomes cold because the dissolution of ammonium nitrate is an endothermic process that removes thermal energy from the water. The cold pack then removes thermal energy from your body. By: Rice University [Openstax CC BY NC SA](#)

## Solution

We assume that the calorimeter prevents heat transfer between the solution and its external environment (including the calorimeter itself), in which case:

$$q_{\text{rxn}} = -q_{\text{soln}}$$

with “rxn” and “soln” used as shorthand for “reaction” and “solution,” respectively.

Assuming also that the specific heat of the solution is the same as that for water, we have:

$$\begin{aligned}
 q_{\text{rxn}} &= -q_{\text{soln}} = -(c \times m \times \Delta T)_{\text{soln}} \\
 &= -[(4.184 \text{ J/g } ^\circ\text{C}) \times (53.2 \text{ g}) \times (20.3 ^\circ\text{C} - 24.9 ^\circ\text{C})] \\
 &= -[(4.184 \text{ J/g } ^\circ\text{C}) \times (53.2 \text{ g}) \times (-4.6 ^\circ\text{C})] \\
 &+ 1.0 \times 10^3 \text{ J} = +1.0 \text{ kJ}
 \end{aligned}$$

The positive sign for  $q$  indicates that the dissolution is an endothermic process.

### Check Your Learning

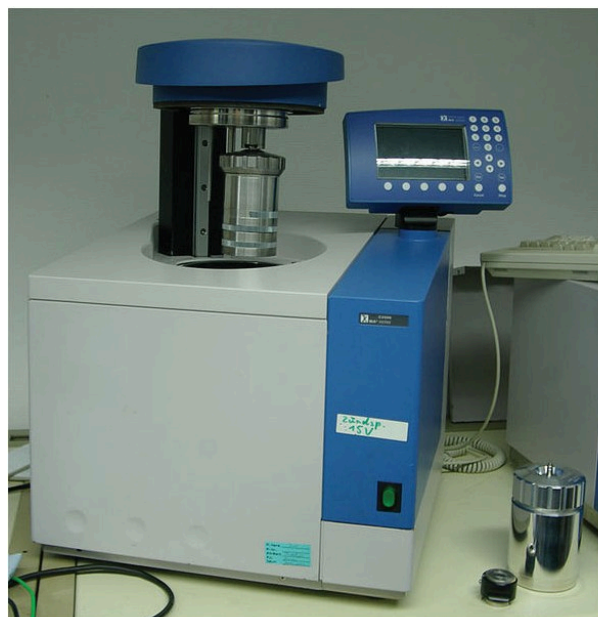
When a 3.00-g sample of KCl was added to  $3.00 \times 10^2$  g of water in a coffee cup calorimeter, the temperature decreased by  $1.05 ^\circ\text{C}$ . How much heat is involved in the dissolution of the KCl? What assumptions did you make?

**Answer:** 1.33 kJ; assume that the calorimeter prevents heat transfer between the solution and its external environment (including the calorimeter itself) and that the specific heat of the solution is the same as that for water.

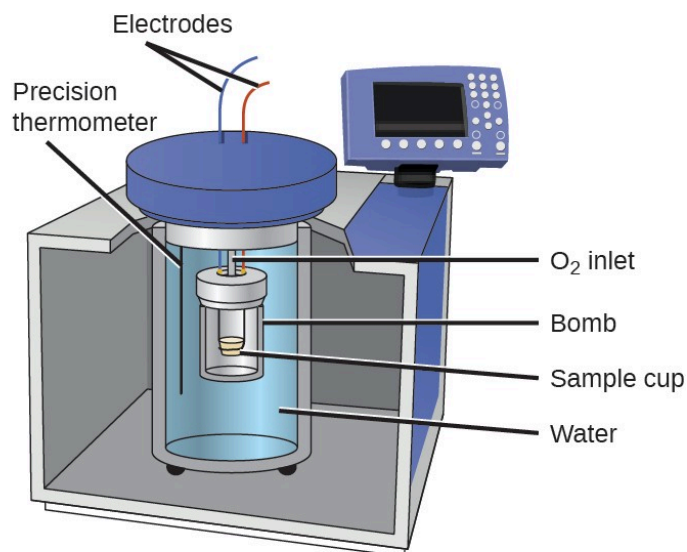
If the amount of heat absorbed by a calorimeter is too large to neglect or if we require more accurate results, then we must take into account the heat absorbed both by the solution and by the calorimeter.

The calorimeters described are designed to operate at constant (atmospheric) pressure and are convenient to measure heat flow accompanying processes that occur in solution. A different type of calorimeter that operates at constant volume, colloquially known as a **bomb calorimeter**, is used to measure the energy produced by reactions that yield large amounts of heat and gaseous products, such as combustion reactions. (The term “bomb” comes from the observation that these reactions can be vigorous enough to resemble explosions that would damage other calorimeters.) This type of calorimeter consists of a robust steel container (the “bomb”) that contains the reactants and is itself submerged in water (**Figure 9.17**). The sample is placed in the bomb, which is then filled with oxygen at high pressure. A small electrical spark is used to ignite the sample. The energy produced by the reaction is absorbed by the steel bomb and the surrounding water. The temperature increase is measured and, along with the known heat capacity of the calorimeter, is used to calculate the energy produced by the reaction. Bomb calorimeters require calibration to determine the heat capacity of the calorimeter and ensure accurate results. The calibration is accomplished using a reaction with a known  $q$ , such as a measured quantity of benzoic acid ignited by a spark from a nickel fuse wire that is weighed before and after the reaction. The temperature change produced by the known reaction is used to determine the heat capacity

of the calorimeter. The calibration is generally performed each time before the calorimeter is used to gather research data.



(a)



(b)

**Figure 9.17** (a) A bomb calorimeter is used to measure heat produced by reactions involving gaseous reactants or products, such as combustion. (b) The reactants are contained in the gas-tight “bomb,” which is submerged in water and surrounded by insulating materials. By: Rice University [Openstax CC BY NC SA](#)

### Link to Learning

[Click on this link](#) to view how a bomb calorimeter is prepared for action. [This site](#) shows calorimetric calculations using sample data.

## EXAMPLE 9.7

## Bomb Calorimetry

When 3.12 g of glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ , is burned in a bomb calorimeter, the temperature of the calorimeter increases from  $23.8^\circ\text{C}$  to  $35.6^\circ\text{C}$ . The calorimeter contains 775 g of water, and the bomb itself has a heat capacity of  $893 \text{ J}/^\circ\text{C}$ . How much heat was produced by the combustion of the glucose sample?

## Solution

The combustion produces heat that is primarily absorbed by the water and the bomb. (The amounts of heat absorbed by the reaction products and the unreacted excess oxygen are relatively small and dealing with them is beyond the scope of this text. We will neglect them in our calculations.)

The heat produced by the reaction is absorbed by the water and the bomb:

$$\begin{aligned} q_{\text{rxn}} &= -(q_{\text{water}} + q_{\text{bomb}}) \\ &= -[(4.184 \text{ J/g } ^\circ\text{C}) \times (775 \text{ g}) \times (35.6^\circ\text{C} - 23.8^\circ\text{C}) + 893 \text{ J}/^\circ\text{C} \times (35.6^\circ\text{C} - 23.8^\circ\text{C})] \\ &= -(38,300 \text{ J} + 10,500 \text{ J}) \\ &= -48,800 \text{ J} = -48.8 \text{ kJ} \end{aligned}$$

This reaction released 48.7 kJ of heat when 3.12 g of glucose was burned.

## Check Your Learning

When 0.963 g of benzene,  $\text{C}_6\text{H}_6$ , is burned in a bomb calorimeter, the temperature of the calorimeter increases by  $8.39^\circ\text{C}$ . The bomb has a heat capacity of  $784 \text{ J}/^\circ\text{C}$  and is submerged in 925 mL of water. How much heat was produced by the combustion of the glucose sample?

**Answer:** 39.0 kJ

## Chemistry in Everyday Life

### Measuring Nutritional Calories

In your day-to-day life, you may be more familiar with energy being given in Calories, or nutritional calories, which are used to quantify the amount of energy in foods. One calorie (cal) = exactly 4.184 joules, and one Calorie (note the capitalization) = 1000 cal, or 1 kcal. (This is approximately the amount of energy needed to heat 1 kg of water by 1 °C.) The macronutrients in food are proteins, carbohydrates, and fats or oils. Proteins provide about 4 Calories per gram, carbohydrates also provide about 4 Calories per gram, and fats and oils provide about 9 Calories/g. Nutritional labels on food packages show the caloric content of one serving of the food, as well as the breakdown into Calories from each of the three macronutrients (**Figure 9.18**).



(a)

Sample label for macaroni & cheese

Nutrition Facts	
① Start here	Serving Size 1 cup (228g) Servings Per Container 2
② Check Calories	Amount Per Serving <b>Calories 250</b> Calories from Fat 110
③ Limit these nutrients	<b>% Daily Value*</b>
	<b>Total Fat 12g</b> 18%
	Saturated Fat 3g 15%
	Trans Fat 3g
	<b>Cholesterol 30mg</b> 10%
	<b>Sodium 470mg</b> 20%
	<b>Total Carbohydrates 31g</b> 10%
	Dietary Fiber 0g 0%
	Sugars 5g
④ Get enough of these nutrients	<b>Protein 5g</b>
	Vitamin A 4%
	Vitamin C 2%
	Calcium 20%
	Iron 4%
⑤ Footnote	*Percent Daily Values are based on a 2,000 calorie diet. Your Daily Values may be higher or lower depending on your calorie needs.
	Calories 2,000 2,500
	Total Fat Less than 65g 80g
	Sat Fat Less than 20g 25g
	Cholesterol Less than 300mg 300mg
	Sodium Less than 2,400mg 2,400mg
	Total Carbohydrate 300g 375g
	Dietary Fiber 25g 30g

⑥ Quick guide to % DV  
• 5% or less is low  
• 20% or more is high

(b)

**Figure 9.18** (a) Macaroni and cheese contain energy in the form of the macronutrients in the food. (b) The food's nutritional information is shown on the package label. In the US, the energy content is given in Calories (per serving); the rest of the world usually uses kilojoules. By: Rice University [Openstax CC BY-NC-SA](#)

For the example shown in (b), the total energy per 228-g portion is calculated by:

$$(5 \text{ g protein} \times 4 \text{ Calories/g}) + (31 \text{ g carb} \times 4 \text{ Calories/g}) + (12 \text{ g fat} \times 9 \text{ Calories/g}) = 252 \text{ Calories}$$

So, you can use food labels to count your Calories. But where do the values come from? And how accurate are they? The caloric content of foods can be determined by using bomb calorimetry; that is, by burning the food and measuring the energy it contains. A sample of food is weighed, mixed in a blender, freeze-dried, ground into powder, and formed into a pellet. The pellet is burned inside a bomb calorimeter, and the measured temperature change is converted into energy per gram of food.

Today, the caloric content on food labels is derived using a method called the Atwater system that uses the average caloric content of the different chemical constituents of food, protein, carbohydrate, and fats. The average amounts are those given in the equation and are derived from the various results given by the bomb calorimetry of whole foods. The carbohydrate amount is discounted a certain amount for the fiber content, which is an indigestible carbohydrate. To determine the energy content of a food, the quantities of carbohydrate, protein, and fat are each multiplied by the average Calories per gram for each and the products summed to obtain the total energy.

## Link to Learning

[Click on this link](#) to access the US Department of Agriculture (USDA) National Nutrient Database, containing nutritional information on over 8000 foods.

# ENTHALPY (9.3)

OpenStax

---

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

- State the first law of thermodynamics
- Define enthalpy and explain its classification as a state function
- Write and balance thermochemical equations
- Calculate enthalpy changes for various chemical reactions
- Explain Hess's law and use it to compute reaction enthalpies

Thermochemistry is a branch of **chemical thermodynamics**, the science that deals with the relationships between heat, work, and other forms of energy in the context of chemical and physical processes. As we concentrate on thermochemistry in this chapter, we need to consider some widely used concepts of thermodynamics.

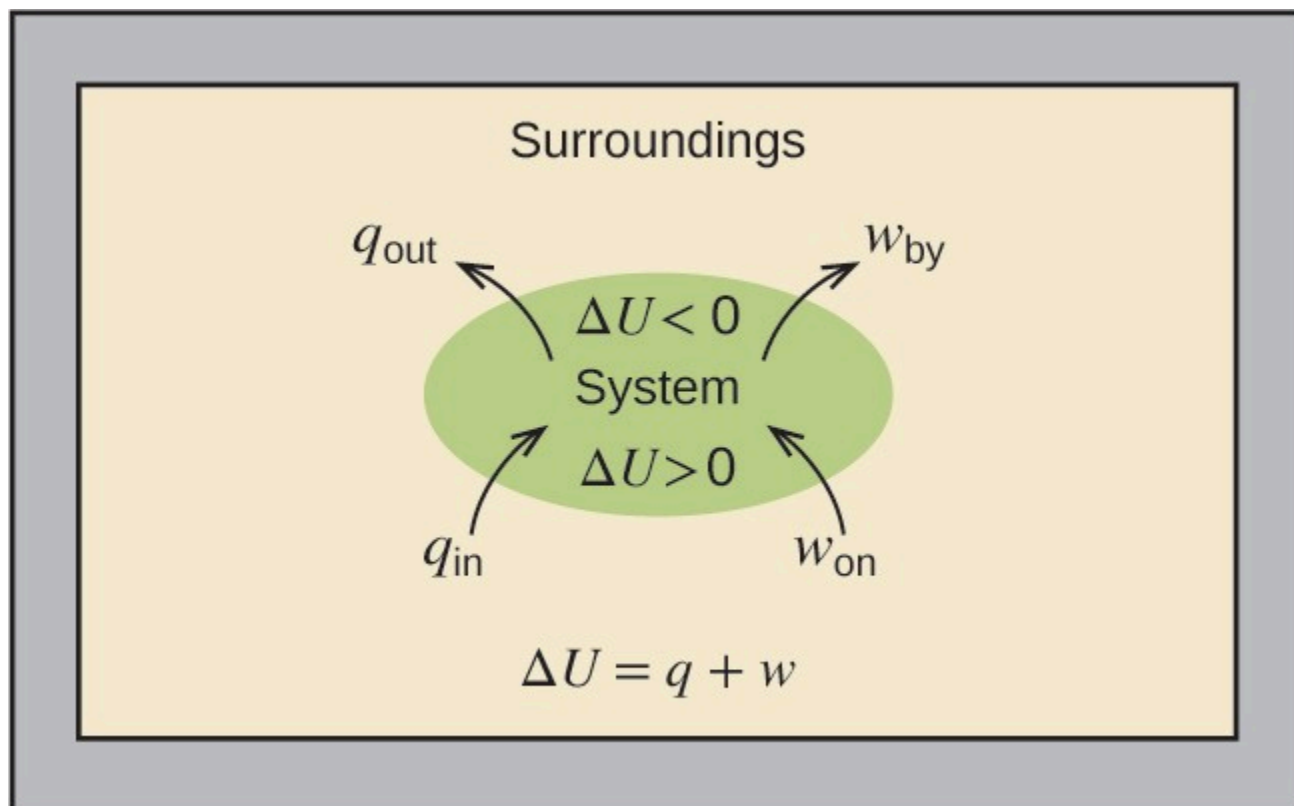
Substances act as reservoirs of energy, meaning that energy can be added to them or removed from them. Energy is stored in a substance when the kinetic energy of its atoms or molecules is raised. The greater kinetic energy may be in the form of increased translations (travel or straight-line motions), vibrations, or rotations of the atoms or molecules. When thermal energy is lost, the intensities of these motions decrease and the kinetic energy falls. The total of all possible kinds of energy present in a substance is called the **internal energy ( $U$ )**, sometimes symbolized as  $E$ .

As a system undergoes a change, its internal energy can change, and energy can be transferred from the system to the surroundings or from the surroundings to the system. Energy is transferred into a system when it absorbs heat ( $q$ ) from the surroundings or when the surroundings do work ( $w$ ) on the system. For example, energy is transferred into room-temperature metal wire if it is immersed in hot water (the wire absorbs heat from the water), or if you rapidly bend the wire back and forth (the wire becomes warmer because of the work done on it). Both processes increase the internal energy of the wire, which is reflected in an increase in the wire's temperature. Conversely, energy is transferred out of a system when heat is lost from the system, or when the system does work on the surroundings.

The relationship between internal energy, heat, and work can be represented by the equation:

$$\Delta U = q + w$$

as shown in **Figure 9.19**. This is one version of the **first law of thermodynamics**, and it shows that the internal energy of a system changes through heat flow into or out of the system (positive  $q$  is heat flow in; negative  $q$  is heat flow out) or work done on or by the system. The work,  $w$ , is positive if it is done on the system and negative if it is done by the system.



**Figure 9.19** The internal energy,  $U$ , of a system can be changed by heat flow and work. If heat flows into the system,  $q_{\text{in}}$ , or work is done on the system,  $w_{\text{on}}$ , its internal energy increases,  $\Delta U > 0$ . If heat flows out of the system,  $q_{\text{out}}$ , or work is done by the system,  $w_{\text{by}}$ , its internal energy decreases,  $\Delta U < 0$ . By: Rice University OpenStax [Openstax CC BY NC SA](https://openstax.org)

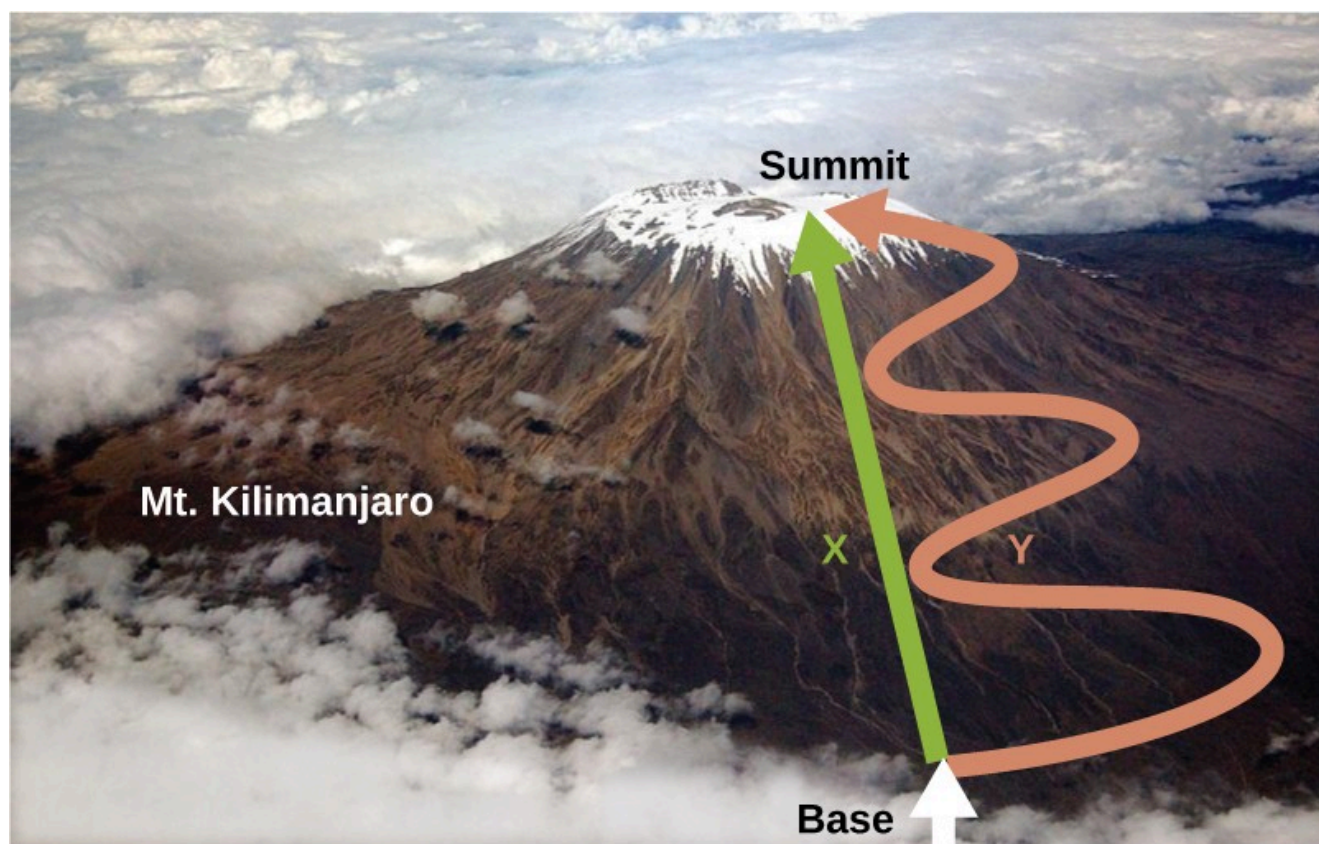
A type of work called **expansion work** (or pressure-volume work) occurs when a system pushes back the surroundings against a restraining pressure or when the surroundings compress the system. An example of this occurs during the operation of an internal combustion engine. The reaction of gasoline and oxygen is exothermic. Some of this energy is given off as heat, and some does work by pushing the piston in the cylinder. The substances involved in the reaction are the system, and the engine and the rest of the universe are the surroundings. The system loses energy by both heating and doing work on the surroundings, and its internal energy decreases. (The engine is able to keep the car moving because this process is repeated many times per second while the engine is running.) We will consider how to determine the amount of work involved in a chemical or physical change in the chapter on thermodynamics.



## Link to Learning

[This view of an internal combustion engine](#) illustrates the conversion of energy produced by the exothermic combustion reaction of a fuel such as gasoline into energy of motion.

As discussed, the relationship between internal energy, heat, and work can be represented as  $\Delta U = q + w$ . Internal energy is an example of a **state function** (or state variable), whereas heat and work are not state functions. The value of a state function depends only on the state that a system is in and not on how that state is reached. If a quantity is not a state function, then its value *does* depend on how the state is reached. An example of a state function is altitude or elevation. If you stand on the summit of Mt. Kilimanjaro, you are at an altitude of 5895 m, and it does not matter whether you hiked there or parachuted there. The distance you traveled to the top of Kilimanjaro, however, is not a state function. You could climb to the summit by a direct route or by a more roundabout, circuitous path (**Figure 9.20**). The distances traveled would differ (distance is not a state function), but the elevation reached would be the same (altitude is a state function).



**Figure 9.20** Paths X and Y represent two different routes to the summit of Mt. Kilimanjaro. Both have the same change in elevation (altitude or elevation on a mountain is a state function; it does not depend on a path), but they have very different distances traveled (distance walked is not a state function; it depends on the path). By: Rice University [Openstax CC BY NC SA](#)

Chemists ordinarily use a property known as **enthalpy ( $H$ )** to describe the thermodynamics of chemical and physical processes. Enthalpy is defined as the sum of a system's internal energy ( $U$ ) and the mathematical product of its pressure ( $P$ ) and volume ( $V$ ):

$$H = U + PV$$

Enthalpy is also a state function. Enthalpy values for specific substances cannot be measured directly; only enthalpy *changes* for chemical or physical processes can be determined. For processes that take place at constant pressure (a common condition for many chemical and physical changes), the **enthalpy change ( $\Delta H$ )** is:

$$\Delta H = \Delta U + P\Delta V$$

The mathematical product  $P\Delta V$  represents work ( $w$ ), namely, expansion or pressure-volume work as noted. By their definitions, the arithmetic signs of  $\Delta V$  and  $w$  will always be opposite:

$$P\Delta V = -w$$

Substituting this equation and the definition of internal energy into the enthalpy-change equation yields:

$$\begin{aligned}\Delta H &= \Delta U + P\Delta V \\ &= q_p + w - w \\ &= q_p\end{aligned}$$

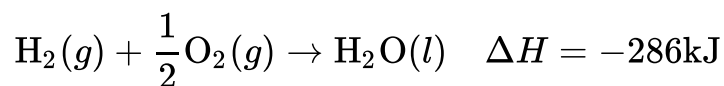
where  $q_p$  is the heat of reaction under conditions of constant pressure.

And so, if a chemical or physical process is carried out at constant pressure with the only work done caused by expansion or contraction, then the heat flow ( $q_p$ ) and enthalpy change ( $\Delta H$ ) for the process are equal.

The heat given off when you operate a Bunsen burner is equal to the enthalpy change of the methane combustion reaction that takes place, since it occurs at the essentially constant pressure of the atmosphere. On the other hand, the heat produced by a reaction measured in a bomb calorimeter (**Figure 9.17**) is not equal to  $\Delta H$  because the closed, constant-volume metal container prevents the pressure from remaining constant (it may increase or decrease if the reaction yields increased or decreased amounts of gaseous species). 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 changes for chemical reactions.

The following conventions apply when using  $\Delta H$ :

- A negative value of an enthalpy change,  $\Delta H < 0$ , indicates an exothermic reaction; a positive value,  $\Delta H > 0$ , indicates an endothermic reaction. If the direction of a chemical equation is reversed, the arithmetic sign of its  $\Delta H$  is changed (a process that is endothermic in one direction is exothermic in the opposite direction).
- 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  $\Delta H$  value following the equation for the reaction. This  $\Delta H$  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:



This equation indicates that when 1 mole of hydrogen gas and  $\frac{1}{2}$  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 ( $\Delta H$  is an extensive property):

(two-fold increase in amounts)

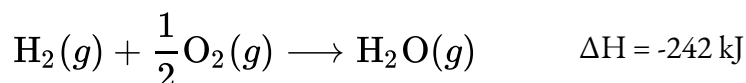
(two-fold increase in amounts)



(two-fold decrease in amounts)



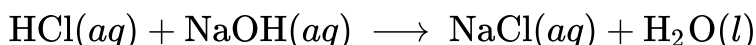
- The enthalpy change of a reaction depends on the physical states of the reactants and products, so these must be shown. For example, when 1 mole of hydrogen gas and  $\frac{1}{2}$  mole of oxygen gas change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released. If gaseous water forms, only 242 kJ of heat are released.



## EXAMPLE 9.8

### Writing Thermochemical Equations

When 0.0500 mol of  $\text{HCl}(aq)$  reacts with 0.0500 mol of  $\text{NaOH}(aq)$  to form 0.0500 mol of  $\text{NaCl}(aq)$ , 2.9 kJ of heat are produced. Write a balanced thermochemical equation for the reaction of one mole of  $\text{HCl}$ .

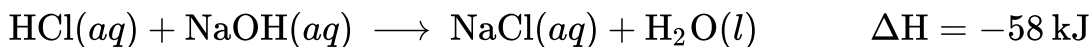


### Solution

For the reaction of 0.0500 mol acid ( $\text{HCl}$ ),  $q = -2.9 \text{ kJ}$ . The reactants are provided in stoichiometric amounts (same molar ratio as in the balanced equation), and so the amount of acid may be used to calculate a molar enthalpy change. Since  $\Delta H$  is an extensive property, it is proportional to the amount of acid neutralized:

$$\Delta H = 1 \text{ mol HCl} \times \frac{-2.9 \text{ kJ}}{0.0500 \text{ mol HCl}} = -58 \text{ kJ}$$

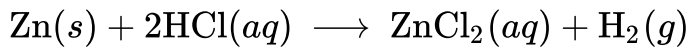
The thermochemical equation is then



Formula does not parse

### Check Your Learning

When 1.34 g  $\text{Zn}(s)$  reacts with 60.0 mL of 0.750 M  $\text{HCl}(aq)$ , 3.14 kJ of heat are produced. Determine the enthalpy change per mole of zinc reacting for the reaction:



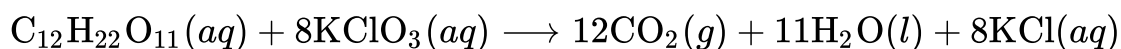
**Answer:**  $\Delta H = -153 \text{ kJ}$

Be sure to take both stoichiometry and limiting reactants into account when determining the  $\Delta H$  for a chemical reaction.

## EXAMPLE 9.9

### Writing Thermochemical Equations

A gummy bear contains 2.67 g sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ . When it reacts with 7.19 g potassium chlorate,  $\text{KClO}_3$ , 43.7 kJ of heat are produced. Write a thermochemical equation for the reaction of one mole of sucrose:



### Solution

Unlike the previous example exercise, this one does not involve the reaction of stoichiometric amounts of reactants, and so the *limiting reactant* must be identified (it limits the yield of the reaction and the amount of thermal energy produced or consumed).

The provided amounts of the two reactants are

$$(2.67\text{g})(1\text{mol}/342.3\text{g}) = 0.00780\text{molC}_{12}\text{H}_{22}\text{O}_{11}$$

$$(7.19\text{g})(1\text{mol}/122.5\text{g}) = 0.0587\text{molKClO}_3$$

The provided molar ratio of perchlorate-to-sucrose is then

$$0.0587\text{molKClO}_3 / 0.00780\text{molC}_{12}\text{H}_{22}\text{O}_{11} = 7.52$$

The balanced equation indicates 8 mol  $\text{KClO}_3$  are required for reaction with 1 mol  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ .

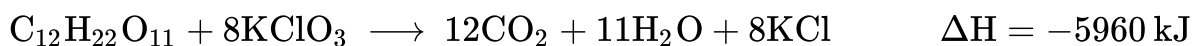
Since the provided amount of  $\text{KClO}_3$  is less than the stoichiometric amount, it is the limiting reactant and may be used to compute the enthalpy change:

$$\Delta H = -43.7\text{kJ} / 0.0587\text{molKClO}_3 = 744\text{kJ/molKClO}_3$$

Because the equation, as written, represents the reaction of 8 mol  $\text{KClO}_3$ , the enthalpy change is

$$(744\text{kJ/molKClO}_3)(8\text{molKClO}_3) = 5960\text{kJ}$$

The enthalpy change for this reaction is  $-5960\text{ kJ}$ , and the thermochemical equation is:



### Check Your Learning

When  $1.42\text{ g}$  of iron reacts with  $1.80\text{ g}$  of chlorine,  $3.22\text{ g}$  of  $\text{FeCl}_2(\text{s})$  and  $8.60\text{ kJ}$  of heat are produced. What is the enthalpy change for the reaction when  $1\text{ mole}$  of  $\text{FeCl}_2(\text{s})$  is produced?

**Answer:**  $\Delta H = -338\text{ kJ}$

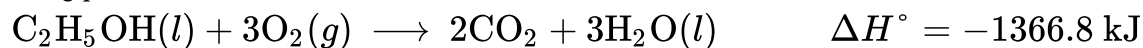
Enthalpy changes are typically tabulated for reactions in which both the reactants and products are in the same conditions. A **standard state** is a commonly accepted set of conditions used as a reference point for the determination of properties under other different conditions. For chemists, the IUPAC standard state refers to materials under a pressure of  $1\text{ bar}$  and solutions at  $1\text{ M}$  and does not specify a temperature. Many thermochemical tables list values with a standard state of  $1\text{ atm}$ . Because the  $\Delta H$  of a reaction changes very little with such small changes in pressure ( $1\text{ bar} = 0.987\text{ atm}$ ),  $\Delta H$  values (except for the most precisely measured values) are essentially the same under both sets of standard conditions. We will include a superscripted “o” in the enthalpy change symbol to designate a standard state. Since the usual (but not technically standard) temperature is  $298.15\text{ K}$ , this temperature will be assumed unless some other temperature is specified. Thus, the symbol ( $\Delta H^\circ$ ) is used to indicate an enthalpy change for a process occurring under these conditions. (The symbol  $\Delta H$  is used to indicate an enthalpy change for a reaction occurring under nonstandard conditions.)

The enthalpy changes for many types of chemical and physical processes are available in the reference literature, including those for combustion reactions, phase transitions, and formation reactions. As we discuss these quantities, it is important to pay attention to the *extensive* nature of enthalpy and enthalpy changes. Since the enthalpy change for a given reaction is proportional to the amounts of substances involved, it may be reported on that basis (i.e., as the  $\Delta H$  for specific amounts of reactants). However, we often find it more useful to divide one extensive property ( $\Delta H$ ) by another (amount of substance), and report a per-amount *intensive* value of  $\Delta H$ , often “normalized” to a per-mole basis. (Note that this is similar to determining the intensive property-specific heat from the extensive property heat capacity, as seen previously.)

## Standard Enthalpy of Combustion

**Standard enthalpy of combustion** ( $\Delta H^\circ_{\text{C}}$ ) is the enthalpy change when  $1\text{ mole}$  of a substance burns

(combines vigorously with oxygen) under standard state conditions; it is sometimes called “heat of combustion.” For example, the enthalpy of combustion of ethanol,  $-1366.8 \text{ kJ/mol}$ , is the amount of heat produced when one mole of ethanol undergoes complete combustion at  $25^\circ\text{C}$  and 1 atmosphere pressure, yielding products also at  $25^\circ\text{C}$  and 1 atm.



Enthalpies of combustion for many substances have been measured; a few of these are listed in [Table 9.2](#). Many readily available substances with large enthalpies of combustion are used as fuels, including hydrogen, carbon (as coal or charcoal), and **hydrocarbons** (compounds containing only hydrogen and carbon), such as methane, propane, and the major components of gasoline.

**Table 9.2 Standard Molar Enthalpies of Combustion By: Rice University [OpenStax](#) CC BY-NC-SA 4.0**

Substance	Combustion Reaction	Enthalpy of Combustion
carbon	$\text{C}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g)$	−393.5
hydrogen	$\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(l)$	−285.8
magnesium	$\text{Mg}(s) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{MgO}(s)$	−601.6
sulfur	$\text{S}(s) + \text{O}_2(g) \rightarrow \text{SO}_2(g)$	−296.8
carbon monoxide	$\text{CO}(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{CO}_2(g)$	−283.0
methane	$\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)$	−890.8
acetylene	$\text{C}_2\text{H}_2(g) + \frac{5}{2} \text{O}_2(g) \rightarrow 2\text{CO}_2(g) + \text{H}_2\text{O}(l)$	−1301.1
ethanol	$\text{C}_2\text{H}_5\text{OH}(l) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 3\text{H}_2\text{O}(l)$	−1366.8
methanol	$\text{CH}_3\text{OH}(l) + \frac{3}{2} \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)$	−726.1
isooctane	$\text{C}_8\text{H}_{18}(l) + \frac{25}{2} \text{O}_2(g) \rightarrow 8\text{CO}_2(g) + 9\text{H}_2\text{O}(l)$	−5461



## EXAMPLE 9.10

## Using Enthalpy of Combustion

As **Figure 9.21** suggests, the combustion of gasoline is a highly exothermic process. Let us determine the approximate amount of heat produced by burning 1.00 L of gasoline, assuming the enthalpy of combustion of gasoline is the same as that of isooctane, a common component of gasoline. The density of isooctane is 0.692 g/mL.



**Figure 9.21** The combustion of gasoline is very exothermic. By: Rice University [Openstax CC BY NC SA](#)

## Solution

Starting with a known amount (1.00 L of isooctane), we can perform conversions between units until we arrive at the desired amount of heat or energy. The enthalpy of combustion of isooctane provides one of the necessary conversions. Table 9.2 gives this value as  $-5460 \text{ kJ}$  per 1 mole of isooctane ( $\text{C}_8\text{H}_{18}$ ).

Using these data,

$$1.00 \text{ L C}_8\text{H}_{18} \times \frac{1000 \text{ mL C}_8\text{H}_{18}}{1 \text{ L C}_8\text{H}_{18}} \times \frac{0.692 \text{ g C}_8\text{H}_{18}}{1 \text{ mL C}_8\text{H}_{18}} \times \frac{1 \text{ mol C}_8\text{H}_{18}}{114 \text{ g C}_8\text{H}_{18}} \times \frac{-5460 \text{ kJ}}{1 \text{ mol C}_8\text{H}_{18}} = -3.31 \times 10^4 \text{ kJ}$$

$$1.00 \text{ L C}_8\text{H}_{18} \times \frac{1000 \text{ mL C}_8\text{H}_{18}}{1 \text{ L C}_8\text{H}_{18}} \times \frac{0.692 \text{ g C}_8\text{H}_{18}}{1 \text{ mL C}_8\text{H}_{18}} \times \frac{1 \text{ mol C}_8\text{H}_{18}}{114 \text{ g C}_8\text{H}_{18}} \times \frac{-5460 \text{ kJ}}{1 \text{ mol C}_8\text{H}_{18}} = -3.31 \times 10^4 \text{ kJ}$$

The combustion of 1.00 L of isooctane produces 33,100 kJ of heat. (This amount of energy is enough to melt 99.2 kg, or about 218 lbs, of ice.)

Note: If you do this calculation one step at a time, you will find:

$$1.00 \text{ L C}_8\text{H}_{18} \longrightarrow 1.00 \times 10^3 \text{ mL C}_8\text{H}_{18}$$

$$1.00 \times 10^3 \text{ mL C}_8\text{H}_{18} \longrightarrow 692 \text{ g C}_8\text{H}_{18}$$

$$692 \text{ g C}_8\text{H}_{18} \longrightarrow 6.07 \text{ mol C}_8\text{H}_{18}$$

$$6.07 \text{ mol C}_8\text{H}_{18} \longrightarrow -3.31 \times 10^4 \text{ kJ}$$

### Check Your Learning

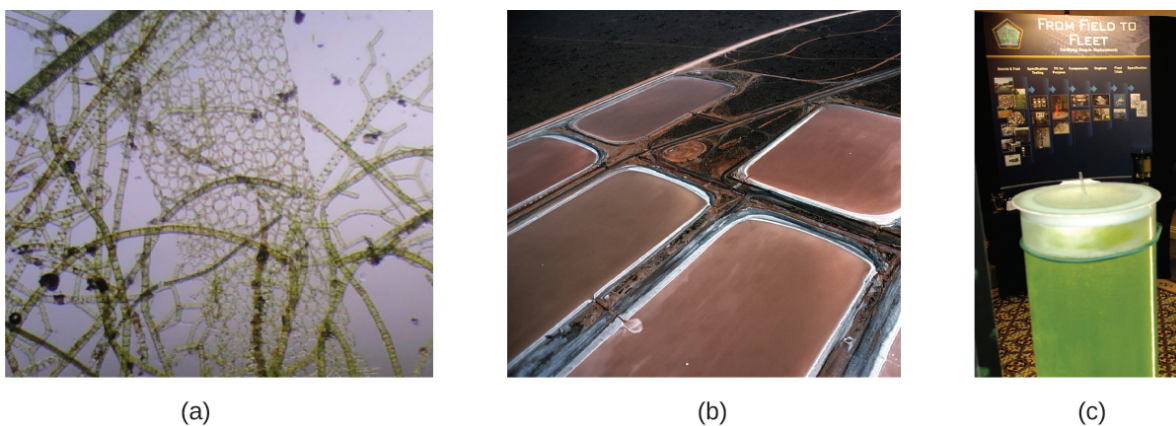
How much heat is produced by the combustion of 125 g of acetylene?

**Answer:**  $6.25 \times 10^3 \text{ kJ}$

## CHEMISTRY IN EVERYDAY LIFE

### Emerging Algae-Based Energy Technologies (Biofuels)

As reserves of fossil fuels diminish and become more costly to extract, the search is ongoing for replacement fuel sources for the future. Among the most promising biofuels are those derived from algae (**Figure 9.22**). The species of algae used are nontoxic, biodegradable, and among the world's fastest-growing organisms. About 50% of algal weight is oil, which can be readily converted into fuel such as biodiesel. Algae can yield 26,000 gallons of biofuel per hectare—much more energy per acre than other crops. Some strains of algae can flourish in brackish water that is not usable for growing other crops. Algae can produce biodiesel, biogasoline, ethanol, butanol, methane, and even jet fuel.



**Figure 9.22** (a) Tiny algal organisms can be (b) grown in large quantities and eventually (c) turned into a useful fuel such as biodiesel. By: Rice University [Openstax CC BY NC SA](#)

According to the US Department of Energy, only 39,000 square kilometers (about 0.4% of the land mass of the US or less than  $\frac{1}{7}$  of the area used to grow corn) can produce enough algal fuel to replace all the petroleum-based fuel used in the US. The cost of algal fuels is becoming more competitive—for instance, the US Air Force is producing jet fuel from algae at a total cost of under \$5 per gallon.<sup>1</sup> The process used to produce algal fuel is as follows: grow the algae (which use sunlight as their energy source and CO<sub>2</sub> as a raw material), harvest the algae, extract the fuel compounds (or precursor compounds), process as necessary (e.g., perform a transesterification reaction to make biodiesel), purify, and distribute (**Figure 9.23**).

## LINK TO LEARNING

Click [here](#) to learn more about the process of creating algae biofuel.

1. For more on algal fuel, see “Algae to solve the Pentagon’s jet fuel problem” in The Guardian.

## Standard Enthalpy of Formation

A standard enthalpy of formation

$\Delta H_f^\circ$  is an enthalpy change for a reaction in which exactly 1 mole of a pure substance is formed from free elements in their most stable states under standard state conditions. These values are especially useful for computing or predicting enthalpy changes for chemical reactions that are impractical or dangerous to carry out, or for processes for which it is difficult to make measurements. If we have values for the appropriate standard enthalpies of formation, we can determine the enthalpy change for any reaction, which we will practice in the next section on Hess's law.

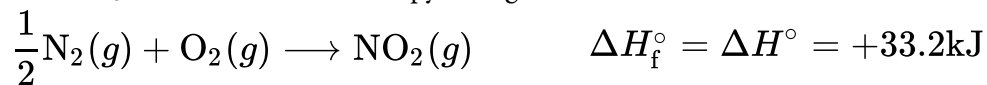
The standard enthalpy of formation of  $\text{CO}_2(g)$  is  $-393.5 \text{ kJ/mol}$ . This is the enthalpy change for the exothermic reaction:



starting with the reactants at a pressure of 1 atm and  $25^\circ\text{C}$  (with the carbon present as graphite, the most stable form of carbon under these conditions) and ending with one mole of  $\text{CO}_2$ , also at 1 atm and  $25^\circ\text{C}$ . For nitrogen dioxide,  $\text{NO}_2(g)$ ,

$$\Delta H_f^\circ$$

is  $33.2 \text{ kJ/mol}$ . This is the enthalpy change for the reaction:



A reaction equation with  $\frac{1}{2}$  mole of  $\text{N}_2$  and 1 mole of  $\text{O}_2$  is correct in this case because the standard enthalpy of formation always refers to 1 mole of product,  $\text{NO}_2(g)$ .

You will find a table of standard enthalpies of the formation of many common substances in [Appendix G](#). These values indicate that formation reactions range from highly exothermic (such as  $-2984 \text{ kJ/mol}$  for the formation of  $\text{P}_4\text{O}_{10}$ ) to strongly endothermic (such as  $+226.7 \text{ kJ/mol}$  for the formation of acetylene,  $\text{C}_2\text{H}_2$ ). By definition, the standard enthalpy of the formation of an element in its most stable form is equal to zero under standard conditions, which is 1 atm for gases and 1 M for solutions.

### EXAMPLE 9.11

#### Evaluating an Enthalpy of Formation

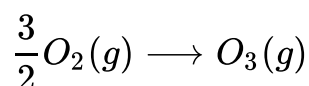
Ozone,  $\text{O}_3(g)$ , forms from oxygen,  $\text{O}_2(g)$ , by an endothermic process. Ultraviolet radiation is the source of the energy that drives this reaction in the upper atmosphere. Assuming that both the

reactants and products of the reaction are in their standard states, determine the standard enthalpy of formation  $\Delta H_f^\circ$  of ozone from the following information:



### Solution

$\Delta H_f^\circ$  is the enthalpy change for the formation of one mole of a substance in its standard state from the elements in their standard states. Thus,  $\Delta H_f^\circ$  for  $\text{O}_3(g)$  is the enthalpy change for the reaction:



For the formation of 2 mol of  $\text{O}_3(g)$ ,

$\Delta H^\circ = +286 \text{ kJ}$ . This ratio,

$\left( \frac{286 \text{ kJ}}{2 \text{ mol O}_3} \right)$ , can be used as a conversion factor to find the heat produced when 1 mole of  $\text{O}_3(g)$  is formed, which is the enthalpy of formation for  $\text{O}_3(g)$ :

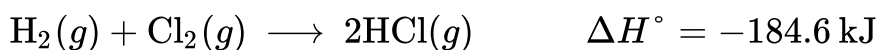
$$\Delta H^\circ \text{ for 1 mole of O}_3(g) = 1 \text{ mol O}_3 \times \frac{286 \text{ kJ}}{2 \text{ mol O}_3} = 143 \text{ kJ}$$

Therefore,  $\Delta H_f^\circ [\text{O}_3(g)] = +143 \text{ kJ/mol}$ .

### Check Your Learning

Hydrogen gas,  $\text{H}_2$ , reacts explosively with gaseous chlorine,  $\text{Cl}_2$ , to form hydrogen chloride,  $\text{HCl}(g)$ . What is the enthalpy change for the reaction of 1 mole of  $\text{H}_2(g)$  with 1 mole of  $\text{Cl}_2(g)$  if both the reactants and products are at standard state conditions? The standard enthalpy of formation of  $\text{HCl}(g)$  is  $-92.3 \text{ kJ/mol}$ .

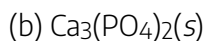
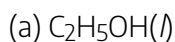
**Answer:** For the reaction



## EXAMPLE 9.12

Writing Reaction Equations for  $\Delta H_f^\circ$ 

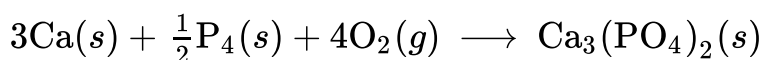
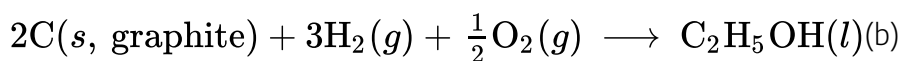
Write the heat of formation reaction equations for:



## Solution

Remembering that  $\Delta H_f^\circ$  reaction equations are for forming 1 mole of the compound from its constituent elements under standard conditions, we have:

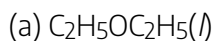
(a)



Note: The standard state of carbon is graphite, and phosphorus exists as  $\text{P}_4$ .

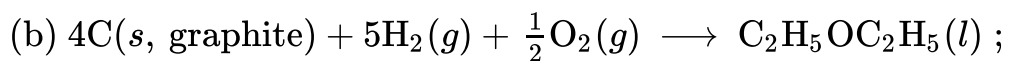
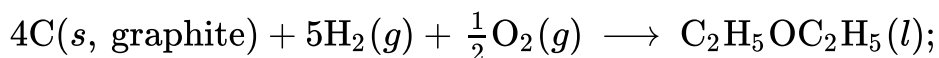
## Check Your Learning

Write the heat of formation reaction equations for:



## Answer:

(a)

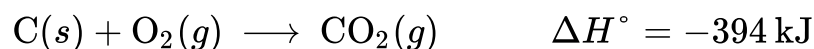


(b)

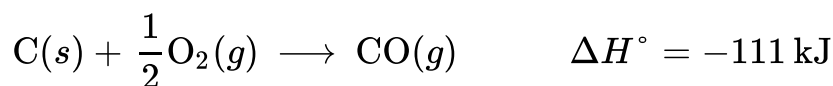
## Hess's Law

There are two ways to determine the amount of heat involved in a chemical change: measure it experimentally, or calculate it from other experimentally determined enthalpy changes. Some reactions are difficult, if not impossible, to investigate and make accurate measurements for experimentally. And even when a reaction is not hard to perform or measure, it is convenient to be able to determine the heat involved in a reaction without having to perform an experiment.

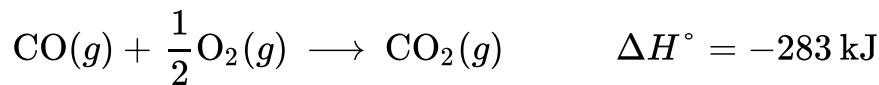
This type of calculation usually involves the use of Hess's law, which states: *If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps.* Hess's law is valid because enthalpy is a state function: Enthalpy changes depend only on where a chemical process starts and ends but not on the path it takes from start to finish. For example, we can think of the reaction of carbon with oxygen to form carbon dioxide as occurring either directly or by a two-step process. The direct process is written:



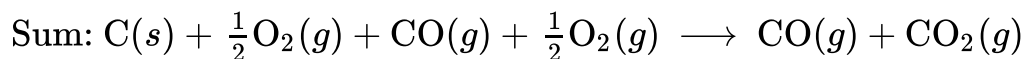
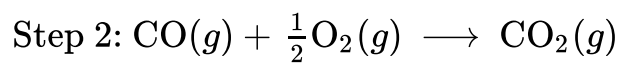
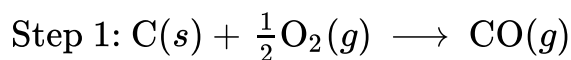
In the two-step process, first carbon monoxide is formed:



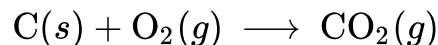
Then, carbon monoxide reacts further to form carbon dioxide:



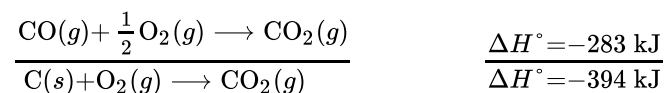
The equation describing the overall reaction is the sum of these two chemical changes:



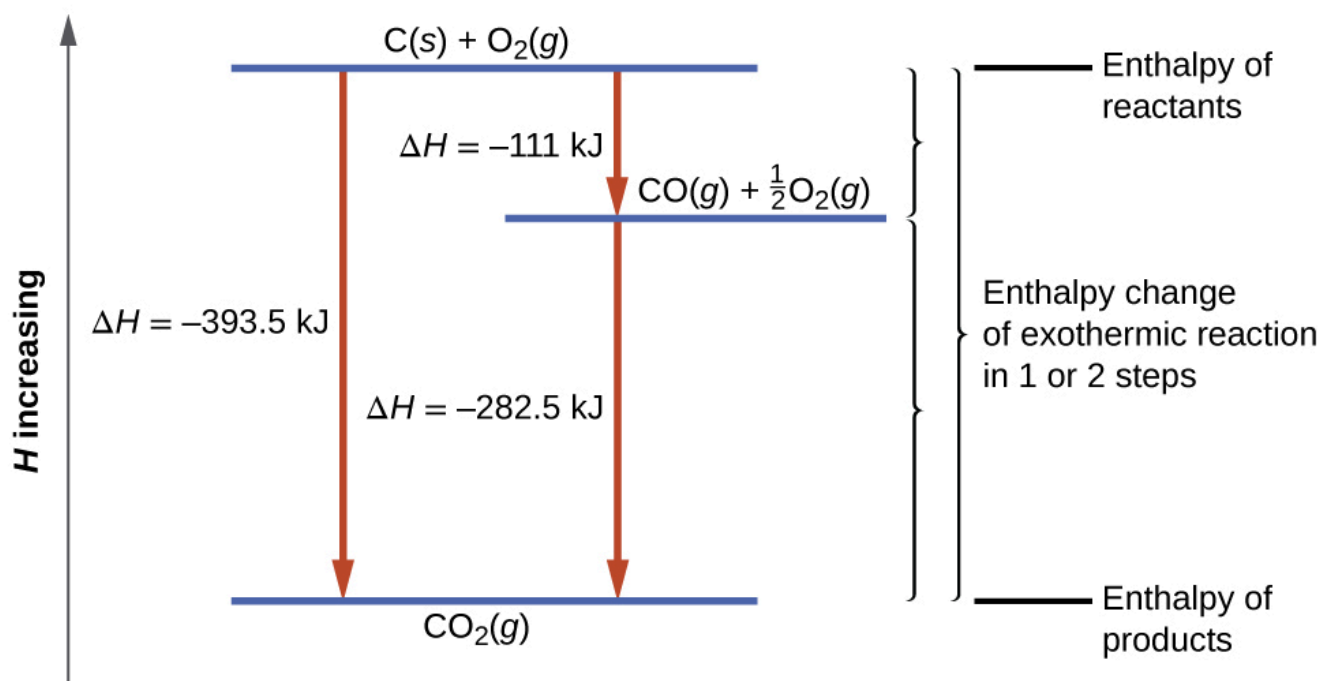
Because the CO produced in Step 1 is consumed in Step 2, the net change is:



According to Hess's law, the enthalpy change of the reaction will equal the sum of the enthalpy changes of the steps.



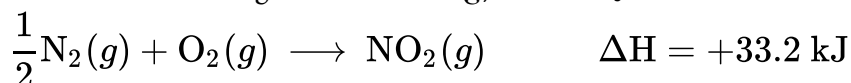
The result is shown in **Figure 9.24**. We see that  $\Delta H$  of the overall reaction is the same whether it occurs in one step or two. This finding (overall  $\Delta H$  for the reaction = sum of  $\Delta H$  values for reaction “steps” in the overall reaction) is true in general for chemical and physical processes.



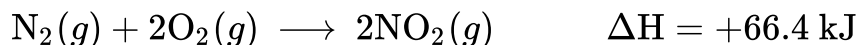
**Figure 9.24** The formation of  $\text{CO}_2(g)$  from its elements can be thought of as occurring in two steps, which sum to the overall reaction, as described by Hess's law. The horizontal blue lines represent enthalpies. For an exothermic process, the products are at a lower enthalpy than are the reactants. By: Rice University Openstax CC BY NC SA

Before we further practice using Hess's law, let us recall two important features of  $\Delta H$ .

1.  $\Delta H$  is directly proportional to the quantities of reactants or products. For example, the enthalpy change for the reaction forming 1 mole of  $\text{NO}_2(g)$  is +33.2 kJ:

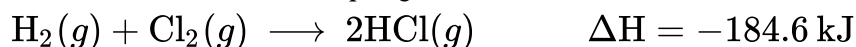


When 2 moles of  $\text{NO}_2$  (twice as much) are formed, the  $\Delta H$  will be twice as large:



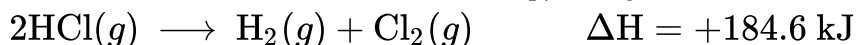
In general, if we multiply or divide an equation by a number, then the enthalpy change should also be multiplied or divided by the same number.

2.  $\Delta H$  for a reaction in one direction is equal in magnitude and opposite in sign to  $\Delta H$  for the reaction in the reverse direction. For example, given that:





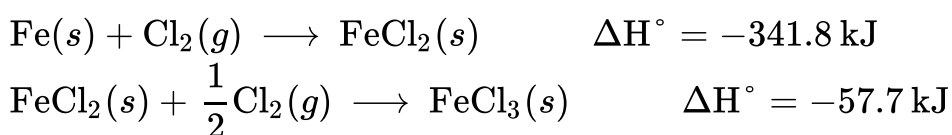
Then, for the “reverse” reaction, the enthalpy change is also “reversed”:



### EXAMPLE 9.13

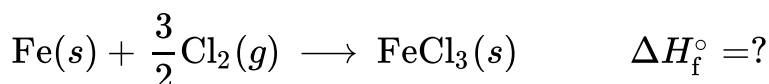
#### Stepwise Calculation of $\Delta H_f^\circ$ Using Hess's Law

Determine the enthalpy of formation,  $\Delta H_f^\circ$  of  $\text{FeCl}_3(s)$  from the enthalpy changes of the following two-step process that occurs under standard state conditions:

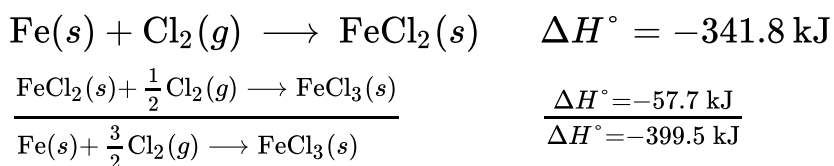


#### Solution

We are trying to find the standard enthalpy of the formation of  $\text{FeCl}_3(s)$ , which is equal to  $\Delta H^\circ$  for the reaction:



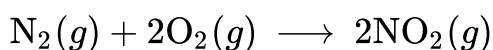
Looking at the reactions, we see that the reaction for which we want to find  $\Delta H^\circ$  is the sum of the two reactions with known  $\Delta H$  values, so we must sum their  $\Delta H$ s:



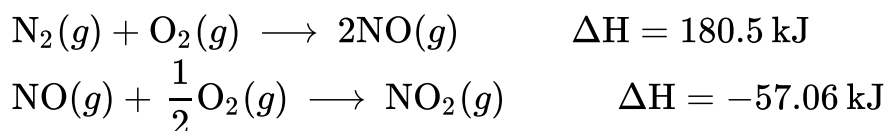
The enthalpy of formation,  $\Delta H_f^\circ$  of  $\text{FeCl}_3(s)$  is  $-399.5 \text{ kJ/mol}$

#### Check Your Learning

Calculate  $\Delta H$  for the process:



from the following information:



**Answer:** 66.4 kJ

Here is a less straightforward example that illustrates the thought process involved in solving many Hess's law problems. It shows how we can find many standard enthalpies of formation (and other values of  $\Delta H$ ) if they are difficult to determine experimentally.

### EXAMPLE 9.14

#### A More Challenging Problem Using Hess's Law

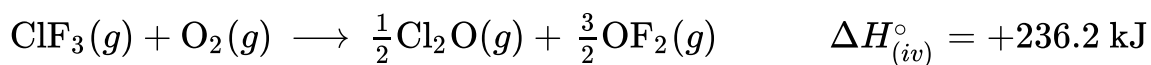
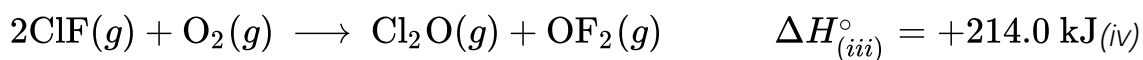
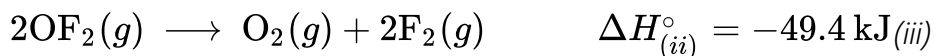
Chlorine monofluoride can react with fluorine to form chlorine trifluoride:

(i)



Use the reactions here to determine the  $\Delta H^\circ$  for reaction (i):

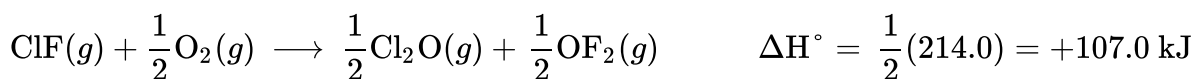
(ii)



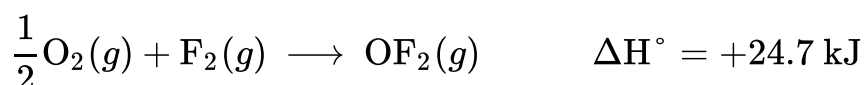
#### Solution

Our goal is to manipulate and combine reactions (ii), (iii), and (iv) such that they add up to reaction (i). Going from left to right in (i), we first see that  $\text{ClF}(g)$  is needed as a reactant. This

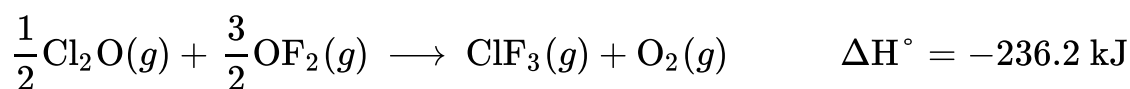
can be obtained by multiplying reaction (iii) by  $\frac{1}{2}$  which means that the  $\Delta H^\circ$  change is also multiplied by  $\frac{1}{2}$



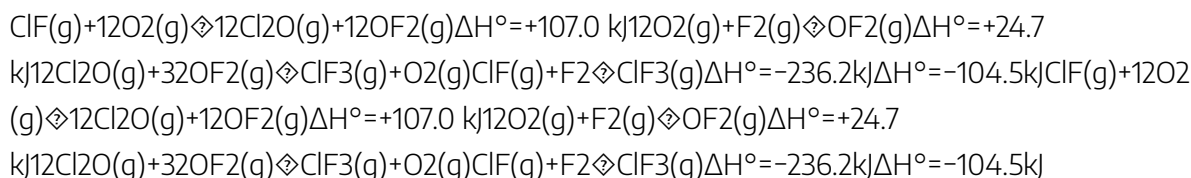
Next, we see that  $\text{F}_2$  is also needed as a reactant. To get this, reverse and halve reaction (ii), which means that the  $\Delta H^\circ$  changes sign and is halved:



To get  $\text{ClF}_3$  as a product, reverse (iv), changing the sign of  $\Delta H^\circ$ :



Now check to make sure that these reactions add up to the reaction we want:



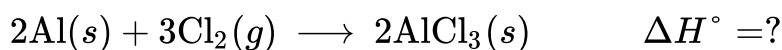
Reactants  $\frac{1}{2}\text{O}_2$  and  $\frac{1}{2}\text{O}_2$  cancel out product  $\text{O}_2$ ; product  $\frac{1}{2}\text{Cl}_2\text{O}$  cancels reactant  $\frac{1}{2}\text{Cl}_2\text{O}$ ; and reactant  $\frac{3}{2}\text{OF}_2$  is by products  $\frac{1}{2}\text{OF}_2$  and  $\text{OF}_2$ . This leaves only reactants  $\text{ClF}(g)$  and  $\text{F}_2(g)$  and product  $\text{ClF}_3(g)$ , which are what we want. Since summing these three modified reactions yields the reaction of interest, summing the three modified  $\Delta H^\circ$  values will give the desired  $\Delta H^\circ$ :

$$\Delta H^\circ = (+107.0 \text{ kJ}) + (24.7 \text{ kJ}) + (-236.2 \text{ kJ}) = -104.5 \text{ kJ}$$

### Check Your Learning

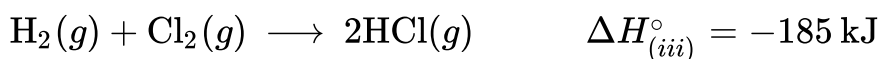
Aluminum chloride can be formed from its elements:

(i)

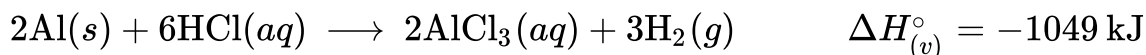


Use the reactions here to determine the  $\Delta H^\circ$  for reaction (i):

(ii)



(iv)

**Answer:** -1407 kJ

We also can use Hess's law to determine the enthalpy change of any reaction if the corresponding enthalpies of formation of the reactants and products are available. The stepwise reactions we consider are: (i) decompositions of the reactants into their component elements (for which the enthalpy changes are proportional to the negative of the enthalpies of formation of the reactants), followed by (ii) re-combinations of the elements to give the products (with the enthalpy changes proportional to the enthalpies of formation of the products). The standard enthalpy change of the overall reaction is therefore equal to: (ii) the sum of the standard enthalpies of formation of all the products plus (i) the sum of the negatives of the standard enthalpies of formation of the reactants. This is usually rearranged slightly to be written as follows, with  $\Sigma$  representing "the sum of" and  $n$  standing for the stoichiometric coefficients:

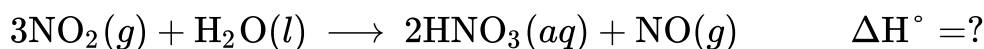
$$\Delta H_{\text{reaction}}^{\circ} = \sum n \times \Delta H_{\text{f}}^{\circ}(\text{products}) - \sum n \times \Delta H_{\text{f}}^{\circ}(\text{reactants})$$

The following example shows in detail why this equation is valid and how to use it to calculate the enthalpy change for a reaction of interest.

## EXAMPLE 9.15

### Using Hess's Law

What is the standard enthalpy change for the reaction:



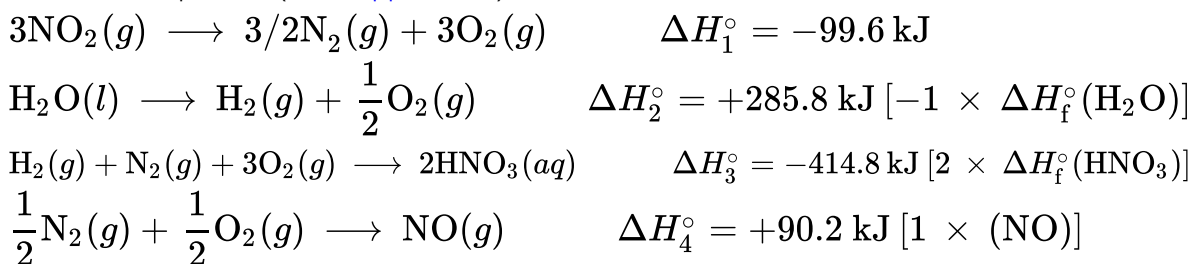
### Solution: Using the Equation

Use the special form of Hess's law given previously and values from [Appendix G](#):

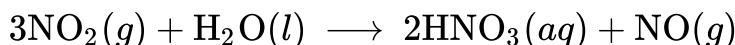
$$\begin{aligned}\Delta H_{\text{reaction}} &= \sum n \times \Delta H_{\text{f}}^{\circ}(\text{products}) - \sum n \times \Delta H_{\text{f}}^{\circ}(\text{reactants}) \\&= \left[ 2 \cancel{\text{mol HNO}_3(\text{aq})} \times \frac{-207.4 \text{ kJ}}{\cancel{\text{mol HNO}_3(\text{aq})}} + 1 \cancel{\text{mol NO}(g)} \times \frac{+90.2 \text{ kJ}}{\cancel{\text{mol NO}(g)}} \right] \\&\quad - \left[ 3 \cancel{\text{mol NO}_2(g)} \times \frac{+33.2 \text{ kJ}}{\cancel{\text{mol NO}_2(g)}} + 1 \cancel{\text{mol H}_2\text{O}(l)} \times \frac{-285.8 \text{ kJ}}{\cancel{\text{mol H}_2\text{O}(l)}} \right] \\&= [2 \times (-206.64) + 90.25] - [3 \times 33.2 + -(-285.83)] \\&= -323.03 + 186.23 \\&= -136.80 \text{ kJ}\end{aligned}$$

### Solution: Supporting Why the General Equation Is Valid

Alternatively, we can write this reaction as the sum of the decompositions of  $3\text{NO}_2(g)$  and  $1\text{H}_2\text{O}(l)$  into their constituent elements and the formation of  $2\text{HNO}_3(aq)$  and  $1\text{NO}(g)$  from their constituent elements. Writing out these reactions, and noting their relationships to the values for these compounds (from [Appendix G](#)), we have:



Summing these reaction equations gives the reaction we are interested in:



Summing their enthalpy changes gives the value we want to determine:

$$\begin{aligned}\Delta H_{\text{rxn}}^{\circ} &= \Delta H_1^{\circ} + \Delta H_2^{\circ} + \Delta H_3^{\circ} + \Delta H_4^{\circ} = (-99.6 \text{ kJ}) + (+285.8 \text{ kJ}) + (-414.8 \text{ kJ}) + (+90.2 \text{ kJ}) \\&= -138.4 \text{ kJ}\end{aligned}$$

So the standard enthalpy change for this reaction is  $\Delta H^\circ = -138.4 \text{ kJ}$ .

Note that this result was obtained by (1) multiplying the  $\Delta H_f^\circ$  of each product by its stoichiometric coefficient and summing those values, (2) multiplying the  $\Delta H_f^\circ$  of each reactant by its stoichiometric coefficient and summing those values, and then (3) subtracting the result found in (2) from the result found in (1). This is also the procedure in using the general equation, as shown.

### Check Your Learning

Calculate the heat of combustion of 1 mole of ethanol,  $\text{C}_2\text{H}_5\text{OH}(l)$ , when  $\text{H}_2\text{O}(l)$  and  $\text{CO}_2(g)$  are formed. Use the following enthalpies of formation:  $\text{C}_2\text{H}_5\text{OH}(l)$ ,  $-278 \text{ kJ/mol}$ ;  $\text{H}_2\text{O}(l)$ ,  $-286 \text{ kJ/mol}$ ; and  $\text{CO}_2(g)$ ,  $-394 \text{ kJ/mol}$ .

**Answer:**  $-1368 \text{ kJ/mol}$

# STRENGTHS OF IONIC AND COVALENT BONDS (9.4)

OpenStax

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

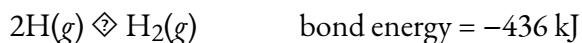
- Describe the energetics of covalent and ionic bond formation and breakage
- Use the Born-Haber cycle to compute lattice energies for ionic compounds
- Use average covalent bond energies to estimate enthalpies of reaction

A bond's strength describes how strongly each atom is joined to another atom and therefore how much energy is required to break the bond between the two atoms.

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  $\text{H}_2$ , 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:



Conversely, the same amount of energy is released when one mole of  $\text{H}_2$  molecules forms from two moles of H atoms:

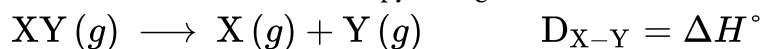


## Bond Strength: Covalent Bonds

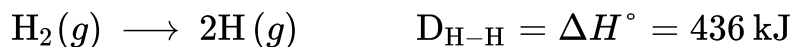
Stable molecules exist because covalent bonds hold the atoms together. We measure the strength of a covalent bond by the energy required to break it, that is, the energy necessary to separate the bonded atoms. Separating any pair of bonded atoms requires energy (see **Figure 4.4**). The stronger a bond, the greater the energy required to break it.

The energy required to break a specific covalent bond in one mole of gaseous molecules is called

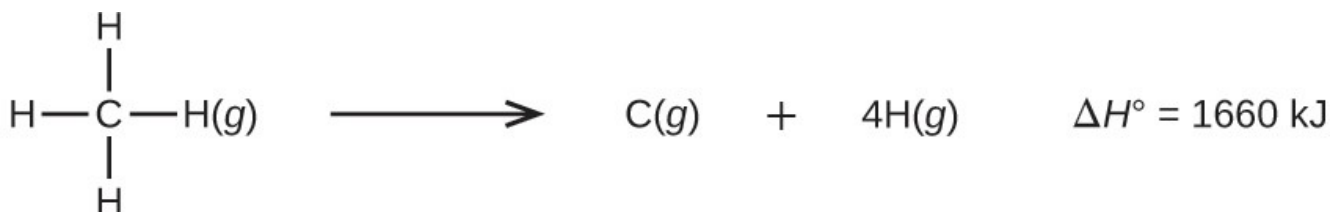
the bond energy or the bond dissociation energy. The bond energy for a diatomic molecule,  $D_{X-Y}$ , is defined as the standard enthalpy change for the endothermic reaction:



For example, the bond energy of the pure covalent H–H bond,  $D_{H-H}$ , is 436 kJ per mole of H–H bonds broken:



Molecules with three or more atoms have two or more bonds. The sum of all bond energies in such a molecule is equal to the standard enthalpy change for the endothermic reaction that breaks all the bonds in the molecule. For example, the sum of the four C–H bond energies in  $CH_4$ , 1660 kJ, is equal to the standard enthalpy change of the reaction:



**Figure 9.25** By: Rice University [Openstax CC BY NC SA](#)

The average C–H bond energy,  $D_{C-H}$ , is  $1660/4 = 415$  kJ/mol because there are four moles of C–H bonds broken per mole of the reaction. Although the four C–H bonds are equivalent in the original molecule, they do not each require the same energy to break; once the first bond is broken (which requires 439 kJ/mol), the remaining bonds are easier to break. The 415 kJ/mol value is the average, not the exact value required to break any one bond.

The strength of a bond between two atoms increases as the number of electron pairs in the bond increases. Generally, as the bond strength increases, the bond length decreases. Thus, we find that triple bonds are stronger and shorter than double bonds between the same two atoms; likewise, double bonds are stronger and shorter than single bonds between the same two atoms. Average bond energies for some common bonds appear in **Table 9.3**, and a comparison of bond lengths and bond strengths for some common bonds appears in **Table 9.4**. When one atom bonds to various atoms in a group, the bond strength typically decreases as we move down the group. For example, C–F is 439 kJ/mol, C–Cl is 330 kJ/mol, and C–Br is 275 kJ/mol.



**Table 9.3 Bond Energies (kJ/mol) By: Rice University [OpenStax CC BY-NC-SA 4.0](#)**

Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Energy
H-H	436	C-S	260	F-Cl	255
H-C	415	C-Cl	330	F-Br	235
H-N	390	C-Br	275	Si-Si	230
H-O	464	C-I	240	Si-P	215
H-F	569	N-N	160	Si-S	225
H-Si	395	N = N	418	Si-Cl	359
H-P	320	N $\equiv$ N	946	Si-Br	290
H-S	340	N-O	200	Si-I	215
H-Cl	432	N-F	270	P-P	215
H-Br	370	N-P	210	P-S	230
H-I	295	N-Cl	200	P-Cl	330
C-C	345	N-Br	245	P-Br	270
C = C	611	O-O	140	P-I	215
C $\equiv$ C	837	O = O	498	S-S	215
C-N	290	O-F	160	S-Cl	250
C = N	615	O-Si	370	S-Br	215
C $\equiv$ N	891	O-P	350	Cl-Cl	243
C-O	350	O-Cl	205	Cl-Br	220
C = O	741	O-I	200	Cl-I	210
C $\equiv$ O	1080	F-F	160	Br-Br	190
C-F	439	F-Si	540	Br-I	180
C-Si	360	F-P	489	I-I	150

C–P	265	F–S	285		
-----	-----	-----	-----	--	--

**Table 9.4 Average Bond Lengths and Bond Energies for Some Common Bonds By: Rice University [OpenStax](#) CC BY-NC-SA 4.0**

Bond	Bond Length (Å)	Bond Energy (kJ/mol)
C–C	1.54	345
C = C	1.34	611
C ≡ C	1.20	837
C–N	1.43	290
C = N	1.38	615
C ≡ N	1.16	891
C–O	1.43	350
C = O	1.23	741
C ≡ O	1.13	1080

The bond energy is the difference between the energy minimum (which occurs at the bond distance) and the energy of the two separated atoms. This is the quantity of energy released when the bond is formed. Conversely, the same amount of energy is required to break the bond. For the  $\text{H}_2$  molecule shown in **Figure 5.2**, at the bond distance of 74 pm, the system is  $7.24 \times 10^{-19}$  J lower in energy than the two separated hydrogen atoms. This may seem like a small number. However, as we will learn in more detail later, bond energies are often discussed on a per-mole basis. For example, it requires  $7.24 \times 10^{-19}$  J to break one H–H bond, but it takes  $4.36 \times 10^5$  J to break 1 mole of H–H bonds. A comparison of some bond lengths and energies is shown in **Figure 5.2** and **Table 9.3**. We can find many of these bonds in a variety of molecules, and this table provides average values. For example, breaking the first C–H bond in  $\text{CH}_4$  requires 439.3 kJ/mol, while breaking the first C–H bond in  $\text{H–CH}_2\text{C}_6\text{H}_5$  (a common paint thinner) requires 375.5 kJ/mol.

As seen in **Table 9.3** and **Table 9.4**, an average carbon-carbon single bond is 347 kJ/mol, while in a carbon-carbon double bond, the  $\pi$  bond increases the bond strength by 267 kJ/mol. Adding an additional  $\pi$  bond causes a further increase of 225 kJ/mol. We can see a similar pattern when we compare other  $\sigma$  and  $\pi$  bonds. Thus, each individual  $\pi$  bond is generally weaker than a corresponding  $\sigma$  bond between the same two atoms. In a  $\sigma$  bond, there is a greater degree of orbital overlap than in a  $\pi$  bond.

We can use bond energies to calculate approximate enthalpy changes for reactions where enthalpies of formation are not available. Calculations of this type will also tell us whether a reaction is exothermic or

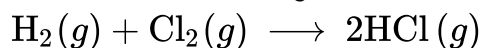
endothermic. An exothermic reaction ( $\Delta H$  negative, heat produced) results when the bonds in the products are stronger than the bonds in the reactants. An endothermic reaction ( $\Delta H$  positive, heat absorbed) results when the bonds in the products are weaker than those in the reactants.

The enthalpy change,  $\Delta H$ , for a chemical reaction is approximately equal to the sum of the energy required to break all bonds in the reactants (energy “in,” positive sign) plus the energy released when all bonds are formed in the products (energy “out,” negative sign). This can be expressed mathematically in the following way:

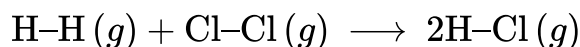
$$\Delta H = \Sigma D_{\text{bonds broken}} - \Sigma D_{\text{bonds formed}}$$

In this expression, the symbol  $\Sigma$  means “the sum of,” and  $D$  represents the bond energy in kilojoules per mole, which is always a positive number. The bond energy is obtained from a table (like **Table 9.4**) and will depend on whether the particular bond is a single, double, or triple bond. Thus, in calculating enthalpies in this manner, it is important that we consider the bonding in all reactants and products. Because  $D$  values are typically averages for one type of bond in many different molecules, this calculation provides a rough estimate, not an exact value, for the enthalpy of reaction.

Consider the following reaction:



or



To form two moles of  $\text{HCl}$ , one mole of  $\text{H}-\text{H}$  bonds and one mole of  $\text{Cl}-\text{Cl}$  bonds must be broken. The energy required to break these bonds is the sum of the bond energy of the  $\text{H}-\text{H}$  bond (436 kJ/mol) and the  $\text{Cl}-\text{Cl}$  bond (243 kJ/mol). During the reaction, two moles of  $\text{H}-\text{Cl}$  bonds are formed (bond energy = 432 kJ/mol), releasing  $2 \times 432$  kJ, or 864 kJ. Because the bonds in the products are stronger than those in the reactants, the reaction releases more energy than it consumes:

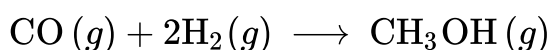
$$\begin{aligned} \Delta H &= \Sigma D_{\text{bonds broken}} - \Sigma D_{\text{bonds formed}} \\ \Delta H &= [D_{\text{H}-\text{H}} + D_{\text{Cl}-\text{Cl}}] - 2D_{\text{H}-\text{Cl}} \\ &= [436 + 243] - 2(432) = -185\text{kJ} \end{aligned}$$

This excess energy is released as heat, so the reaction is exothermic. **Appendix G** gives a value for the standard molar enthalpy of formation of  $\text{HCl}(g)$ ,  $\Delta H^\circ_f$ , of  $-92.307$  kJ/mol. Twice that value is  $-184.6$  kJ, which agrees well with the answer obtained earlier for the formation of two moles of  $\text{HCl}$ .

## EXAMPLE 9.16

## Using Bond Energies to Calculate Approximate Enthalpy Changes

Methanol,  $\text{CH}_3\text{OH}$ , may be an excellent alternative fuel. The high-temperature reaction of steam and carbon produces a mixture of the gases carbon monoxide,  $\text{CO}$ , and hydrogen,  $\text{H}_2$ , from which methanol can be produced. Using the bond energies in Table 9.4, calculate the approximate enthalpy change,  $\Delta H$ , for the reaction here:



## Solution

First, we need to write the Lewis structures of the reactants and the products:

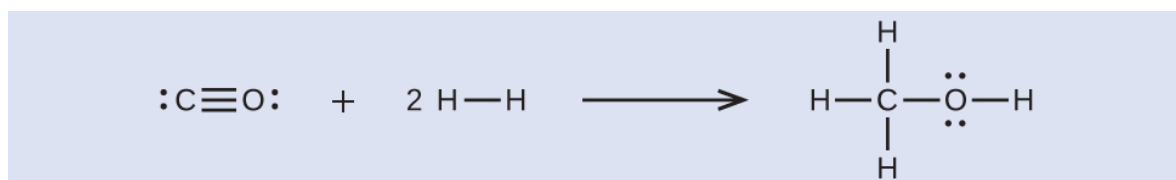


Figure 9.26 By: Rice University Openstax CC BY NC SA

From this, we see that  $\Delta H$  for this reaction involves the energy required to break a C–O triple bond and two H–H single bonds, as well as the energy produced by the formation of three C–H single bonds, a C–O single bond, and an O–H single bond. We can express this as follows:

$$\begin{aligned} \$\Delta H &= \Sigma D_{\text{bonds broken}} - \Sigma D_{\text{bonds formed}} \$ \\ \$\Delta H &= [D_{\text{C}\equiv\text{O}} + 2(D_{\text{H}-\text{H}})] - [3(D_{\text{C}-\text{H}}) + D_{\text{C}-\text{O}} + D_{\text{O}-\text{H}}] \$ \end{aligned}$$

Using the bond energy values in **Table 9.4**, we obtain:

$$\begin{aligned} \$\Delta H &= [1080 + 2(436)] - [3(415) + 350 + 464] \$ \\ &= -107\text{kJ} \end{aligned}$$

We can compare this value to the value calculated based on

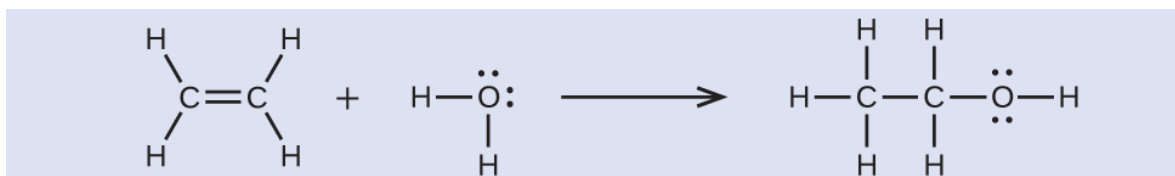
$$\begin{aligned} \Delta H &= [\Delta H_f^\circ \text{CH}_3\text{OH}(g)] - [\Delta H_f^\circ \text{CO}(g) + 2 \times \Delta H_f^\circ \text{H}_2] \\ &= [-201.0] - [-110.52 + 2 \times 0] \quad \text{Note that there} \\ &= -90.5 \text{ kJ} \end{aligned}$$

is a fairly significant gap between the values calculated using the two different methods. This

occurs because D values are the *average* of different bond strengths; therefore, they often give only rough agreement with other data.

### Check Your Learning

Ethyl alcohol,  $\text{CH}_3\text{CH}_2\text{OH}$ , was one of the first organic chemicals deliberately synthesized by humans. It has many uses in industry, and it is the alcohol contained in alcoholic beverages. It can be obtained by the fermentation of sugar or synthesized by the hydration of ethylene in the following reaction:



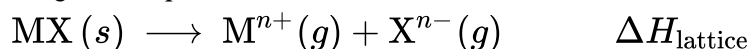
**Figure 9.27** By: Rice University [Openstax CC BY NC SA](#)

Using the bond energies in Table 9.4, calculate an approximate enthalpy change,  $\Delta H$ , for this reaction.

**Answer:**  $-35 \text{ kJ}$

## Ionic Bond Strength and Lattice Energy

An ionic compound is stable because of the electrostatic attraction between its positive and negative ions. The lattice energy of a compound is a measure of the strength of this attraction. The **lattice energy** ( $\Delta H_{\text{lattice}}$ ) of an ionic compound is defined as the energy required to separate one mole of the solid into its component gaseous ions. For the ionic solid  $\text{MX}$ , the lattice energy is the enthalpy change of the process:



Note that we are using the convention where the ionic solid is separated into ions, so our lattice energies will be *endothermic* (positive values). Some texts use the equivalent but opposite convention, defining lattice energy as the energy released when separate ions combine to form a lattice and give negative (exothermic) values. Thus, if you are looking up lattice energies in another reference, be certain to check which definition is being used. In both cases, a larger magnitude for lattice energy indicates a more stable ionic compound. For sodium chloride,

$\Delta H_{\text{lattice}} = 769 \text{ kJ}$ . Thus, it requires 769 kJ to separate one mole of solid NaCl into gaseous  $\text{Na}^+$  and  $\text{Cl}^-$  ions. When one mole of gaseous  $\text{Na}^+$  and  $\text{Cl}^-$  ions form solid NaCl, 769 kJ of heat is released.

The lattice energy  $\Delta H_{\text{lattice}}$  of an ionic crystal can be expressed by the following equation (derived from Coulomb's law, governing the forces between electric charges):

$$\Delta H_{\text{lattice}} = \frac{C (Z^+) (Z^-)}{R_o}$$

in which  $C$  is a constant that depends on the type of crystal structure,  $Z^+$  and  $Z^-$  are the charges on the ions, and  $R_o$  is the interionic distance (the sum of the radii of the positive and negative ions). Thus, the lattice energy of an ionic crystal increases rapidly as the charges of the ions increase and the sizes of the ions decrease. When all other parameters are kept constant, doubling the charge of both the cation and anion quadruples the lattice energy. For example, the lattice energy of LiF ( $Z^+$  and  $Z^- = 1$ ) is 1023 kJ/mol, whereas that of MgO ( $Z^+$  and  $Z^- = 2$ ) is 3900 kJ/mol ( $R_o$  is nearly the same—about 200 pm for both compounds).

Different interatomic distances produce different lattice energies. For example, we can compare the lattice energy of  $\text{MgF}_2$  (2957 kJ/mol) to that of  $\text{MgI}_2$  (2327 kJ/mol) to observe the effect on lattice energy of the smaller ionic size of  $\text{F}^-$  as compared to  $\text{I}^-$ .

## EXAMPLE 9.17

### Lattice Energy Comparisons

The precious gem ruby is aluminum oxide,  $\text{Al}_2\text{O}_3$ , containing traces of  $\text{Cr}^{3+}$ . The compound  $\text{Al}_2\text{Se}_3$  is used in the fabrication of some semiconductor devices. Which has the larger lattice energy,  $\text{Al}_2\text{O}_3$  or  $\text{Al}_2\text{Se}_3$ ?

### Solution

In these two ionic compounds, the charges  $Z^+$  and  $Z^-$  are the same, so the difference in lattice energy will depend upon  $R_o$ . The  $\text{O}^{2-}$  ion is smaller than the  $\text{Se}^{2-}$  ion. Thus,  $\text{Al}_2\text{O}_3$  would have a shorter interionic distance than  $\text{Al}_2\text{Se}_3$ , and  $\text{Al}_2\text{O}_3$  would have a larger lattice energy.

### Check Your Learning

Zinc oxide,  $\text{ZnO}$ , is a very effective sunscreen. How would the lattice energy of  $\text{ZnO}$  compare to that of  $\text{NaCl}$ ?

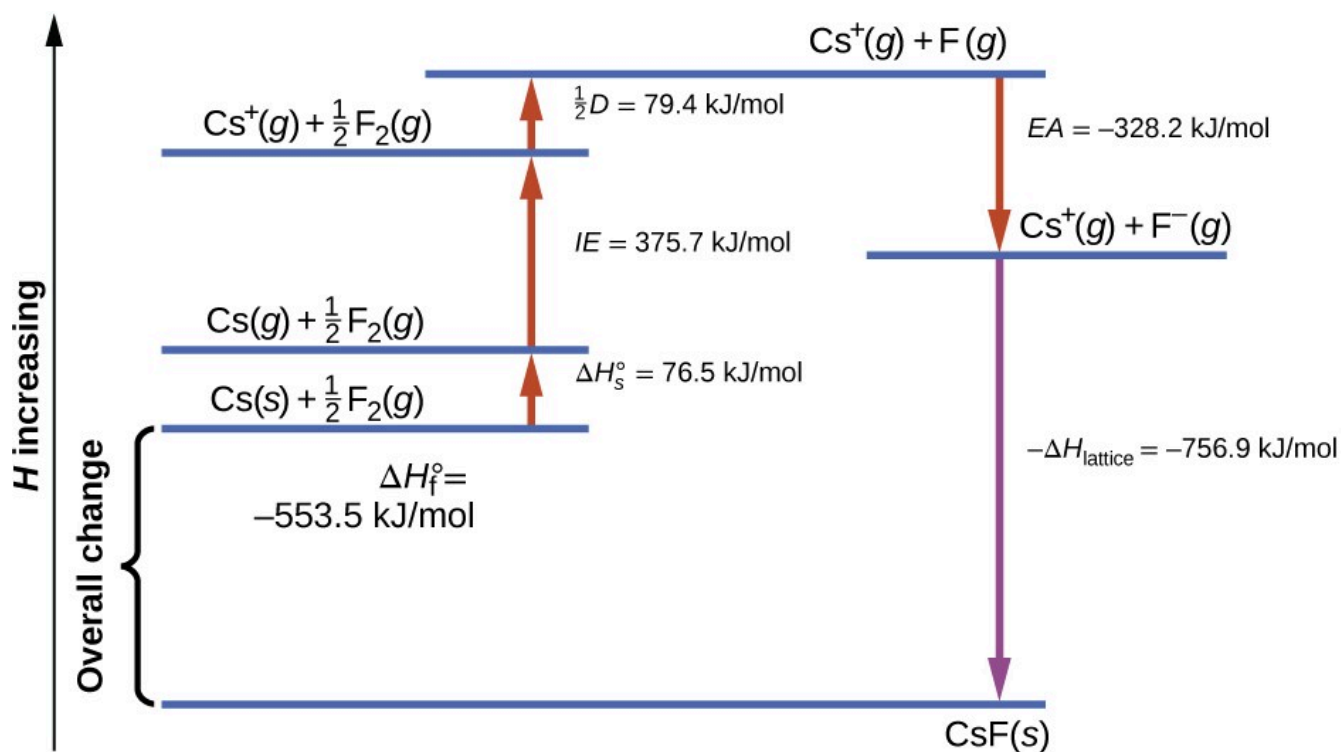
**Answer:** ZnO would have the larger lattice energy because the Z values of both the cation and the anion in ZnO are greater, and the interionic distance of ZnO is smaller than that of NaCl.

## The Born-Haber Cycle

It is not possible to measure lattice energies directly. However, the lattice energy can be calculated using the equation given in the previous section or by using a thermochemical cycle. The **Born-Haber cycle** is an application of Hess's law that breaks down the formation of an ionic solid into a series of individual steps:

- $\Delta H^\circ_f$ , the standard enthalpy of formation of the compound
- $IE$ , the ionization energy of the metal
- $EA$ , the electron affinity of the nonmetal
- $\Delta H^\circ_s$ , the enthalpy of sublimation of the metal
- $D$ , the bond dissociation energy of the nonmetal
- $\Delta H_{\text{lattice}}$ , the lattice energy of the compound

**Figure 9.25** diagrams the Born-Haber cycle for the formation of solid cesium fluoride.



**Figure 9.28** The Born-Haber cycle shows the relative energies of each step involved in the formation of an ionic solid from the necessary elements in their reference states. By: Rice University [Openstax CC BY NC SA](#)

We begin with the elements in their most common states,  $\text{Cs}(s)$  and  $\text{F}_2(g)$ . The  $\Delta H_s^\circ$  represents the conversion of solid cesium into a gas, and then the ionization energy converts the gaseous cesium atoms into cations. In the next step, we account for the energy required to break the F–F bond to produce fluorine atoms. Converting one mole of fluorine atoms into fluoride ions is an exothermic process, so this step gives off energy (the electron affinity) and is shown as decreasing along the  $y$ -axis. We now have one mole of Cs cations and one mole of F anions. These ions combine to produce solid cesium fluoride. The enthalpy change in this step is the negative of the lattice energy, so it is also an exothermic quantity. The total energy involved in this conversion is equal to the experimentally determined enthalpy of formation,  $\Delta H_f^\circ$ , of the compound from its elements. In this case, the overall change is exothermic.

Hess's law can also be used to show the relationship between the enthalpies of the individual steps and the enthalpy of formation. **Table 9.5** shows this for cesium fluoride, CsF.



**Table 9.5 By: Rice University** [OpenStax CC BY-NC-SA 4.0](#)

Enthalpy of sublimation of Cs(s)	$\text{Cs}(s) \rightarrow \text{Cs}(g)$	$\Delta H = \Delta H^\circ_s = 76.5 \text{ kJ/mol}$
One-half of the bond energy of F <sub>2</sub>	$\frac{1}{2} \text{F}_2(g) \rightarrow \text{F}(g)$	$\Delta H = \frac{1}{2} D = 79.4 \text{ kJ/mol}$
Ionization energy of Cs(g)	$\text{Cs}(g) \rightarrow \text{Cs}^+(g) + e^-$	$\Delta H = IE = 375.7 \text{ kJ/mol}$
Negative of the electron affinity of F	$\text{F}(g) + e^- \rightarrow \text{F}^-(g)$	$\Delta H = -EA = -328.2 \text{ kJ/mol}$
Negative of the lattice energy of CsF(s)	$\text{Cs}^+(g) + \text{F}^-(g) \rightarrow \text{CsF}(s)$	$\Delta H = -\Delta H_{\text{lattice}} = ?$
Enthalpy of formation of CsF(s), add steps 1–5	$\Delta H = \Delta H^\circ_f = \Delta H^\circ_s + \frac{1}{2} D + IE + (-EA) + (-\Delta H_{\text{lattice}})$ $\text{Cs}(s) + \frac{1}{2} \text{F}_2(g) \rightarrow \text{CsF}(s)$	$\Delta H = -553.5 \text{ kJ/mol}$

Thus, the lattice energy can be calculated from other values. For cesium fluoride, using this data, the lattice energy is:

$$\Delta H_{\text{lattice}} = 76.5 + 79.4 + 375.7 + (-328.2) - (-553.5) = 756.9 \text{ kJ/mol}$$

The Born-Haber cycle may also be used to calculate any one of the other quantities in the equation for lattice energy, provided that the remainder is known. For example, if the relevant enthalpy of sublimation  $\Delta H^\circ_s$ , ionization energy (IE), bond dissociation enthalpy (D), lattice energy  $\Delta H_{\text{lattice}}$ , and standard enthalpy of formation  $\Delta H^\circ_f$  are known, the Born-Haber cycle can be used to determine the electron affinity of an atom.

Lattice energies calculated for ionic compounds are typically much higher than bond dissociation energies measured for covalent bonds. Whereas lattice energies typically fall in the range of 600–4000 kJ/mol (some even higher), covalent bond dissociation energies are typically between 150–400 kJ/mol for single bonds. Keep in mind, however, that these are not directly comparable values. For ionic compounds, lattice energies are associated with many interactions, as cations and anions pack

together in an extended lattice. For covalent bonds, the bond dissociation energy is associated with the interaction of just two atoms.

# APPENDIX A – THE PERIODIC TABLE

OpenStax

Period

Group

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

1	<b>H</b> 1.008 hydrogen																	2	<b>He</b> 4.003 helium
2	3	4											5	6	7	8	9	10	
	<b>Li</b> 6.94 lithium	<b>Be</b> 9.012 beryllium											<b>B</b> 10.81 boron	<b>C</b> 12.01 carbon	<b>N</b> 14.01 nitrogen	<b>O</b> 16.00 oxygen	<b>F</b> 19.00 fluorine	<b>Ne</b> 20.18 neon	
3	11	12											13	14	15	16	17	18	
	<b>Na</b> 22.99 sodium	<b>Mg</b> 24.31 magnesium											<b>Al</b> 26.98 aluminum	<b>Si</b> 28.09 silicon	<b>P</b> 30.97 phosphorus	<b>S</b> 32.06 sulfur	<b>Cl</b> 35.45 chlorine	<b>Ar</b> 39.95 argon	
4	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	
	<b>K</b> 39.10 potassium	<b>Ca</b> 40.08 calcium	<b>Sc</b> 44.96 scandium	<b>Ti</b> 47.87 titanium	<b>V</b> 50.94 vanadium	<b>Cr</b> 52.00 chromium	<b>Mn</b> 54.94 manganese	<b>Fe</b> 55.85 iron	<b>Co</b> 58.93 cobalt	<b>Ni</b> 58.69 nickel	<b>Cu</b> 63.55 copper	<b>Zn</b> 65.38 zinc	<b>Ga</b> 69.72 gallium	<b>Ge</b> 72.63 germanium	<b>As</b> 74.92 arsenic	<b>Se</b> 78.97 selenium	<b>Br</b> 79.90 bromine	<b>Kr</b> 83.80 krypton	
5	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	
	<b>Rb</b> 85.47 rubidium	<b>Sr</b> 87.62 strontium	<b>Y</b> 88.91 yttrium	<b>Zr</b> 91.22 zirconium	<b>Nb</b> 92.91 niobium	<b>Mo</b> 95.95 molybdenum	<b>Tc</b> [97] technetium	<b>Ru</b> 101.1 ruthenium	<b>Rh</b> 102.9 rhodium	<b>Pd</b> 106.4 palladium	<b>Ag</b> 107.9 silver	<b>Cd</b> 112.4 cadmium	<b>In</b> 114.8 indium	<b>Sn</b> 118.7 tin	<b>Sb</b> 121.8 antimony	<b>Te</b> 127.6 tellurium	<b>I</b> 126.9 iodine	<b>Xe</b> 131.3 xenon	
6	55	56	57-71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	
	<b>Cs</b> 132.9 cesium	<b>Ba</b> 137.3 barium	<b>La-Lu</b> *	<b>Hf</b> 178.5 hafnium	<b>Ta</b> 180.9 tantalum	<b>W</b> 183.8 tungsten	<b>Re</b> 186.2 rhenium	<b>Os</b> 190.2 osmium	<b>Ir</b> 192.2 iridium	<b>Pt</b> 195.1 platinum	<b>Au</b> 197.0 gold	<b>Hg</b> 200.6 mercury	<b>Tl</b> 204.4 thallium	<b>Pb</b> 207.2 lead	<b>Bi</b> 209.0 bismuth	<b>Po</b> [209] polonium	<b>At</b> [210] astatine	<b>Rn</b> [222] radon	
7	87	88	89-103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	
	<b>Fr</b> [223] francium	<b>Ra</b> [226] radium	<b>Ac-Lr</b> **	<b>Rf</b> [267] rutherfordium	<b>Db</b> [270] dubnium	<b>Sg</b> [271] seaborgium	<b>Bh</b> [270] bohrium	<b>Hs</b> [277] hassium	<b>Mt</b> [276] meitnerium	<b>Ds</b> [281] darmstadtium	<b>Rg</b> [282] roentgenium	<b>Cn</b> [285] copernicium	<b>Nh</b> [285] nihonium	<b>Fl</b> [289] flerovium	<b>Mc</b> [288] moscovium	<b>Lv</b> [293] livermorium	<b>Ts</b> [294] tennessine	<b>Og</b> [294] oganesson	
			*	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	
				<b>La</b> 138.9 lanthanum	<b>Ce</b> 140.1 cerium	<b>Pr</b> 140.9 praseodymium	<b>Nd</b> 144.2 neodymium	<b>Pm</b> [145] promethium	<b>Sm</b> 150.4 samarium	<b>Eu</b> 152.0 europium	<b>Gd</b> 157.3 gadolinium	<b>Tb</b> 158.9 terbium	<b>Dy</b> 162.5 dysprosium	<b>Ho</b> 164.9 holmium	<b>Er</b> 167.3 erbium	<b>Tm</b> 168.9 thulium	<b>Yb</b> 173.1 ytterbium	<b>Lu</b> 175.0 lutetium	
			**	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	
				<b>Ac</b> [227] actinium	<b>Th</b> 232.0 thorium	<b>Pa</b> 231.0 protactinium	<b>U</b> 238.0 uranium	<b>Np</b> [237] neptunium	<b>Pu</b> [244] plutonium	<b>Am</b> [243] americium	<b>Cm</b> [247] curium	<b>Bk</b> [247] berkelium	<b>Cf</b> [251] californium	<b>Es</b> [252] einsteinium	<b>Fm</b> [257] fermium	<b>Md</b> [258] mendelevium	<b>No</b> [259] nobelium	<b>Lr</b> [262] lawrencium	

Atomic number → 1

Symbol → **H**

Atomic mass → 1.008

Name → hydrogen

Color Code	
<span style="background-color: #d9ead3; border: 1px solid #ccc; display: inline-block; width: 15px; height: 10px;"></span> Metal	<b>Solid</b>
<span style="background-color: #f4cccc; border: 1px solid #ccc; display: inline-block; width: 15px; height: 10px;"></span> Metalloid	<b>Liquid</b>
<span style="background-color: #cfe2f3; border: 1px solid #ccc; display: inline-block; width: 15px; height: 10px;"></span> Nonmetal	<b>Gas</b>

# APPENDIX B – ESSENTIAL MATHEMATICS

OpenStax

---

## 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 equal to or 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:

$$1000 = 1 \times 10^3$$

$$100 = 1 \times 10^2$$

$$1 = 1 \times 10^0$$

$$0.1 = 1 \times 10^{-1}$$

$$0.001 = 1 \times 10^{-3}$$

$$2386 = 2.386 \times 1000 = 2.386 \times 10^3$$

$$0.123 = 1.23 \times 0.1 = 1.23 \times 10^{-1}$$

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 a particularly useful notation for very large and very small numbers. For example,  $1,230,000,000 = 1.23 \times 10^9$ , and  $0.00000000036 = 3.6 \times 10^{-10}$ .

## 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.

### Example B1

#### **Adding Exponentials**

Add  $5.00 \times 10^{-5}$  and  $3.00 \times 10^{-3}$

#### **Solution**

$$3.00 \times 10^{-3} = 300 \times 10^{-5}$$

$$(5.00 \times 10^{-5}) + (300 \times 10^{-5}) = 305 \times 10^{-5} = 3.05 \times 10^{-3}$$

## 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.

### Example B2

#### Subtracting Exponentials

Subtract  $4.0 \times 10^{-7}$  from  $5.0 \times 10^{-6}$

#### Solution

$$4.0 \times 10^{-7} = 0.40 \times 10^{-6}$$

$$(5.0 \times 10^{-6}) - (0.40 \times 10^{-6}) = 4.6 \times 10^{-6}$$

## Multiplication of Exponentials

Multiply the digit terms in the usual way and add the exponents of the exponential terms.

### Example B3

#### Multiplying Exponentials

Multiply  $4.2 \times 10^{-8}$  by  $2.0 \times 10^3$

#### Solution

$$(4.2 \times 10^{-8}) \times (2.0 \times 10^{-3}) = (4.2 \times 2.0) \times 10^{(-8)+(-3)} = 8.4 \times 10^{-5}$$

## 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.

### Example B4

#### Division of Exponentials

Divide  $3.6 \times 10^5$  by  $6.0 \times 10^{-4}$

#### Solution

$$\frac{3.6 \times 10^5}{6.0 \times 10^{-4}} = \left( \frac{3.6}{6.0} \right) \times 10^{(5)-(-4)} = 0.60 \times 10^{-1} = 6.0 \times 10^{-2}$$

## Squaring of Exponentials

Square the digit term in the usual way and multiply the exponent of the exponential term by 2.

### Example B5

#### Squaring Exponentials

Square the number  $4.0 \times 10^{-6}$

#### Solution

$$(4.0 \times 10^{-6})^2 = 4 \times 4 \times 10^{2 \times (-6)} = 10^{-12} = 1.6 \times 10^{-11}$$

## Cubing of Exponentials

Cube the digit term in the usual way and multiply the exponent of the exponential term by 3.

### Example B6

#### **Cubing Exponentials**

Cube the number  $2 \times 10^4$ .

#### **Solution**

$$(2 \times 10^4)^3 = 2 \times 2 \times 2 \times 10^{3 \times 4} = 8 \times 10^{12}$$

## 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.

### Example B7

#### **Finding the Square Root of Exponentials**

Find the square root of  $1.6 \times 10^{-7}$

#### **Solution**

$$\begin{aligned} 1.6 \times 10^{-7} &= 16 \times 10^{-8} \\ \sqrt{16 \times 10^{-8}} &= \sqrt{16} \times \sqrt{10^{-8}} = \sqrt{16} \times 10^{-\frac{8}{2}} = 4.0 \times 10^{-4} \end{aligned}$$

## 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 reasonable 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 useful meaning in this situation. When reporting quantities, 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).

### Example B8

#### **Addition and Subtraction with Significant Figures**

add 4.383 g and 0.0023

#### **Solution**

$$\begin{array}{r} 4.\underline{383} \text{ g} \\ 0.0023 \text{ g} \\ \hline 4.385 \text{ g} \end{array}$$

In multiplication and division, the product or quotient should contain no more digits than that in the factor containing the least number of significant figures.

### Example B9

#### **Multiplication and Division with Significant Figures**

Multiply 0.6238 by 6.6

#### **Solution**

$$0.6238 \times 6.\underline{6} = 4.1$$



When rounding numbers, increase the retained digit by 1 if it is followed by a number larger than 5 (“round up”). Do not change the retained digit if the digits that follow are less than 5 (“round down”). If the retained digit is followed by 5, round up if the retained digit is odd or round down if it is even (after rounding, the retained digit will thus always be even).

## 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 table

Number	Number Expressed Exponentially	Common Logarithm
<b>1000</b>	$10^3$	3
<b>10</b>	$10^1$	1
<b>1</b>	$10^0$	0
<b>0.1</b>	$10^{-1}$	-1
<b>0.001</b>	$10^{-3}$	-3

What is the common logarithm of 60? Because 60 lies between 10 and 100, which have logarithms of 1 and 2, respectively, the logarithm of 60 is 1.7782; that is,  
 $60 = 10^{1.7782}$

The common logarithm of a number less than 1 has a negative value. The logarithm of 0.03918 is  $-1.4069$ , or

$$0.03918 = 10^{-1.4069} = \frac{1}{10^{1.4069}}$$

To obtain the common logarithm of a number, use the  $\log$  button on your calculator. To calculate a number from its logarithm, take the inverse log of the logarithm, or calculate  $10^x$  (where  $x$  is the logarithm of the number).

The natural logarithm of a number ( $\ln$ ) is the power to which  $e$  must be raised to equal the number;  $e$  is the constant 2.7182818. For example, the natural logarithm of 10 is 2.303; that is,  
 $10 = e^{2.303} = 2.7182818^{2.303}$

To obtain the natural logarithm of a number, use the  $\ln$  button on your calculator. To calculate a number

from its natural logarithm, enter the natural logarithm and take the inverse  $\ln$  of the natural logarithm or calculate  $e^x$  (where  $x$  is the natural logarithm of the number).

Logarithms are exponents; thus, operations involving logarithms follow the same rules as operations involving exponents.

1. The logarithm of a product of two numbers is the sum of the logarithms of the two numbers.

$$\log xy = \log x + \log y, \text{ and } \ln xy = \ln x + \ln y$$

2. The logarithm of the number resulting from the division of two numbers is the difference between the logarithms of the two numbers.

$$\log \frac{x}{y} = \log x - \log y, \text{ and } \ln \frac{x}{y} = \ln x - \ln y$$

3. The logarithm of a number raised to an exponent is the product of the exponent and the logarithm of the number.

$$\log x^n = n \log x \text{ and } \ln x^n = n \ln x$$

## The Solution of Quadratic Equations

Mathematical functions of this form are known as second-order polynomials or, more commonly, quadratic functions.

$$ax^2 + bx + c = 0$$

The solution or roots for any quadratic equation can be calculated using the following formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

### Example B10

#### Solving Quadratic Equations

Solve the quadratic equation  $3x^2 + 13x - 10 = 0$

#### Solution

Substituting the values  $a = 3$ ,  $b = 13$ ,  $c = -10$  in the formula, we obtain

$$x = \frac{-13 \pm \sqrt{(13)^2 - 4 \times 3 \times (-10)}}{2 \times 3}$$

$$x = \frac{-13 \pm \sqrt{169 + 120}}{6} = \frac{-13 \pm \sqrt{289}}{6} = \frac{-13 \pm 17}{6}$$

The two roots are therefore

$$x = \frac{-13 + 17}{6} = \frac{2}{3} \text{ and } x = \frac{-13 - 17}{6} = -5$$

Quadratic equations constructed on physical data always have real roots, and of these real roots, often only those having positive values are of any significance.

## 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 ( $y$ ).

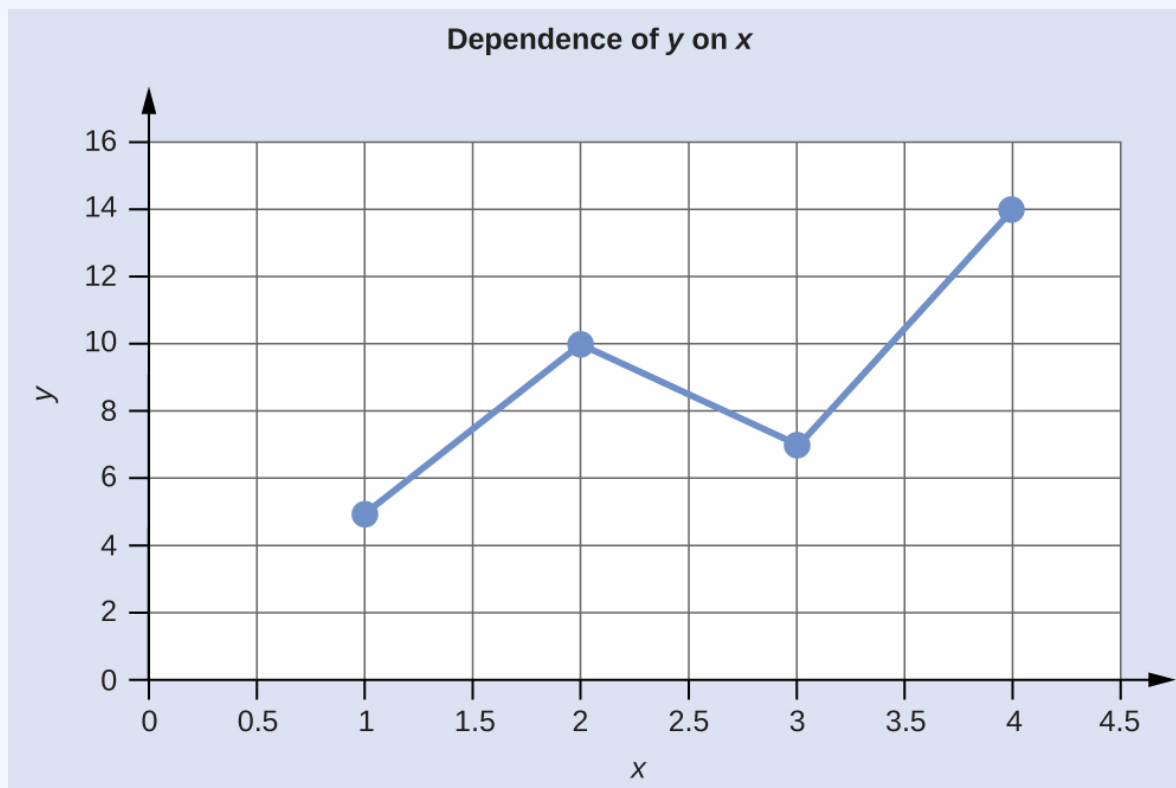
When the value of  $y$  is changing as a function of  $x$  (that is, different values of  $x$  correspond to different values of  $y$ ), a graph of this change can be plotted or sketched. The graph can be produced by using specific values for ( $x,y$ ) data pairs.

### Example B11

#### Graphing the Dependence of $y$ on $x$

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  $x$ .

$x$	$y$
1	5
2	10
3	7
4	14



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

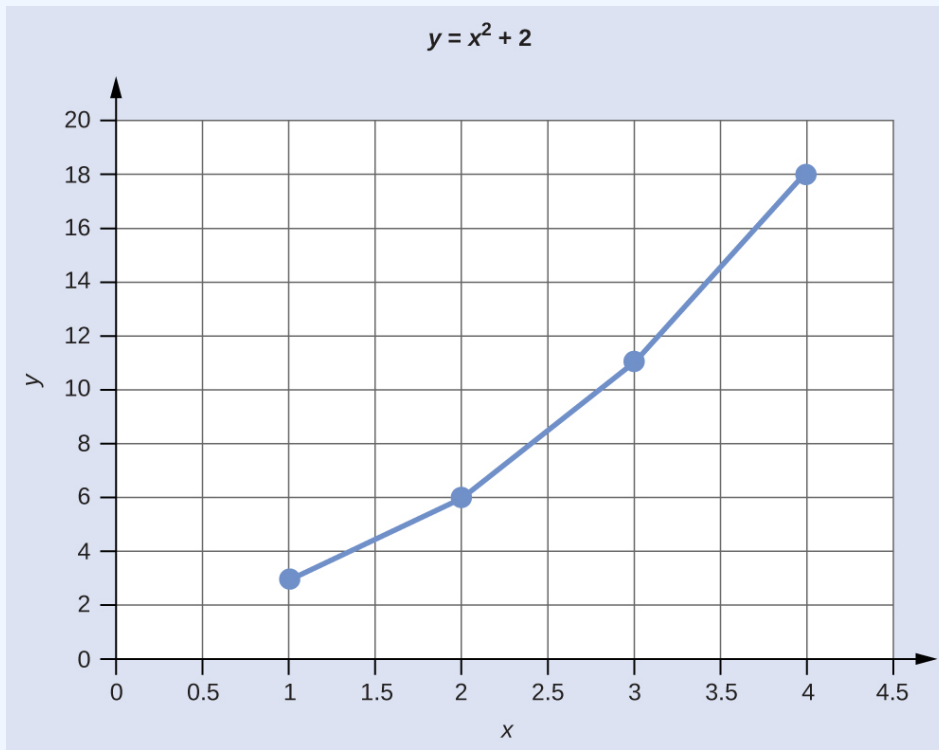
## Example B12

### 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.

A table of  $x$  and  $y$  coordinate data that is visually represented in the image below. The value of the  $y$  coordinate is determined by  $x$  in the equation " $y = x^2 + 2$ "

$x$	$y = x^2 + 2$
1	3
2	6
3	11
4	18



A line graph with the data in the table above is visualized. The value of  $y$  is determined by  $x$  and the equation  $x$  squared plus 2.

# APPENDIX C – UNITS AND CONVERSION FACTORS

OpenStax

---

## Units of Length

meter (m)	= 39.37 inches (in.) = 1.094 yards (yd)
centimeter (cm)	= 0.01 m (exact, definition)
millimeter (mm)	= 0.001 m (exact, definition)
kilometer (km)	= 1000 m (exact, definition)
angstrom ( $\text{\AA}$ )	= $10^{-8}$ cm (exact, definition) = $10^{-10}$ m (exact, definition)
yard (yd)	= 0.9144 m
inch (in.)	= 2.54 cm (exact, definition)
mile (US)	= 1.60934 km

## Units of Volume

<b>liter (L)</b>	= 0.001 m <sup>3</sup> (exact, definition) = 1000 cm <sup>3</sup> (exact, definition) = 1.057 (US) quarts
milliliter (mL)	= 0.001 L (exact, definition) = 1 cm <sup>3</sup> (exact, definition)
microliter (μL)	= 10 <sup>−6</sup> L (exact, definition) = 10 <sup>−3</sup> cm <sup>3</sup> (exact, definition)
liquid quart (US)	= 32 (US) liquid ounces (exact, definition) = 0.25 (US) gallon (exact, definition) = 0.9463 L
dry quart	= 1.1012 L
cubic foot (US)	= 28.316 L

## Units of Mass

gram (g)	= 0.001 kg (exact, definition)
milligram (mg)	= 0.001 g (exact, definition)
kilogram (kg)	= 1000 g (exact, definition) = 2.205 lb <sup>1</sup>

---

1. Strictly speaking, the ounce and pound are units of weight,  $W$  (a force equal to the product of mass and gravitational acceleration,  $W = mg$ ). The conversion relations in this table are commonly used to equate masses and weight assuming a nominal value for  $g$  at the surface of the earth.

## Units of Mass

ton (metric)	=1000 kg (exact, definition) = 2204.62 lb
ounce (oz)	= 28.35 g
pound (lb)	= 0.4535924 kg
ton (short)	=2000 lb (exact, definition) = 907.185 kg
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)	= $4.184 \times 10^7$ erg
erg	= $10^{-7}$ J (exact, definition)
electron-volt (eV)	= $1.60218 \times 10^{-19}$ J = 23.061 kcal mol <sup>-1</sup>
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 <sup>2</sup>

---

2. 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.



## Units of Pressure

torr	= 1 mm Hg (exact, definition)
pascal (Pa)	= N m <sup>-2</sup> (exact, definition) = kg m <sup>-1</sup> s <sup>-2</sup> (exact, definition)
atmosphere (atm)	= 760 mm Hg (exact, definition) = 760 torr (exact, definition) = 101,325 N m <sup>-2</sup> (exact, definition) = 101,325 Pa (exact, definition)
bar	= 10 <sup>5</sup> Pa (exact, definition) = 10 <sup>5</sup> kg m <sup>-1</sup> s <sup>-2</sup> (exact, definition)

# APPENDIX D – FUNDAMENTAL PHYSICAL CONSTANTS

OpenStax

---

## Fundamental Physical Constants

Name and Symbol	Value
atomic mass unit (amu)	$1.6605402 \times 10^{-27} \text{ kg}$
Avogadro's number	$6.0221367 \times 10^{23} \text{ mol}^{-1}$
Boltzmann's constant ( $k$ )	$1.380658 \times 10^{-23} \text{ J K}^{-1}$
charge-to-mass ratio for electron ( $e/m_e$ )	$1.75881962 \times 10^{11} \text{ C kg}^{-1}$
electron charge ( $e$ )	$1.60217733 \times 10^{-19} \text{ C}$
electron rest mass ( $m_e$ )	$9.1093897 \times 10^{-31} \text{ kg}$
Faraday's constant ( $F$ )	$9.6485309 \times 10^4 \text{ C mol}^{-1}$
gas constant ( $R$ )	$8.205784 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1} = 8.314510 \text{ J mol}^{-1} \text{ K}^{-1}$
molar volume of an ideal gas, 1 atm, 0 °C	$22.41409 \text{ L mol}^{-1}$
molar volume of an ideal gas, 1 bar, 0 °C	$22.71108 \text{ L mol}^{-1}$
neutron rest mass ( $m_n$ )	$1.6749274 \times 10^{-27} \text{ kg}$
Planck's constant ( $h$ )	$6.6260755 \times 10^{-34} \text{ J s}$
proton rest mass ( $m_p$ )	$1.6726231 \times 10^{-27} \text{ kg}$
Rydberg constant ( $R$ )	$1.0973731534 \times 10^7 \text{ m}^{-1} = 2.1798736 \times 10^{-18} \text{ J}$
speed of light (in vacuum) ( $c$ )	$2.99792458 \times 10^8 \text{ m s}^{-1}$

# APPENDIX E – WATER PROPERTIES

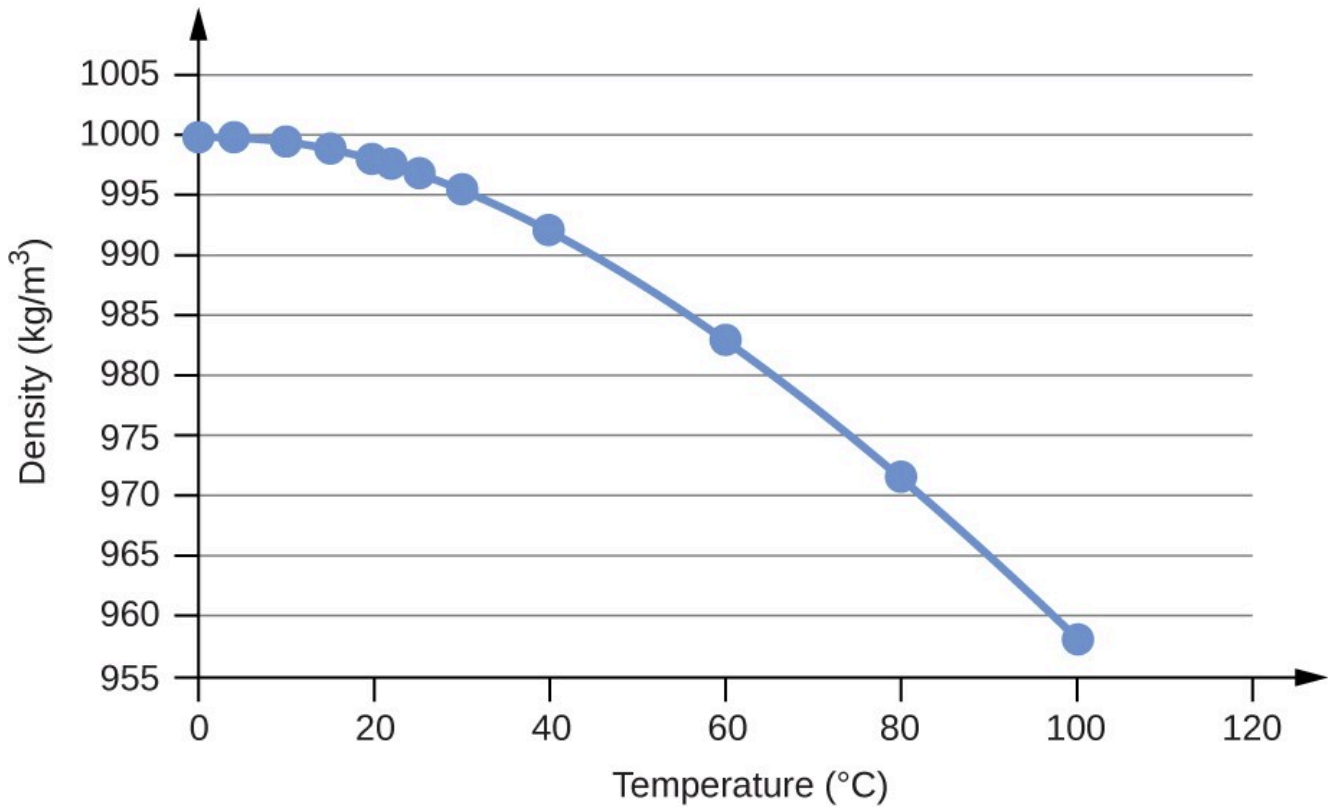
OpenStax

---

## Water Density (g/mL) at Different Temperatures (°C)

Temperature	Density (g/mL)
0	0.9998395
4	0.9999720 (density maximum)
10	0.9997026
15	0.9991026
20	0.9982071
22	0.9977735
25	0.9970479
30	0.9956502
40	0.9922
60	0.9832
80	0.9718
100	0.9584

Density of Water as a Function of Temperature

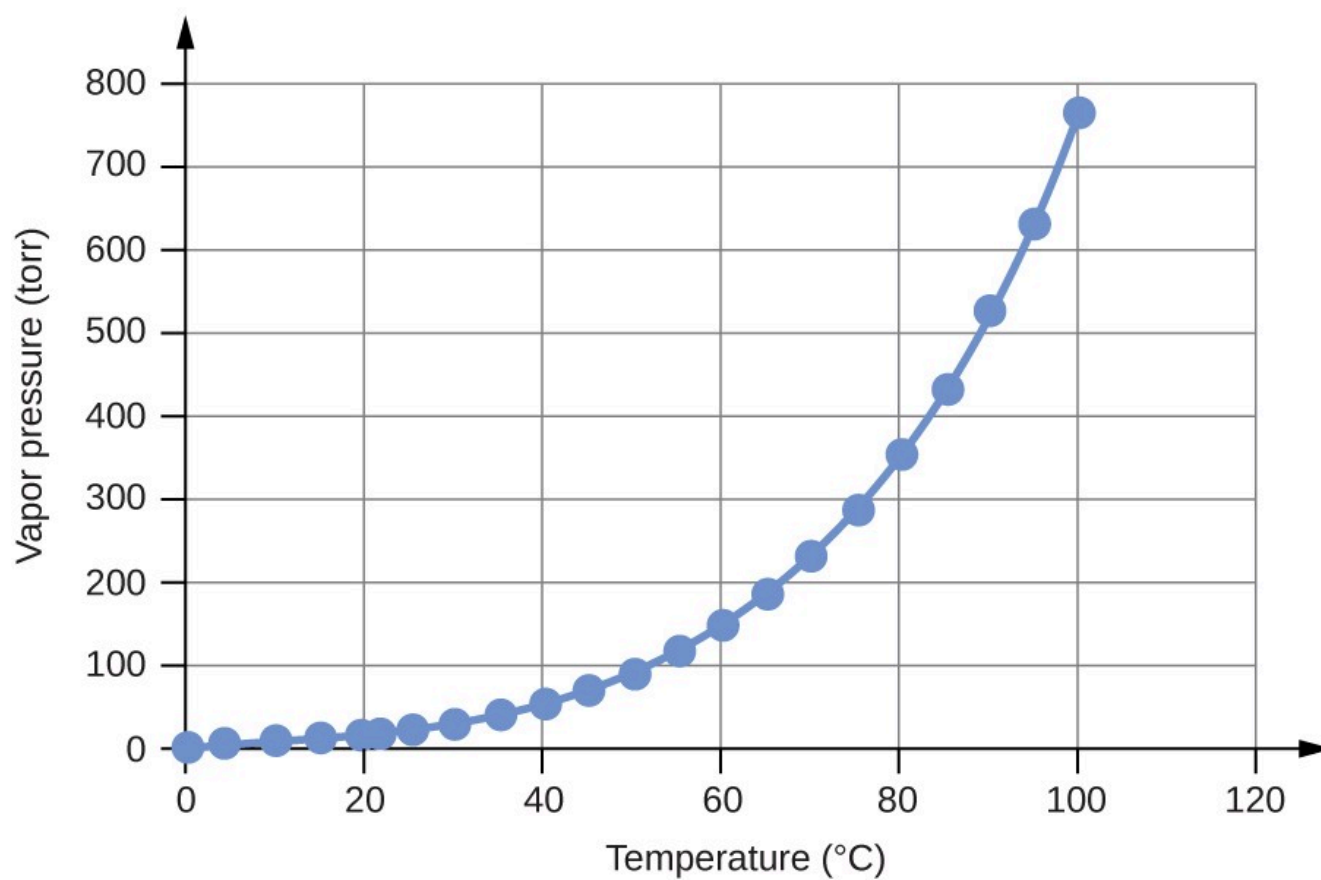


# Water Vapor Pressure at Different Temperatures (°C)

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

**Vapor Pressure as a Function of Temperature**



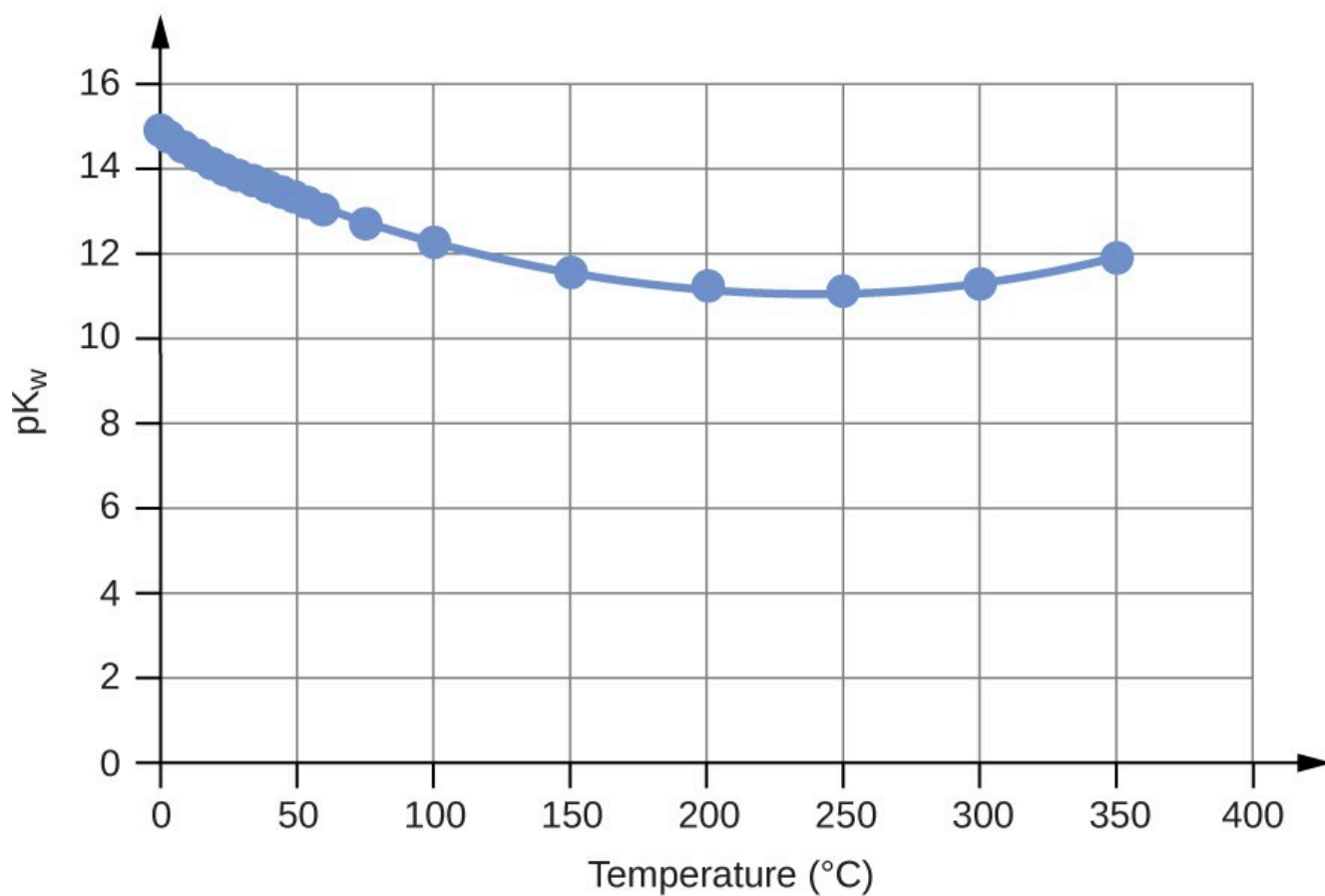
## Water $K_w$ and $pK_w$ at Different Temperatures (°C)

$$pK_w = -\log_{10}(K_w)$$



Temperature	$K_w$ 10 <sup>-14</sup>	pK <sub>w</sub>
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

### Water $pK_w$ as a Function of Temperature



### Specific Heat Capacity for Water

$C^\circ(\text{H}_2\text{O}(l)) = 4.184 \text{ J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1}$
$C^\circ(\text{H}_2\text{O}(s)) = 1.864 \text{ J} \cdot \text{K}^{-1} \cdot \text{g}^{-1}$
$C^\circ(\text{H}_2\text{O}(g)) = 2.093 \text{ J} \cdot \text{K}^{-1} \cdot \text{g}^{-1}$

## Standard Water Melting and Boiling Temperatures and Enthalpies of the Transitions

Temperature (K)	$\Delta H$ (kJ/mol)
Melting – 273.15	Boiling – 6.088
boiling – 373.15	40.656 (44.016 at 298 K)

## Water Cryoscopic (Freezing Point Depression) and Ebullioscopic (Boiling Point Elevation) Constants

$K_f = 1.86^\circ\text{C}\cdot\text{kg}\cdot\text{mol}^{-1}$ (cryoscopic constant)
$K_b = 0.51^\circ\text{C}\cdot\text{kg}\cdot\text{mol}^{-1}$ (ebullioscopic constant)

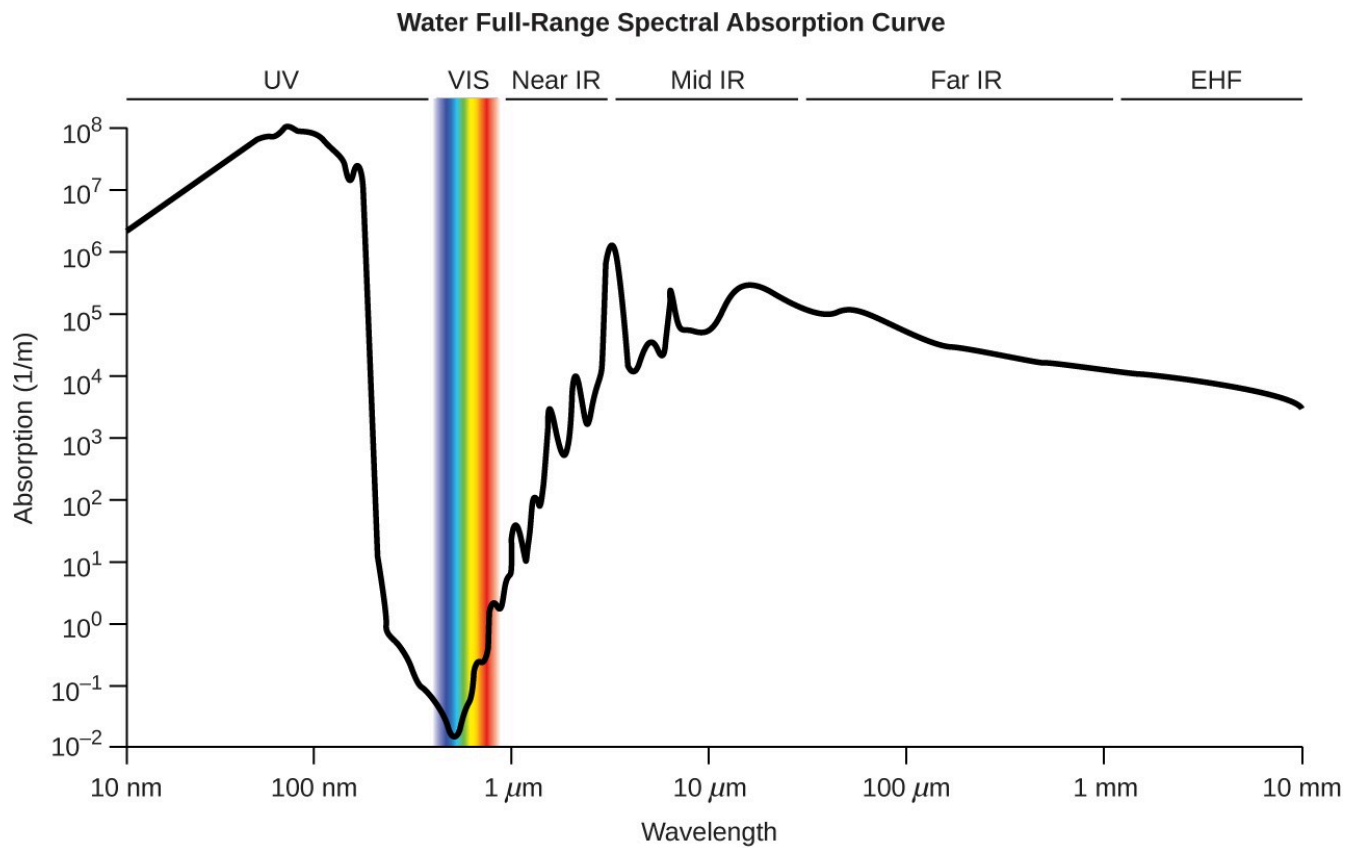


Figure E1 The plot shows the extent of light absorption versus wavelength for water. Absorption is reported in reciprocal meters and corresponds to the inverse of the distance light may travel through water before its intensity is diminished by  $1/e$  (~37%).

# APPENDIX F – COMPOSITION OF COMMERCIAL ACIDS AND BASES

OpenStax

## Composition Of Commercial Acids And Bases

Acid or Base <sup>1</sup>	Density (g/mL) <sup>2</sup>	Percentage by Mass	Molarity
acetic acid, glacial	1.05	99.5%	17.4
aqueous ammonia <sup>3</sup>	0.90	28%	14.8
hydrochloric acid	1.18	36%	11.6
nitric acid	1.42	71%	16.0
perchloric acid	1.67	70%	11.65
phosphoric acid	1.70	85%	14.7
sodium hydroxide	1.53	50%	19.1
sulfuric acid	1.84	96%	18.0

1. Acids and bases are commercially available as aqueous solutions. This table lists the properties (densities and concentrations) of common acid and base solutions. Nominal values are provided in cases where the manufacturer cites a range of concentrations and densities.
2. This column contains specific gravity data. In the case of this table, specific gravity is the ratio of the density of a substance to the density of pure water at the same conditions. Specific gravity is often cited on commercial labels.
3. This solution is sometimes called “ammonium hydroxide,” although this term is not chemically accurate.

# APPENDIX G – STANDARD THERMODYNAMIC PROPERTIES FOR SELECTED SUBSTANCES

OpenStax

---

## Standard Thermodynamic Properties For Aluminum

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
$\text{Al}(s)$	0	0	28.3
$\text{Al}(g)$	324.4	285.7	164.54
$\text{Al}^{3+}(aq)$	-531	-485	-321.7
$\text{Al}_2\text{O}_3(s)$	-1676	-1582	50.92
$\text{AlF}_3(s)$	-1510.4	-1425	66.5
$\text{AlCl}_3(s)$	-704.2	-628.8	110.67
$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}(s)$	-2691.57	-2269.40	376.56
$\text{Al}_2\text{S}_3(s)$	-724.0	-492.4	116.9
$\text{Al}_2(\text{SO}_4)_3(s)$	-3445.06	-3506.61	239.32

## Standard Thermodynamic Properties For Antimony

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
$\text{Sb}(s)$	0	0	45.69
$\text{Sb}(g)$	262.34	222.17	180.16
$\text{Sb}_4\text{O}_6(s)$	-1440.55	-1268.17	220.92
$\text{SbCl}_3(g)$	-313.8	-301.2	337.80
$\text{SbCl}_5(g)$	-394.34	-334.29	401.94
$\text{Sb}_2\text{S}_3(s)$	-174.89	-173.64	182.00
$\text{SbCl}_3(s)$	-382.17	-323.72	184.10
$\text{SbOCl}(s)$	-374.0	—	—

## Standard Thermodynamic Properties for Arsenic

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
As( <i>s</i> )	0	0	35.1
As( <i>g</i> )	302.5	261.0	174.21
As <sub>4</sub> ( <i>g</i> )	143.9	92.4	314
As <sub>4</sub> O <sub>6</sub> ( <i>s</i> )	−1313.94	−1152.52	214.22
As <sub>2</sub> O <sub>5</sub> ( <i>s</i> )	−924.87	−782.41	105.44
AsCl <sub>3</sub> ( <i>g</i> )	−261.50	−248.95	327.06
As <sub>2</sub> S <sub>3</sub> ( <i>s</i> )	−169.03	−168.62	163.59
AsH <sub>3</sub> ( <i>g</i> )	66.44	68.93	222.78
H <sub>3</sub> AsO <sub>4</sub> ( <i>s</i> )	−906.3	—	—



## Standard Thermodynamic Properties for Barium

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
Ba( <i>s</i> )	0	0	62.5
Ba( <i>g</i> )	180	146	170.24
Ba <sup>2+</sup> ( <i>aq</i> )	−537.6	−560.8	9.6
BaO( <i>s</i> )	−548.0	−520.3	72.1
BaCl <sub>2</sub> ( <i>s</i> )	−855.0	−806.7	123.7
BaSO <sub>4</sub> ( <i>s</i> )	−1473.2	−1362.3	132.2

## Standard Thermodynamic Properties for Beryllium

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
Be( <i>s</i> )	0	0	9.50
Be( <i>g</i> )	324.3	286.6	136.27
BeO( <i>s</i> )	−609.4	−580.1	13.8

## Standard Thermodynamic Properties for Bismuth

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
Bi( <i>s</i> )	0	0	56.74
Bi( <i>g</i> )	207.1	168.2	187.00
Bi <sub>2</sub> O <sub>3</sub> ( <i>s</i> )	−573.88	−493.7	151.5
BiCl <sub>3</sub> ( <i>s</i> )	−379.07	−315.06	176.98
Bi <sub>2</sub> S <sub>3</sub> ( <i>s</i> )	−143.1	−140.6	200.4

## Standard Thermodynamic Properties for Boron

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
B( <i>s</i> )	0	0	5.86
B( <i>g</i> )	565.0	521.0	153.4
B <sub>2</sub> O <sub>3</sub> ( <i>s</i> )	−1273.5	−1194.3	53.97
B <sub>2</sub> H <sub>6</sub> ( <i>g</i> )	36.4	87.6	232.1
H <sub>3</sub> BO <sub>3</sub> ( <i>s</i> )	−1094.33	−968.92	88.83
BF <sub>3</sub> ( <i>g</i> )	−1136.0	−1119.4	254.4
BCl <sub>3</sub> ( <i>g</i> )	−403.8	−388.7	290.1
B <sub>3</sub> N <sub>3</sub> H <sub>6</sub> ( <i>l</i> )	−540.99	−392.79	199.58
HBO <sub>2</sub> ( <i>s</i> )	−794.25	−723.41	37.66

## Standard Thermodynamic Properties for Bromine

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
$\text{Br}_2(l)$	0	0	152.23
$\text{Br}_2(g)$	30.91	3.142	245.5
$\text{Br}(g)$	111.88	82.429	175.0
$\text{Br}^-(aq)$	-120.9	-102.82	80.71
$\text{BrF}_3(g)$	-255.60	-229.45	292.42
$\text{HBr}(g)$	-36.3	-53.43	198.7

## Standard Thermodynamic Properties for Cadmium

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
$\text{Cd}(s)$	0	0	51.76
$\text{Cd}(g)$	112.01	77.41	167.75
$\text{Cd}^{2+}(aq)$	-75.90	-77.61	-73.2
$\text{CdO}(s)$	-258.2	-228.4	54.8
$\text{CdCl}_2(s)$	-391.5	-343.9	115.3
$\text{CdSO}_4(s)$	-933.3	-822.7	123.0
$\text{CdS}(s)$	-161.9	-156.5	64.9

## Standard Thermodynamic Properties for Calcium

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
$\text{Ca}(s)$	0	0	41.6
$\text{Ca}(g)$	178.2	144.3	154.88
$\text{Ca}^{2+}(aq)$	-542.96	-553.04	-55.2
$\text{CaO}(s)$	-634.9	-603.3	38.1
$\text{Ca}(\text{OH})_2(s)$	-985.2	-897.5	83.4
$\text{CaSO}_4(s)$	-1434.5	-1322.0	106.5
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(s)$	-2022.63	-1797.45	194.14
$\text{CaCO}_3(s)$ (calcite)	-1220.0	-1081.4	110.0
$\text{CaSO}_3 \cdot \text{H}_2\text{O}(s)$	-1752.68	-1555.19	184.10

## Standard Thermodynamic Properties for Carbon

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
C(s) (graphite)	0	0	5.740
C(s) (diamond)	1.89	2.90	2.38
C(g)	716.681	671.2	158.1
CO(g)	-110.52	-137.15	197.7
CO <sub>2</sub> (g)	-393.51	-394.36	213.8
CO <sub>3</sub> <sup>2-</sup> (aq)	-677.1	-527.8	-56.9
CH <sub>4</sub> (g)	-74.6	-50.5	186.3
CH <sub>3</sub> OH(l)	-239.2	-166.6	126.8
CH <sub>3</sub> OH(g)	-201.0	-162.3	239.9
CCl <sub>4</sub> (l)	-128.2	-62.5	214.4
CCl <sub>4</sub> (g)	-95.7	-58.2	309.7
CHCl <sub>3</sub> (l)	-134.1	-73.7	201.7
CHCl <sub>3</sub> (g)	-103.14	-70.34	295.71
CS <sub>2</sub> (l)	89.70	65.27	151.34
CS <sub>2</sub> (g)	116.9	66.8	238.0
C <sub>2</sub> H <sub>2</sub> (g)	227.4	209.2	200.9
C <sub>2</sub> H <sub>4</sub> (g)	52.4	68.4	219.3
C <sub>2</sub> H <sub>6</sub> (g)	-84.0	-32.0	229.2

$\text{CH}_3\text{CO}_2\text{H}(l)$	-484.3	-389.9	159.8
$\text{CH}_3\text{CO}_2\text{H}(g)$	-434.84	-376.69	282.50
$\text{C}_2\text{H}_5\text{OH}(l)$	-277.6	-174.8	160.7
$\text{C}_2\text{H}_5\text{OH}(g)$	-234.8	-167.9	281.6
$\text{HCO}_3^-(aq)$	-691.11	-587.06	95
$\text{C}_3\text{H}_8(g)$	-103.8	-23.4	270.3
$\text{C}_6\text{H}_6(g)$	82.927	129.66	269.2
$\text{C}_6\text{H}_6(l)$	49.1	124.50	173.4
$\text{CH}_2\text{Cl}_2(l)$	-124.2	-63.2	177.8
$\text{CH}_2\text{Cl}_2(g)$	-95.4	-65.90	270.2
$\text{CH}_3\text{Cl}(g)$	-81.9	-60.2	234.6
$\text{C}_2\text{H}_5\text{Cl}(l)$	-136.52	-59.31	190.79
$\text{C}_2\text{H}_5\text{Cl}(g)$	-112.17	-60.39	276.00
$\text{C}_2\text{N}_2(g)$	308.98	297.36	241.90
$\text{HCN}(l)$	108.9	125.0	112.8
$\text{HCN}(g)$	135.5	124.7	201.8

## Standard Thermodynamic Properties for Cesium

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
$\text{Cs}(aq)$	-248	-282.0	133

## Standard Thermodynamic Properties for Chlorine

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
$\text{Cl}_2(g)$	0	0	223.1
$\text{Cl}(g)$	121.3	105.70	165.2
$\text{Cl}^-(aq)$	-167.2	-131.2	56.5
$\text{ClF}(g)$	-54.48	-55.94	217.78
$\text{ClF}_3(g)$	-158.99	-118.83	281.50
$\text{Cl}_2\text{O}(g)$	80.3	97.9	266.2
$\text{Cl}_2\text{O}_7(l)$	238.1	—	—
$\text{Cl}_2\text{O}_7(g)$	272.0	—	—
$\text{HCl}(g)$	-92.307	-95.299	186.9
$\text{HClO}_4(l)$	-40.58	—	—



## Standard Thermodynamic Properties for Chromium

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
Cr( <i>s</i> )	0	0	23.77
Cr( <i>g</i> )	396.6	351.8	174.50
CrO <sub>4</sub> <sup>2-</sup> ( <i>aq</i> )	-881.2	-727.8	50.21
Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> ( <i>aq</i> )	-1490.3	-1301.1	261.9
Cr <sub>2</sub> O <sub>3</sub> ( <i>s</i> )	-1139.7	-1058.1	81.2
CrO <sub>3</sub> ( <i>s</i> )	-589.5	—	—
(NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> ( <i>s</i> )	-1806.7	—	—

## Standard Thermodynamic Properties of Cobalt

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
Co( <i>s</i> )	0	0	30.0
Co <sup>2+</sup> ( <i>aq</i> )	-67.4	-51.5	-155
Co <sup>3+</sup> ( <i>aq</i> )	92	134	-305.0
CoO( <i>s</i> )	-237.9	-214.2	52.97
Co <sub>3</sub> O <sub>4</sub> ( <i>s</i> )	-910.02	-794.98	114.22
Co(NO <sub>3</sub> ) <sub>2</sub> ( <i>s</i> )	-420.5	—	—

## Standard Thermodynamic Properties for Copper

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
$\text{Cu}(s)$	0	0	33.15
$\text{Cu}(g)$	338.32	298.58	166.38
$\text{Cu}^+(aq)$	51.9	50.2	−26
$\text{Cu}^{2+}(aq)$	64.77	65.49	−99.6
$\text{CuO}(s)$	−157.3	−129.7	42.63
$\text{Cu}_2\text{O}(s)$	−168.6	−146.0	93.14
$\text{CuS}(s)$	−53.1	−53.6	66.5
$\text{Cu}_2\text{S}(s)$	−79.5	−86.2	120.9
$\text{CuSO}_4(s)$	−771.36	−662.2	109.2
$\text{Cu}(\text{NO}_3)_2(s)$	−302.9	—	—

## Standard Thermodynamic Properties of Fluorine

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
$\text{F}_2(g)$	0	0	202.8
$\text{F}(g)$	79.4	62.3	158.8
$\text{F}^-(aq)$	-332.6	-278.8	-13.8
$\text{F}_2\text{O}(g)$	24.7	41.9	247.43
$\text{HF}(g)$	-273.3	-275.4	173.8

## Standard Thermodynamic Properties for Hydrogen

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
$\text{H}_2(g)$	0	0	130.7
$\text{H}(g)$	217.97	203.26	114.7
$\text{H}^+(aq)$	0	0	0
$\text{OH}^-(aq)$	-230.0	-157.2	-10.75
$\text{H}_3\text{O}^+(aq)$	-285.8		69.91
$\text{H}_2\text{O}(l)$	-285.83	-237.1	70.0
$\text{H}_2\text{O}(g)$	-241.82	-228.59	188.8
$\text{H}_2\text{O}_2(l)$	-187.78	-120.35	109.6
$\text{H}_2\text{O}_2(g)$	-136.3	-105.6	232.7
$\text{HF}(g)$	-273.3	-275.4	173.8
$\text{HCl}(g)$	-92.307	-95.299	186.9
$\text{HBr}(g)$	-36.3	-53.43	198.7
$\text{HI}(g)$	26.48	1.70	206.59
$\text{H}_2\text{S}(g)$	-20.6	-33.4	205.8
$\text{H}_2\text{Se}(g)$	29.7	15.9	219.0

## Standard Thermodynamic Properties for Iodine

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
$\text{I}_2(s)$	0	0	116.14
$\text{I}_2(g)$	62.438	19.3	260.7
$\text{I}(g)$	106.84	70.2	180.8
$\text{I}-(aq)$	-55.19	-51.57	11.13
$\text{IF}(g)$	95.65	-118.49	236.06
$\text{ICl}(g)$	17.78	-5.44	247.44
$\text{IBr}(g)$	40.84	3.72	258.66
$\text{IF}_7(g)$	-943.91	-818.39	346.44
$\text{HI}(g)$	26.48	1.70	206.59

## Standard Thermodynamic Properties of Iron

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
Fe( <i>s</i> )	0	0	27.3
Fe( <i>g</i> )	416.3	370.7	180.5
Fe <sup>2+</sup> ( <i>aq</i> )	−89.1	−78.90	−137.7
Fe <sup>3+</sup> ( <i>aq</i> )	−48.5	−4.7	−315.9
Fe <sub>2</sub> O <sub>3</sub> ( <i>s</i> )	−824.2	−742.2	87.40
Fe <sub>3</sub> O <sub>4</sub> ( <i>s</i> )	−1118.4	−1015.4	146.4
Fe(CO) <sub>5</sub> ( <i>l</i> )	−774.04	−705.42	338.07
Fe(CO) <sub>5</sub> ( <i>g</i> )	−733.87	−697.26	445.18
FeCl <sub>2</sub> ( <i>s</i> )	−341.79	−302.30	117.95
FeCl <sub>3</sub> ( <i>s</i> )	−399.49	−334.00	142.3
FeO( <i>s</i> )	−272.0	−255.2	60.75
Fe(OH) <sub>2</sub> ( <i>s</i> )	−569.0	−486.5	88.
Fe(OH) <sub>3</sub> ( <i>s</i> )	−823.0	−696.5	106.7
FeS( <i>s</i> )	−100.0	−100.4	60.29
Fe <sub>3</sub> C( <i>s</i> )	25.10	20.08	104.60

## Standard Thermodynamic Properties for Lead

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
Pb( <i>s</i> )	0	0	64.81
Pb( <i>g</i> )	195.2	162.	175.4
Pb <sup>2+</sup> ( <i>aq</i> )	−1.7	−24.43	10.5
PbO( <i>s</i> ) (yellow)	−217.32	−187.89	68.70
PbO( <i>s</i> ) (red)	−218.99	−188.93	66.5
Pb(OH) <sub>2</sub> ( <i>s</i> )	−515.9	—	—
PbS( <i>s</i> )	−100.4	−98.7	91.2
Pb(NO <sub>3</sub> ) <sub>2</sub> ( <i>s</i> )	−451.9	—	—
PbO <sub>2</sub> ( <i>s</i> )	−277.4	−217.3	68.6
PbCl <sub>2</sub> ( <i>s</i> )	−359.4	−314.1	136.0

## Standard Thermodynamic Properties for Lithium

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
Li(s)	0	0	29.1
Li(g)	159.3	126.6	138.8
Li+(aq)	-278.5	-293.3	13.4
LiH(s)	-90.5	-68.3	20.0
Li(OH)(s)	-487.5	-441.5	42.8
LiF(s)	-616.0	-587.5	35.7
Li <sub>2</sub> CO <sub>3</sub> (s)	-1216.04	-1132.19	90.17

## Standard Thermodynamic Properties for Magnesium

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
Mg <sup>2+</sup> (aq)	-466.9	-454.8	-138.1



## Standard Thermodynamic Properties for Manganese

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
$\text{Mn}(s)$	0	0	32.0
$\text{Mn}(g)$	280.7	238.5	173.7
$\text{Mn}^{2+}(aq)$	-220.8	-228.1	-73.6
$\text{MnO}(s)$	-385.2	-362.9	59.71
$\text{MnO}_2(s)$	-520.03	-465.1	53.05
$\text{Mn}_2\text{O}_3(s)$	-958.97	-881.15	110.46
$\text{Mn}_3\text{O}_4(s)$	-1378.83	-1283.23	155.64
$\text{MnO}_4^-(aq)$	-541.4	-447.2	191.2
$\text{MnO}_4^{2-}(aq)$	-653.0	-500.7	59

## Standard Thermodynamic Properties for Mercury

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
Hg( <i>l</i> )	0	0	75.9
Hg( <i>g</i> )	61.4	31.8	175.0
Hg <sub>2</sub> <sup>+</sup> ( <i>aq</i> )		164.8	
Hg <sub>2</sub> <sup>+</sup> ( <i>aq</i> )	172.4	153.9	84.5
HgO( <i>s</i> ) (red)	−90.83	−58.5	70.29
HgO( <i>s</i> ) (yellow)	−90.46	−58.43	71.13
HgCl <sub>2</sub> ( <i>s</i> )	−224.3	−178.6	146.0
Hg <sub>2</sub> Cl <sub>2</sub> ( <i>s</i> )	−265.4	−210.7	191.6
HgS( <i>s</i> ) (red)	−58.16	−50.6	82.4
HgS( <i>s</i> ) (black)	−53.56	−47.70	88.28
HgSO <sub>4</sub> ( <i>s</i> )	−707.51	−594.13	0.00

## Standard Thermodynamic Properties for Nickel

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
Ni <sub>2</sub> <sup>+</sup> ( <i>aq</i> )	−64.0	−46.4	−159

## Standard Thermodynamic Properties for Nitrogen

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
$\text{N}_2(g)$	0	0	191.6
$\text{N}(g)$	472.704	455.5	153.3
$\text{NO}(g)$	90.25	87.6	210.8
$\text{NO}_2(g)$	33.2	51.30	240.1
$\text{N}_2\text{O}(g)$	81.6	103.7	220.0
$\text{N}_2\text{O}_3(g)$	83.72	139.41	312.17
$\text{NO}_3^-(aq)$	-205.0	-108.7	146.4
$\text{N}_2\text{O}_4(g)$	11.1	99.8	304.4
$\text{N}_2\text{O}_5(g)$	11.3	115.1	355.7
$\text{NH}_3(g)$	-45.9	-16.5	192.8
$\text{NH}_4^+(aq)$	-132.5	-79.31	113.4
$\text{N}_2\text{H}_4(l)$	50.63	149.43	121.21
$\text{N}_2\text{H}_4(g)$	95.4	159.4	238.5
$\text{NH}_4\text{NO}_3(s)$	-365.56	-183.87	151.08
$\text{NH}_4\text{Cl}(s)$	-314.43	-202.87	94.6
$\text{NH}_4\text{Br}(s)$	-270.8	-175.2	113.0
$\text{NH}_4\text{I}(s)$	-201.4	-112.5	117.0
$\text{NH}_4\text{NO}_2(s)$	-256.5	—	—

$\text{HNO}_3(l)$	-174.1	-80.7	155.6
$\text{HNO}_3(g)$	-133.9	-73.5	266.9

## Standard Thermodynamic Properties for Oxygen

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
$\text{O}_2(g)$	0	0	205.2
$\text{O}(g)$	249.17	231.7	161.1
$\text{O}_3(g)$	142.7	163.2	238.9

## Standard Thermodynamic Properties for Phosphorus

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
$\text{P}_4(s)$	0	0	164.4
$\text{P}_4(g)$	58.91	24.4	280.0
$\text{P}(g)$	314.64	278.25	163.19
$\text{PH}_3(g)$	5.4	13.5	210.2
$\text{PCl}_3(g)$	-287.0	-267.8	311.78
$\text{PCl}_5(g)$	-374.9	-305.0	364.4
$\text{P}_4\text{O}_6(s)$	-1640.1	—	—
$\text{P}_4\text{O}_{10}(s)$	-2984.0	-2697.0	228.86
$\text{PO}_4^{3-}(aq)$	-1277	-1019	-222
$\text{HPO}_3(s)$	-948.5	—	—
$\text{HPO}_4^{2-}(aq)$	-1292.1	-1089.3	-33
$\text{H}_2\text{PO}_4^{2-}(aq)$	-1296.3	-1130.4	90.4
$\text{H}_3\text{PO}_2(s)$	-604.6	—	—
$\text{H}_3\text{PO}_3(s)$	-964.4	—	—
$\text{H}_3\text{PO}_4(s)$	-1279.0	-1119.1	110.50
$\text{H}_3\text{PO}_4(l)$	-1266.9	-1124.3	110.5
$\text{H}_4\text{P}_2\text{O}_7(s)$	-2241.0	—	—
$\text{POCl}_3(l)$	-597.1	-520.8	222.5

$\text{POCl}_3(g)$	-558.5	-512.9	325.5
--------------------	--------	--------	-------

## Standard Thermodynamic Properties of Potassium

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
$\text{K}(s)$	0	0	64.7
$\text{K}(g)$	89.0	60.5	160.3
$\text{K}^+(aq)$	-252.4	-283.3	102.5
$\text{KF}(s)$	-576.27	-537.75	66.57
$\text{KCl}(s)$	-436.5	-408.5	82.6

## Standard Thermodynamic Properties for Rubidium

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
$\text{Rb}^+(aq)$	-246	-282.2	124



## Standard Thermodynamic Properties for Silicon

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
Si( <i>s</i> )	0	0	18.8
Si( <i>g</i> )	450.0	405.5	168.0
SiO <sub>2</sub> ( <i>s</i> )	−910.7	−856.3	41.5
SiH <sub>4</sub> ( <i>g</i> )	34.3	56.9	204.6
H <sub>2</sub> SiO <sub>3</sub> ( <i>s</i> )	−1188.67	−1092.44	133.89
H <sub>4</sub> SiO <sub>4</sub> ( <i>s</i> )	−1481.14	−1333.02	192.46
SiF <sub>4</sub> ( <i>g</i> )	−1615.0	−1572.8	282.8
SiCl <sub>4</sub> ( <i>l</i> )	−687.0	−619.8	239.7
SiCl <sub>4</sub> ( <i>g</i> )	−662.75	−622.58	330.62
SiC( <i>s, beta cubic</i> )	−73.22	−70.71	16.61
SiC( <i>s, alpha hexagonal</i> )	−71.55	−69.04	16.48

## Standard Thermodynamic Properties for Silver

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
$\text{Ag}(s)$	0	0	42.55
$\text{Ag}(g)$	284.9	246.0	172.89
$\text{Ag}^+(aq)$	105.6	77.11	72.68
$\text{Ag}_2\text{O}(s)$	-31.05	-11.20	121.3
$\text{AgCl}(s)$	-127.0	-109.8	96.3
$\text{Ag}_2\text{S}(s)$	-32.6	-40.7	144.0

## Standard Thermodynamic Properties for Sodium

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
$\text{Na}(s)$	0	0	51.3
$\text{Na}(g)$	107.5	77.0	153.7
$\text{Na}^+(aq)$	-240.1	-261.9	59
$\text{Na}_2\text{O}(s)$	-414.2	-375.5	75.1
$\text{NaCl}(s)$	-411.2	-384.1	72.1

## Standard Thermodynamic Properties for Strontium

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
$\text{Sr}^{2+}(\text{aq})$	-545.8	-557.3	-32.6

## Standard Thermodynamic Properties for Sulfur

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
$\text{S}_8(s)$ (rhombic)	0	0	256.8
$\text{S}(g)$	278.81	238.25	167.82
$\text{S}_2(aq)$	41.8	83.7	22
$\text{SO}_2(g)$	-296.83	-300.1	248.2
$\text{SO}_3(g)$	-395.72	-371.06	256.76
$\text{SO}_4^{2-}(aq)$	-909.3	-744.5	20.1
$\text{S}_2\text{O}_3^{2-}(aq)$	-648.5	-522.5	67
$\text{H}_2\text{S}(g)$	-20.6	-33.4	205.8
$\text{HS}^-(aq)$	-17.7	12.6	61.1
$\text{H}_2\text{SO}_4(l)$	-813.989	690.00	156.90
$\text{HSO}_4^-(aq)$	-885.75	-752.87	126.9
$\text{H}_2\text{S}_2\text{O}_7(s)$	-1273.6	—	—
$\text{SF}_4(g)$	-728.43	-684.84	291.12
$\text{SF}_6(g)$	-1220.5	-1116.5	291.5
$\text{SCl}_2(l)$	-50	—	—
$\text{SCl}_2(g)$	-19.7	—	—
$\text{S}_2\text{Cl}_2(l)$	-59.4	—	—
$\text{S}_2\text{Cl}_2(g)$	-19.50	-29.25	319.45

$\text{SOCl}_2(g)$	-212.55	-198.32	309.66
$\text{SOCl}_2(l)$	-245.6	—	—
$\text{SO}_2\text{Cl}_2(l)$	-394.1	—	—
$\text{SO}_2\text{Cl}_2(g)$	-354.80	-310.45	311.83

## Standard Thermodynamic Properties for Tin

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
$\text{Sn}(s)$	0	0	51.2
$\text{Sn}(g)$	301.2	266.2	168.5
$\text{SnO}(s)$	-285.8	-256.9	56.5
$\text{SnO}_2(s)$	-577.6	-515.8	49.0
$\text{SnCl}_4(l)$	-511.3	-440.1	258.6
$\text{SnCl}_4(g)$	-471.5	-432.2	365.8

## Standard Thermodynamic Properties for Titanium

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
Ti( <i>s</i> )	0	0	30.7
Ti( <i>g</i> )	473.0	428.4	180.3
TiO <sub>2</sub> ( <i>s</i> )	−944.0	−888.8	50.6
TiCl <sub>4</sub> ( <i>l</i> )	−804.2	−737.2	252.4
TiCl <sub>4</sub> ( <i>g</i> )	−763.2	−726.3	353.2

## Standard Thermodynamic Properties for Tungsten

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
W( <i>s</i> )	0	0	32.6
W( <i>g</i> )	849.4	807.1	174.0
WO <sub>3</sub> ( <i>s</i> )	−842.9	−764.0	75.9

## Standard Thermodynamic Properties for Zinc

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
$\text{Zn}(s)$	0	0	41.6
$\text{Zn}(g)$	130.73	95.14	160.98
$\text{Zn}^{2+}(aq)$	-153.9	-147.1	-112.1
$\text{ZnO}(s)$	-350.5	-320.5	43.7
$\text{ZnCl}_2(s)$	-415.1	-369.43	111.5
$\text{ZnS}(s)$	-206.0	-201.3	57.7
$\text{ZnSO}_4(s)$	-982.8	-871.5	110.5
$\text{ZnCO}_3(s)$	-812.78	-731.57	82.42



## Standard Thermodynamic Properties for Complexes

Substance	$\Delta H^\circ_f(\text{kJ mol}^{-1})$	$\Delta G^\circ_f(\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
$[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{NO}_3$ , <i>cis</i>	–898.7	—	—
$[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{NO}_3$ , <i>trans</i>	–896.2	—	—
$\text{NH}_4[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$	–837.6	—	—
$[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]_3$	–2733.0	—	—
$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ , <i>cis</i>	–874.9	—	—
$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ , <i>trans</i>	–877.4	—	—
$[\text{Co}(\text{en})_2(\text{NO}_2)_2]\text{NO}_3$ , <i>cis</i>	–689.5	—	—
$[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ , <i>cis</i>	–681.2	—	—
$[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ , <i>trans</i>	–677.4	—	—
$[\text{Co}(\text{en})_3](\text{ClO}_4)_3$	–762.7	—	—
$[\text{Co}(\text{en})_3]\text{Br}_2$	–595.8	—	—
$[\text{Co}(\text{en})_3]\text{I}_2$	–475.3	—	—
$[\text{Co}(\text{en})_3]\text{I}_3$	–519.2	—	—
$[\text{Co}(\text{NH}_3)_6](\text{ClO}_4)_3$	–1034.7	–221.1	615
$[\text{Co}(\text{NH}_3)_5\text{NO}_2](\text{NO}_3)_2$	–1088.7	–412.9	331
$[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$	–1282.0	–524.5	448
$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	–1017.1	–582.5	366.1
$[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$	–725.5	—	—

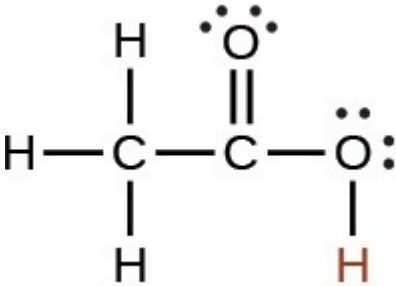
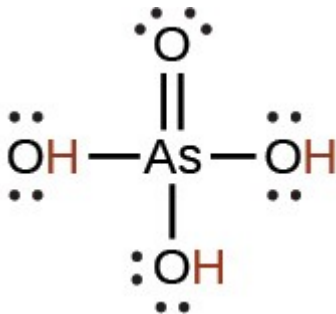
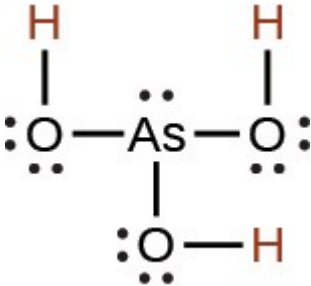
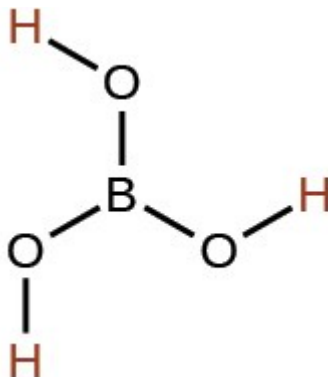
$[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$	-994.1	—	—
$[\text{Ni}(\text{NH}_3)_6]\text{Br}_2$	-923.8	—	—
$[\text{Ni}(\text{NH}_3)_6]\text{I}_2$	-808.3	—	—

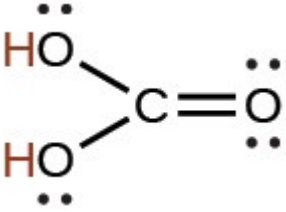
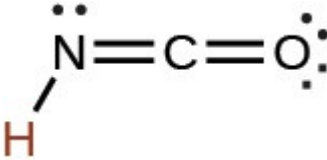
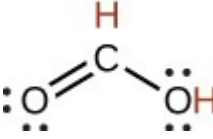

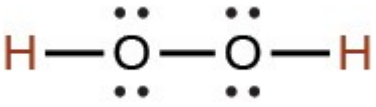
# APPENDIX H – IONIZATION CONSTANTS OF WEAK ACIDS

OpenStax

---

Ionization Constants Of Weak Acids

Acid	Formula	$K_a$ at 25 °C	Lewis Structure
acetic	$\text{CH}_3\text{CO}_2\text{H}$	$1.8 \times 10^{-5}$	
arsenic	$\text{H}_3\text{AsO}_4$	$5.5 \times 10^{-3}$	
	$\text{H}_2\text{AsO}_4^-$	$1.7 \times 10^{-7}$	
	$\text{HAsO}_4^{2-}$	$3.0 \times 10^{-12}$	
arsenous	$\text{H}_3\text{AsO}_3$	$5.1 \times 10^{-10}$	
boric	$\text{H}_3\text{BO}_3$	$5.4 \times 10^{-10}$	

carbonic	$\text{H}_2\text{CO}_3$	$4.3 \times 10^{-7}$	
	$\text{HCO}_3^-$	$4.7 \times 10^{-11}$	
cyanic	$\text{HCNO}$	$2 \times 10^{-4}$	
formic	$\text{HCO}_2\text{H}$	$1.8 \times 10^{-4}$	
hydrazoic	$\text{HN}_3$	$2.5 \times 10^{-5}$	
hydrocyanic	$\text{HCN}$	$4.9 \times 10^{-10}$	
hydrofluoric	$\text{HF}$	$6.4 \times 10^{-4}$	
hydrogen peroxide	$\text{H}_2\text{O}_2$	$2.4 \times 10^{-12}$	
hydrogen selenide	$\text{H}_2\text{Se}$	$1.29 \times 10^{-4}$	
	$\text{HSe}^-$	$1 \times 10^{-12}$	

hydrogen sulfate ion	$\text{HSO}_4^-$	$1.2 \times 10^{-2}$	
hydrogen sulfide	$\text{H}_2\text{S}$	$8.9 \times 10^{-8}$	
	$\text{HS}^-$	$1.0 \times 10^{-19}$	
hydrogen telluride	$\text{H}_2\text{Te}$	$2.3 \times 10^{-3}$	
	$\text{HTe}^-$	$1.6 \times 10^{-11}$	
hypobromous	$\text{HBrO}$	$2.8 \times 10^{-9}$	
hypochlorous	$\text{HClO}$	$2.9 \times 10^{-8}$	
nitrous	$\text{HNO}_2$	$4.6 \times 10^{-4}$	
oxalic	$\text{H}_2\text{C}_2\text{O}_4$	$6.0 \times 10^{-2}$	
	$\text{HC}_2\text{O}_4^-$	$6.1 \times 10^{-5}$	

phosphoric	$\text{H}_3\text{PO}_4$	$7.5 \times 10^{-3}$	
	$\text{H}_2\text{PO}_4^-$	$6.2 \times 10^{-8}$	
	$\text{HPO}_4^{2-}$	$4.2 \times 10^{-13}$	
phosphorous	$\text{H}_3\text{PO}_3$	$5 \times 10^{-2}$	
	$\text{H}_2\text{PO}_3^-$	$2.0 \times 10^{-7}$	
sulfurous	$\text{H}_2\text{SO}_3$	$1.6 \times 10^{-2}$	
	$\text{HSO}_3^-$	$6.4 \times 10^{-8}$	

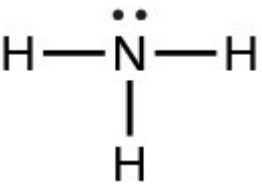
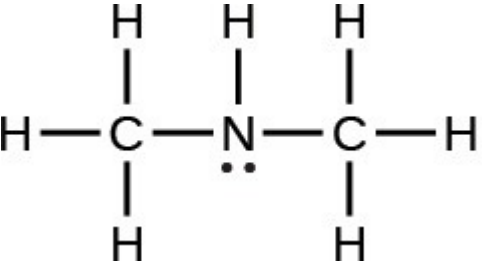
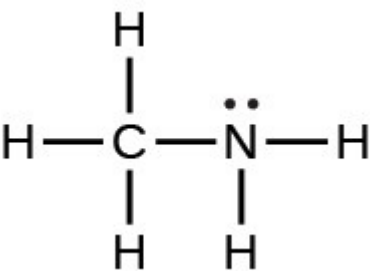
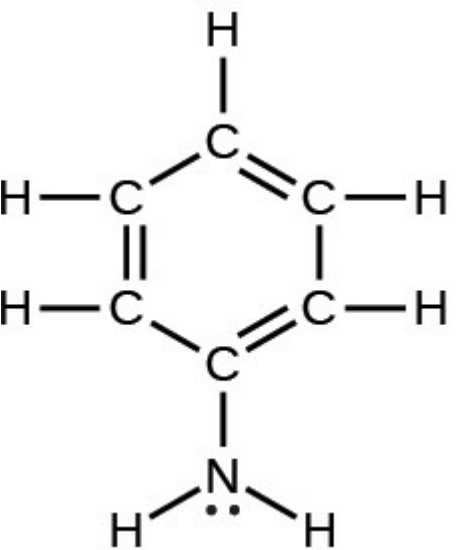


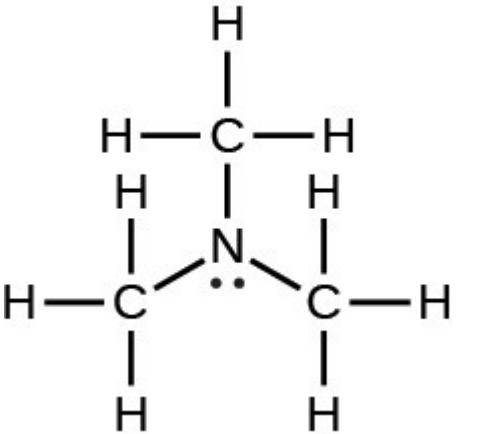
# APPENDIX I – IONIZATION CONSTANTS OF WEAK BASES

OpenStax

---

Ionization Constants of Weak Bases

Base	Lewis Structure	$K_b$ at 25 °C
ammonia		$1.8 \times 10^{-5}$
dimethylamine		$5.9 \times 10^{-4}$
methylamine		$4.4 \times 10^{-4}$
phenylamine (aniline)		$4.3 \times 10^{-10}$

trimethylamine		$6.3 \times 10^{-5}$

# APPENDIX J – SOLUBILITY PRODUCTS

OpenStax

---

## Aluminum Solubility Products

Substance	$K_{sp}$ at 25 °C
$\text{Al}(\text{OH})_3$	$2 \times 10^{-32}$

## Barium Solubility Products

Substance	$K_{sp}$ at 25 °C
barium	
$\text{BaCO}_3$	$1.6 \times 10^{-9}$
$\text{BaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	$1.1 \times 10^{-7}$
$\text{BaSO}_4$	$2.3 \times 10^{-8}$
$\text{BaCrO}_4$	$8.5 \times 10^{-11}$
$\text{BaF}_2$	$2.4 \times 10^{-5}$
$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	$5.0 \times 10^{-3}$
$\text{Ba}_3(\text{PO}_4)_2$	$6 \times 10^{-39}$
$\text{Ba}_3(\text{AsO}_4)_2$	$1.1 \times 10^{-13}$

## Bismuth Solubility Products

Substance	$K_{sp}$ at 25 °C
BiO(OH)	$4 \times 10^{-10}$
BiOCl	$1.8 \times 10^{-31}$
Bi <sub>2</sub> S <sub>3</sub>	$1 \times 10^{-97}$

## Cadmium Solubility Products

Substance	$K_{sp}$ at 25 °C
Cd(OH) <sub>2</sub>	$5.9 \times 10^{-15}$
CdS	$1.0 \times 10^{-28}$
CdCO <sub>3</sub>	$5.2 \times 10^{-12}$

## Calcium Solubility Products

Substance	$K_{sp}$ at 25 °C
Ca(OH) <sub>2</sub>	$1.3 \times 10^{-6}$
CaCO <sub>3</sub>	$8.7 \times 10^{-9}$
CaSO <sub>4</sub> ·2H <sub>2</sub> O	$6.1 \times 10^{-5}$
CaC <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O	$1.96 \times 10^{-8}$
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	$1.3 \times 10^{-32}$
CaHPO <sub>4</sub>	$7 \times 10^{-7}$
CaF <sub>2</sub>	$4.0 \times 10^{-11}$

## Chromium Solubility Products

Substance	$K_{sp}$ at 25 °C
$\text{Cr}(\text{OH})_3$	$6.7 \times 10^{-31}$

## Cobalt Solubility Products

Substance	$K_{sp}$ at 25 °C
$\text{Co}(\text{OH})_2$	$2.5 \times 10^{-16}$
$\text{CoS}(\alpha)$	$5 \times 10^{-22}$
$\text{CoS}(\beta)$	$3 \times 10^{-26}$
$\text{CoCO}_3$	$1.4 \times 10^{-13}$
$\text{Co}(\text{OH})_3$	$2.5 \times 10^{-43}$

## Copper Solubility Products

Substance	$K_{sp}$ at 25 °C
$\text{CuCl}$	$1.2 \times 10^{-6}$
$\text{CuBr}$	$6.27 \times 10^{-9}$
$\text{CuI}$	$1.27 \times 10^{-12}$
$\text{CuSCN}$	$1.6 \times 10^{-11}$
$\text{Cu}_2\text{S}$	$2.5 \times 10^{-48}$
$\text{Cu}(\text{OH})_2$	$2.2 \times 10^{-20}$
$\text{CuS}$	$8.5 \times 10^{-45}$
$\text{CuCO}_3$	$2.5 \times 10^{-10}$

## Iron Product Solubility

Substance	$K_{sp}$ at 25 °C
$\text{Fe}(\text{OH})_2$	$1.8 \times 10^{-15}$
$\text{FeCO}_3$	$2.1 \times 10^{-11}$
$\text{FeS}$	$3.7 \times 10^{-19}$
$\text{Fe}(\text{OH})_3$	$4 \times 10^{-38}$

## Lead Solubility Products

Substance	$K_{sp}$ at 25 °C
$\text{Pb}(\text{OH})_2$	$1.2 \times 10^{-15}$
$\text{PbF}_2$	$4 \times 10^{-8}$
$\text{PbCl}_2$	$1.6 \times 10^{-5}$
$\text{PbBr}_2$	$4.6 \times 10^{-6}$
$\text{PbI}_2$	$1.4 \times 10^{-8}$
$\text{PbCO}_3$	$1.5 \times 10^{-15}$
$\text{PbS}$	$7 \times 10^{-29}$
$\text{PbCrO}_4$	$2 \times 10^{-16}$
$\text{PbSO}_4$	$1.3 \times 10^{-8}$
$\text{Pb}_3(\text{PO}_4)_2$	$1 \times 10^{-54}$

## Magnesium Solubility Products

Substance	$K_{sp}$ at 25 °C
$Mg(OH)_2$	$8.9 \times 10^{-12}$
$MgCO_3 \cdot 3H_2O$	<i>ca</i> $1 \times 10^{-5}$
$MgNH_4PO_4$	$3 \times 10^{-13}$
$MgF_2$	$6.4 \times 10^{-9}$
$MgC_2O_4$	$7 \times 10^{-7}$

## Manganese Solubility Products

Substance	$K_{sp}$ at 25 °C
$Mn(OH)_2$	$2 \times 10^{-13}$
$MnCO_3$	$8.8 \times 10^{-11}$
$MnS$	$2.3 \times 10^{-13}$

## Mercury Solubility Products

Substance	$K_{sp}$ at 25 °C
$Hg_2O \cdot H_2O$	$3.6 \times 10^{-26}$
$Hg_2Cl_2$	$1.1 \times 10^{-18}$
$Hg_2Br_2$	$1.3 \times 10^{-22}$
$Hg_2I_2$	$4.5 \times 10^{-29}$
$Hg_2CO_3$	$9 \times 10^{-15}$
$Hg_2SO_4$	$7.4 \times 10^{-7}$
$Hg_2S$	$1.0 \times 10^{-47}$
$Hg_2CrO_4$	$2 \times 10^{-9}$
$HgS$	$1.6 \times 10^{-54}$



## Nickel Solubility Products

Substance	$K_{sp}$ at 25 °C
$\text{Ni}(\text{OH})_2$	$1.6 \times 10^{-16}$
$\text{NiCO}_3$	$1.4 \times 10^{-7}$
$\text{NiS}(\alpha)$	$4 \times 10^{-20}$
$\text{NiS}(\beta)$	$1.3 \times 10^{-25}$

## Potassium Solubility Products

Substance	$K_{sp}$ at 25 °C
$\text{KClO}_4$	$1.05 \times 10^{-2}$
$\text{K}_2\text{PtCl}_6$	$7.48 \times 10^{-6}$
$\text{KHC}_4\text{H}_4\text{O}_6$	$3 \times 10^{-4}$

## Silver Solubility Products

Substance	$K_{sp}$ at 25 °C
$\text{Ag}_2\text{O}(\text{Ag}^+ + \text{OH}^-)$	$2 \times 10^{-8}$
$\text{AgCl}$	$1.6 \times 10^{-10}$
$\text{AgBr}$	$5.0 \times 10^{-13}$
$\text{AgI}$	$1.5 \times 10^{-16}$
$\text{AgCN}$	$1.2 \times 10^{-16}$
$\text{AgSCN}$	$1.0 \times 10^{-12}$
$\text{Ag}_2\text{S}$	$1.6 \times 10^{-49}$
$\text{Ag}_2\text{CO}_3$	$8.1 \times 10^{-12}$
$\text{Ag}_2\text{CrO}_4$	$9.0 \times 10^{-12}$
$\text{Ag}_4\text{Fe}(\text{CN})_6$	$1.55 \times 10^{-41}$
$\text{Ag}_2\text{SO}_4$	$1.2 \times 10^{-5}$
$\text{Ag}_3\text{PO}_4$	$1.8 \times 10^{-18}$

## Strontium Solubility Products

Substance	$K_{sp}$ at 25 °C
$\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	$3.2 \times 10^{-4}$
$\text{SrCO}_3$	$7 \times 10^{-10}$
$\text{SrCrO}_4$	$3.6 \times 10^{-5}$
$\text{SrSO}_4$	$3.2 \times 10^{-7}$
$\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$	$4 \times 10^{-7}$

## Thallium Solubility Products

Substance	$K_{sp}$ at 25 °C
$\text{TlCl}$	$1.7 \times 10^{-4}$
$\text{TlSCN}$	$1.6 \times 10^{-4}$
$\text{Tl}_2\text{S}$	$6 \times 10^{-22}$
$\text{Tl}(\text{OH})_3$	$6.3 \times 10^{-46}$

## Tin Solubility Products

Substance	$K_{sp}$ at 25 °C
$\text{Sn}(\text{OH})_2$	$3 \times 10^{-27}$
$\text{SnS}$	$1 \times 10^{-26}$
$\text{Sn}(\text{OH})_4$	$1.0 \times 10^{-57}$

## Zinc Solubility Products

Substance	$K_{sp}$ at 25 °C
ZnCO <sub>3</sub>	$2 \times 10^{-10}$

# APPENDIX K – FORMATION CONSTANTS FOR COMPLEX IONS

OpenStax

---

Equilibrium	$K_f$
$\text{Al}^{3+} + 6\text{F}^- \rightleftharpoons [\text{AlF}_6]^{3-}$	$7 \times 10^{19}$
$\text{Cd}^{2+} + 4\text{NH}_3 \rightleftharpoons [\text{Cd}(\text{NH}_3)_4]^{2+}$	$1.3 \times 10^7$
$\text{Cd}^{2+} + 4\text{CN}^- \rightleftharpoons [\text{Cd}(\text{CN})_4]^{2-}$	$3 \times 10^{18}$
$\text{Co}^{2+} + 6\text{NH}_3 \rightleftharpoons [\text{Co}(\text{NH}_3)_6]^{2+}$	$1.3 \times 10^5$
$\text{Co}^{3+} + 6\text{NH}_3 \rightleftharpoons [\text{Co}(\text{NH}_3)_6]^{3+}$	$2.3 \times 10^{33}$
$\text{Cu}^+ + 2\text{CN}^- \rightleftharpoons [\text{Cu}(\text{CN})_2]^-$	$1.0 \times 10^{16}$
$\text{Cu}^{2+} + 4\text{NH}_3 \rightleftharpoons [\text{Cu}(\text{NH}_3)_4]^{2+}$	$1.7 \times 10^{13}$
$\text{Fe}^{2+} + 6\text{CN}^- \rightleftharpoons [\text{Fe}(\text{CN})_6]^{4-}$	$1.5 \times 10^{35}$
$\text{Fe}^{3+} + 6\text{CN}^- \rightleftharpoons [\text{Fe}(\text{CN})_6]^{3-}$	$2 \times 10^{43}$
$\text{Fe}^{3+} + 6\text{SCN}^- \rightleftharpoons [\text{Fe}(\text{SCN})_6]^{3-}$	$3.2 \times 10^3$
$\text{Hg}^{2+} + 4\text{Cl}^- \rightleftharpoons [\text{HgCl}_4]^{2-}$	$1.1 \times 10^{16}$
$\text{Ni}^{2+} + 6\text{NH}_3 \rightleftharpoons [\text{Ni}(\text{NH}_3)_6]^{2+}$	$2.0 \times 10^8$
$\text{Ag}^+ + 2\text{Cl}^- \rightleftharpoons [\text{AgCl}_2]^-$	$1.8 \times 10^5$
$\text{Ag}^+ + 2\text{CN}^- \rightleftharpoons [\text{Ag}(\text{CN})_2]^-$	$1 \times 10^{21}$
$\text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+$	$1.7 \times 10^7$
$\text{Zn}^{2+} + 4\text{CN}^- \rightleftharpoons [\text{Zn}(\text{CN})_4]^{2-}$	$2.1 \times 10^{19}$
$\text{Zn}^{2+} + 4\text{OH}^- \rightleftharpoons [\text{Zn}(\text{OH})_4]^{2-}$	$2 \times 10^{15}$
$\text{Fe}^{3+} + \text{SCN}^- \rightleftharpoons [\text{Fe}(\text{SCN})]^{2+}$	$8.9 \times 10^2$
$\text{Ag}^+ + 4\text{SCN}^- \rightleftharpoons [\text{Ag}(\text{SCN})_4]^{3-}$	$1.2 \times 10^{10}$
$\text{Pb}^{2+} + 4\text{I}^- \rightleftharpoons [\text{PbI}_4]^{2-}$	$3.0 \times 10^4$
$\text{Pt}^{2+} + 4\text{Cl}^- \rightleftharpoons [\text{PtCl}_4]^{2-}$	$1 \times 10^{16}$
$\text{Cu}^{2+} + 4\text{CN}^- \rightleftharpoons [\text{Cu}(\text{CN})_4]^{2-}$	$1.0 \times 10^{25}$
$\text{Co}^{2+} + 4\text{SCN}^- \rightleftharpoons [\text{Co}(\text{SCN})_4]^{2-}$	$1 \times 10^3$

# APPENDIX L – STANDARD ELECTRODE (HALF-CELL) POTENTIALS

OpenStax

---

Half-Reaction	$E^\circ$ (V)
$\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag}$	+0.7996
$\text{AgCl} + \text{e}^- \longrightarrow \text{Ag} + \text{Cl}^-$	+0.22233
$[\text{Ag}(\text{CN})_2]^- + \text{e}^- \longrightarrow \text{Ag} + 2\text{CN}^-$	-0.31
$\text{Ag}_2\text{CrO}_4 + 2\text{e}^- \longrightarrow 2\text{Ag} + \text{CrO}_4^{2-}$	+0.45
$[\text{Ag}(\text{NH}_3)_2]^+ + \text{e}^- \longrightarrow \text{Ag} + 2\text{NH}_3$	+0.373
$[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3+} + \text{e}^- \longrightarrow \text{Ag} + 2\text{S}_2\text{O}_3^{2-}$	+0.017
$[\text{AlF}_6]^{3-} + 3\text{e}^- \longrightarrow \text{Al} + 6\text{F}^-$	-2.07
$\text{Al}^{3+} + 3\text{e}^- \longrightarrow \text{Al}$	-1.662
$\text{Am}^{3+} + 3\text{e}^- \longrightarrow \text{Am}$	-2.048
$\text{Au}^{3+} + 3\text{e}^- \longrightarrow \text{Au}$	+1.498
$\text{Au}^+ + \text{e}^- \longrightarrow \text{Au}$	+1.692
$\text{Ba}^{2+} + 2\text{e}^- \longrightarrow \text{Ba}$	-2.912
$\text{Be}^{2+} + 2\text{e}^- \longrightarrow \text{Be}$	-1.847
$\text{Br}_2(aq) + 2\text{e}^- \longrightarrow 2\text{Br}^-$	+1.0873
$\text{Ca}^{2+} + 2\text{e}^- \longrightarrow \text{Ca}$	-2.868
$\text{Ce}^3 + 3\text{e}^- \longrightarrow \text{Ce}$	-2.483



Half-Reaction	$E^\circ$ (V)
$\text{Ce}^{4+} + \text{e}^- \longrightarrow \text{Ce}^{3+}$	+1.61
$\text{Cd}^{2+} + 2\text{e}^- \longrightarrow \text{Cd}$	-0.4030
$[\text{Cd}(\text{CN})_4]^{2-} + 2\text{e}^- \longrightarrow \text{Cd} + 4\text{CN}^-$	-1.09
$[\text{Cd}(\text{NH}_3)_4]^{2+} + 2\text{e}^- \longrightarrow \text{Cd} + 4\text{NH}_3$	-0.61
$\text{CdS} + 2\text{e}^- \longrightarrow \text{Cd} + \text{S}^{2-}$	-1.17
$\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Cl}^-$	+1.35827
$\text{ClO}_4^- + \text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{ClO}_3^- + 2\text{OH}^-$	+0.36
$\text{ClO}_3^- + \text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{ClO}_2^- + 2\text{OH}^-$	+0.33
$\text{ClO}_2^- + \text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{ClO}^- + 2\text{OH}^-$	+0.66
$\text{ClO}^- + \text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{Cl}^- + 2\text{OH}^-$	+0.89
$\text{ClO}_4^- + 2\text{H}_3\text{O}^+ + 2\text{e}^- \longrightarrow \text{ClO}_3^- + 3\text{H}_2\text{O}$	+1.189
$\text{ClO}_3^- + 3\text{H}_3\text{O}^+ + 2\text{e}^- \longrightarrow \text{HClO}_2 + 4\text{H}_2\text{O}$	+1.21
$\text{HClO} + \text{H}_3\text{O}^+ + 2\text{e}^- \longrightarrow \text{Cl}^- + 2\text{H}_2\text{O}$	+1.482
$\text{HClO} + \text{H}_3\text{O}^+ + \text{e}^- \longrightarrow \frac{1}{2}\text{Cl}_2 + 2\text{H}_2\text{O}$	+1.611
$\text{HClO}_2 + 2\text{H}_3\text{O}^+ + 2\text{e}^- \longrightarrow \text{HClO} + 3\text{H}_2\text{O}$	+1.628
$\text{Co}^{3+} + \text{e}^- \longrightarrow \text{Co}^{2+} \text{ (2 mol // H}_2\text{SO}_4\text{)}$	+1.83

Half-Reaction	$E^\circ$ (V)
$\text{Co}^{2+} + 2\text{e}^- \longrightarrow \text{Co}$	-0.28
$[\text{Co}(\text{NH}_3)_6]^{3+} + \text{e}^- \longrightarrow [\text{Co}(\text{NH}_3)_6]^{2+}$	+0.1
$\text{Co}(\text{OH})_3 + \text{e}^- \longrightarrow \text{Co}(\text{OH})_2 + \text{OH}^-$	+0.17
$\text{Cr}^3 + 3\text{e}^- \longrightarrow \text{Cr}$	-0.744
$\text{Cr}^{3+} + \text{e}^- \longrightarrow \text{Cr}^{2+}$	-0.407
$\text{Cr}^{2+} + 2\text{e}^- \longrightarrow \text{Cr}$	-0.913
$[\text{Cu}(\text{CN})_2]^- + \text{e}^- \longrightarrow \text{Cu} + 2\text{CN}^-$	-0.43
$\text{CrO}_4^{2-} + 4\text{H}_2\text{O} + 3\text{e}^- \longrightarrow \text{Cr}(\text{OH})_3 + 5\text{OH}^-$	-0.13
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}_3\text{O}^+ + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+} + 21\text{H}_2\text{O}$	+1.232
$[\text{Cr}(\text{OH})_4]^- + 3\text{e}^- \longrightarrow \text{Cr} + 4\text{OH}^-$	-1.2
$\text{Cr}(\text{OH})_3 + 3\text{e}^- \longrightarrow \text{Cr} + 3\text{OH}^-$	-1.48
$\text{Cu}^{2+} + \text{e}^- \longrightarrow \text{Cu}^+$	+0.153
$\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$	+0.34
$\text{Cu}^+ + \text{e}^- \longrightarrow \text{Cu}$	+0.521
$\text{F}_2 + 2\text{e}^- \longrightarrow 2\text{F}^-$	+2.866
$\text{Fe}^{2+} + 2\text{e}^- \longrightarrow \text{Fe}$	-0.447

Half-Reaction	$E^\circ$ (V)
$\text{Fe}^{3+} + \text{e}^- \longrightarrow \text{Fe}^{2+}$	+0.771
$[\text{Fe}(\text{CN})_6]^{3-} + \text{e}^- \longrightarrow [\text{Fe}(\text{CN})_6]^{4-}$	+0.36
$\text{Fe}(\text{OH})_2 + 2\text{e}^- \longrightarrow \text{Fe} + 2\text{OH}^-$	-0.88
$\text{FeS} + 2\text{e}^- \longrightarrow \text{Fe} + \text{S}^{2-}$	-1.01
$\text{Ga}^{3+} + 3\text{e}^- \longrightarrow \text{Ga}$	-0.549
$\text{Gd}^{3+} + 3\text{e}^- \longrightarrow \text{Gd}$	-2.279
$\frac{1}{2}\text{H}_2 + \text{e}^- \longrightarrow \text{H}^-$	-2.23
$2\text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{H}_2 + 2\text{OH}^-$	-0.8277
$\text{H}_2\text{O}_2 + 2\text{H}_3\text{O}^+ + 2\text{e}^- \longrightarrow 4\text{H}_2\text{O}$	+1.776
$2\text{H}_3\text{O}^+ + 2\text{e}^- \longrightarrow \text{H}_2 + 2\text{H}_2\text{O}$	0.00
$\text{HO}_2^- + \text{H}_2\text{O} + 2\text{e}^- \longrightarrow 3\text{OH}^-$	+0.878
$\text{Hf}^{4+} + 4\text{e}^- \longrightarrow \text{Hf}$	-1.55
$\text{Hg}^{2+} + 2\text{e}^- \longrightarrow \text{Hg}$	+0.851
$2\text{Hg}^{2+} + 2\text{e}^- \longrightarrow \text{Hg}_2^{2+}$	+0.92
$\text{Hg}_2^{2+} + 2\text{e}^- \longrightarrow 2\text{Hg}$	+0.7973
$[\text{HgBr}_4]^{2-} + 2\text{e}^- \longrightarrow \text{Hg} + 4\text{Br}^-$	+0.21

Half-Reaction	$E^\circ$ (V)
$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Hg} + 2\text{Cl}^-$	+0.26808
$[\text{Hg}(\text{CN})_4]^{2-} + 2\text{e}^- \longrightarrow \text{Hg} + 4\text{CN}^-$	-0.37
$[\text{HgI}_4]^{2-} + 2\text{e}^- \longrightarrow \text{Hg} + 4\text{I}^-$	-0.04
$\text{HgS} + 2\text{e}^- \longrightarrow \text{Hg} + \text{S}^{2-}$	-0.70
$\text{I}_2 + 2\text{e}^- \longrightarrow 2\text{I}^-$	+0.5355
$\text{In}^{3+} + 3\text{e}^- \longrightarrow \text{In}$	-0.3382
$\text{K}^+ + \text{e}^- \longrightarrow \text{K}$	-2.931
$\text{La}^{3+} + 3\text{e}^- \longrightarrow \text{La}$	-2.52
$\text{Li}^+ + \text{e}^- \longrightarrow \text{Li}$	-3.04
$\text{Lu}^{3+} + 3\text{e}^- \longrightarrow \text{Lu}$	-2.28
$\text{Mg}^{2+} + 2\text{e}^- \longrightarrow \text{Mg}$	-2.372
$\text{Mn}^{2+} + 2\text{e}^- \longrightarrow \text{Mn}$	-1.185
$\text{MnO}_2 + 2\text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{Mn}(\text{OH})_2 + 2\text{OH}^-$	-0.05
$\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- \longrightarrow \text{MnO}_2 + 4\text{OH}^-$	+0.558
$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \longrightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$	+1.23
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.507

Half-Reaction	$E^\circ$ (V)
$\text{Na}^+ + \text{e}^- \longrightarrow \text{Na}$	-2.71
$\text{Nd}^{3+} + 3\text{e}^- \longrightarrow \text{Nd}$	-2.323
$\text{Ni}^{2+} + 2\text{e}^- \longrightarrow \text{Ni}$	-0.257
$[\text{Ni}(\text{NH}_3)_6]^{2+} + 2\text{e}^- \longrightarrow \text{Ni} + 6\text{NH}_3$	-0.49
$\text{NiO}_2 + 4\text{H}^+ + 2\text{e}^- \longrightarrow \text{Ni}^{2+} + 2\text{H}_2\text{O}$	+1.593
$\text{NiO}_2 + 2\text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{Ni}(\text{OH})_2 + 2\text{OH}^-$	+0.49
$\text{NiS} + 2\text{e}^- \longrightarrow \text{Ni} + \text{S}^{2-}$	+0.76
$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- \longrightarrow \text{NO} + 2\text{H}_2\text{O}$	+0.957
$\text{NO}_3^- + 3\text{H}^+ + 2\text{e}^- \longrightarrow \text{HNO}_2 + \text{H}_2\text{O}$	+0.92
$\text{NO}_3^- + \text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{NO}_2^- + 2\text{OH}^-$	+0.10
$\text{Np}^{3+} + 3\text{e}^- \longrightarrow \text{Np}$	-1.856
$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \longrightarrow 4\text{OH}^-$	+0.401
$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2\text{O}_2$	+0.695
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \longrightarrow 2\text{H}_2\text{O}$	+1.229
$\text{Pb}^{2+} + 2\text{e}^- \longrightarrow \text{Pb}$	-0.1262
$\text{PbO}_2 + \text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^- \longrightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$	+1.69
$\text{PbS} + 2\text{e}^- \longrightarrow \text{Pb} + \text{S}^{2-}$	-0.95

Half-Reaction	$E^\circ$ (V)
$\text{PbSO}_4 + 2\text{e}^- \longrightarrow \text{Pb} + \text{SO}_4^{2-}$	-0.3505
$\text{Pd}^{2+} + 2\text{e}^- \longrightarrow \text{Pd}$	+0.987
$[\text{PdCl}_4]^{2-} + 2\text{e}^- \longrightarrow \text{Pd} + 4\text{Cl}^-$	+0.591
$\text{Pt}^{2+} + 2\text{e}^- \longrightarrow \text{Pt}$	+1.20
$[\text{PtBr}_4]^{2-} + 2\text{e}^- \longrightarrow \text{Pt} + 4\text{Br}^-$	+0.58
$[\text{PtCl}_4]^{2-} + 2\text{e}^- \longrightarrow \text{Pt} + 4\text{Cl}^-$	+0.755
$[\text{PtCl}_6]^{2-} + 2\text{e}^- \longrightarrow [\text{PtCl}_4]^{2-} + 2\text{Cl}^-$	+0.68
$\text{Pu}^3 + 3\text{e}^- \longrightarrow \text{Pu}$	-2.03
$\text{Ra}^{2+} + 2\text{e}^- \longrightarrow \text{Ra}$	-2.92
$\text{Rb}^+ + \text{e}^- \longrightarrow \text{Rb}$	-2.98
$[\text{RhCl}_6]^{3-} + 3\text{e}^- \longrightarrow \text{Rh} + 6\text{Cl}^-$	+0.44
$\text{S} + 2\text{e}^- \longrightarrow \text{S}^{2-}$	-0.47627
$\text{S} + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2\text{S}$	+0.142
$\text{Sc}^{3+} + 3\text{e}^- \longrightarrow \text{Sc}$	-2.09
$\text{Se} + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2\text{Se}$	-0.399
$[\text{SiF}_6]^{2-} + 4\text{e}^- \longrightarrow \text{Si} + 6\text{F}^-$	-1.2

Half-Reaction	$E^\circ$ (V)
$\text{SiO}_3^{2-} + 3\text{H}_2\text{O} + 4\text{e}^- \longrightarrow \text{Si} + 6\text{OH}^-$	-1.697
$\text{SiO}_2 + 4\text{H}^+ + 4\text{e}^- \longrightarrow \text{Si} + 2\text{H}_2\text{O}$	-0.86
$\text{Sm}^{3+} + 3\text{e}^- \longrightarrow \text{Sm}$	-2.304
$\text{Sn}^{4+} + 2\text{e}^- \longrightarrow \text{Sn}^{2+}$	+0.151
$\text{Sn}^{2+} + 2\text{e}^- \longrightarrow \text{Sn}$	-0.1375
$[\text{SnF}_6]^{2-} + 4\text{e}^- \longrightarrow \text{Sn} + 6\text{F}^-$	-0.25
$\text{SnS} + 2\text{e}^- \longrightarrow \text{Sn} + \text{S}^{2-}$	-0.94
$\text{Sr}^{2+} + 2\text{e}^- \longrightarrow \text{Sr}$	-2.89
$\text{TeO}_2 + 4\text{H}^+ + 4\text{e}^- \longrightarrow \text{Te} + 2\text{H}_2\text{O}$	+0.593
$\text{Th}^{4+} + 4\text{e}^- \longrightarrow \text{Th}$	-1.90
$\text{Ti}^{2+} + 2\text{e}^- \longrightarrow \text{Ti}$	-1.630
$\text{U}^{3+} + 3\text{e}^- \longrightarrow \text{U}$	-1.79
$\text{V}^{2+} + 2\text{e}^- \longrightarrow \text{V}$	-1.19
$\text{Y}^{3+} + 3\text{e}^- \longrightarrow \text{Y}$	-2.37
$\text{Zn}^{2+} + 2\text{e}^- \longrightarrow \text{Zn}$	-0.7618
$[\text{Zn}(\text{CN})_4]^{2-} + 2\text{e}^- \longrightarrow \text{Zn} + 4\text{CN}^-$	-1.26

Half-Reaction	$E^\circ$ (V)
$[\text{Zn}(\text{NH}_3)_4]^{2+} + 2\text{e}^- \longrightarrow \text{Zn} + 4\text{NH}_3$	-1.04
$\text{Zn}(\text{OH})_2 + 2\text{e}^- \longrightarrow \text{Zn} + 2\text{OH}^-$	-1.245
$[\text{Zn}(\text{OH})_4]^{2-} + 2\text{e}^- \longrightarrow \text{Zn} + 4\text{OH}^-$	-1.199
$\text{ZnS} + 2\text{e}^- \longrightarrow \text{Zn} + \text{S}^{2-}$	-1.40
$\text{Zr}^4 + 4\text{e}^- \longrightarrow \text{Zr}$	-1.539





# APPENDIX M – HALF-LIVES FOR SEVERAL RADIOACTIVE ISOTOPES

OpenStax

---

Isotope	Half-Life <sup>[1]</sup>	Type of Emission <sup>[2]</sup>	Isotope	Half-Life <sup>[3]</sup>	Type of Emission <sup>[4]</sup>
$^{14}_6\text{C}$	5730 y	( $\beta^-$ )	$^{210}_{83}\text{Bi}$	5.01 d	( $\beta^-$ )
$^{13}_7\text{N}$	9.97 m	( $\beta^+$ )	$^{212}_{83}\text{Bi}$	60.55 m	( $\alpha$ or $\beta^-$ )
$^{15}_9\text{F}$	$4.1 \times 10^{-22}$ s	( $p$ )	$^{212}_{84}\text{Po}$	138.4 d	( $\alpha$ )
$^{24}_{11}\text{Na}$	15.00 h	( $\beta^-$ )	$^{216}_{84}\text{Po}$	$3 \times 10^{-7}$ s	( $\alpha$ )
$^{32}_{15}\text{P}$	14.29 d	( $\beta^-$ )	$^{218}_{84}\text{Po}$	0.15 s	( $\alpha$ )
$^{40}_{19}\text{K}$	$1.27 \times 10^9$ y	( $\beta$ or <i>E.C.</i> )	$^{215}_{84}\text{At}$	3.05 m	( $\alpha$ )
$^{49}_{26}\text{Fe}$	0.08 s	( $\beta^+$ )	$^{218}_{85}\text{At}$	$1.0 \times 10^{-4}$ s	( $\alpha$ )
$^{60}_{26}\text{Fe}$	$2.6 \times 10^6$ y	( $\beta^-$ )	$^{220}_{85}\text{Rn}$	1.6 s	( $\alpha$ )
$^{60}_{27}\text{Co}$	5.27 y	( $\beta^-$ )	$^{222}_{86}\text{Rn}$	55.6 s	( $\alpha$ )
$^{87}_{37}\text{Rb}$	$4.7 \times 10^{10}$ y	( $\beta^-$ )	$^{224}_{86}\text{Rn}$	3.82 d	( $\alpha$ )
$^{90}_{38}\text{Sr}$	29 y	( $\beta^-$ )	$^{226}_{88}\text{Ra}$	3.66 d	( $\alpha$ )
$^{115}_{49}\text{In}$	$5.1 \times 10^{15}$ y	( $\beta^-$ )	$^{228}_{88}\text{Ra}$	1600 y	( $\alpha$ )

$^{131}_{53}\text{I}$	8.040 d	( $\beta^-$ )	$^{228}_{88}\text{Ra}$	5.75 y	( $\beta^-$ )
$^{142}_{58}\text{Ce}$	$5 \times 10^{15}$ y	( $\alpha$ )	$^{228}_{89}\text{Ac}$	6.13 h	( $\beta^-$ )
$^{208}_{81}\text{Tl}$	3.07 m	( $\beta^-$ )	$^{232}_{90}\text{Th}$	1.913 y	( $\alpha$ )
$^{210}_{82}\text{Pb}$	22.3 y	( $\beta^-$ )	$^{233}_{90}\text{Th}$	$1.4 \times 10^{10}$ y	( $\alpha$ )
$^{212}_{82}\text{Pb}$	10.6 h	( $\beta^-$ )	$^{234}_{90}\text{Th}$	22 m	( $\beta^-$ )
$^{214}_{82}\text{Pb}$	26.8 m	( $\beta^-$ )	$^{233}_{90}\text{Th}$	24.10 d	( $\beta^-$ )
$^{206}_{83}\text{Bi}$	6.243 d	( <i>E.C.</i> )	$^{242}_{91}\text{Pa}$	27 d	( $\beta^-$ )
$^{233}_{92}\text{U}$	$1.59 \times 10^5$ y	( $\alpha$ )	$^{243}_{96}\text{Cm}$	162.8 d	( $\alpha$ )
$^{234}_{92}\text{U}$	$2.45 \times 10^5$ y	( $\alpha$ )	$^{253}_{97}\text{Bk}$	4.5 h	( $\alpha$ or <i>E.C.</i> )
$^{235}_{92}\text{U}$	$7.03 \times 10^8$ y	( $\alpha$ )	$^{254}_{99}\text{Es}$	20.47 d	( $\alpha$ )
$^{238}_{92}\text{U}$	$4.47 \times 10^9$ y	( $\alpha$ )	$^{255}_{100}\text{Fm}$	3.24 h	( $\alpha$ or <i>S.F.</i> )

$^{239}_{92}\text{U}$	23.54 m	( $\beta^-$ )	$^{256}_{100}\text{Fm}$	20.1 h	( $\alpha$ )
$^{239}_{93}\text{Np}$	2.3 d	( $\beta^-$ )	$^{254}_{101}\text{Md}$	76 m	( $\alpha$ or <i>E.C.</i> )
$^{239}_{94}\text{Pu}$	$2.407 \times 10^4$ y	( $\alpha$ )	$^{254}_{102}\text{No}$	55 s	( $\alpha$ )
$^{239}_{94}\text{Pu}$	$6.54 \times 10^3$ y	( $\alpha$ )	$^{257}_{103}\text{Lr}$	0.65 s	( $\alpha$ )
$^{241}_{94}\text{Pu}$	14.4 y	( $\alpha$ or $\beta^-$ )	$^{260}_{105}\text{Ha}$	1.5 s	( $\alpha$ or <i>S.F.</i> )
$^{241}_{95}\text{Am}$	432.2 y	( $\alpha$ )	$^{263}_{106}\text{Sg}$	0.8 s	( $\alpha$ or <i>S.F.</i> )

- y = years, d = days, h = hours, m = minutes, s = seconds
- *E.C.* = electron capture, *S.F.* = Spontaneous fission
- y = years, d = days, h = hours, m = minutes, s = seconds
- *E.C.* = electron capture, *S.F.* = Spontaneous fission

# APPENDIX N: CHECKLIST FOR ACCESSIBILITY

---

This title has been reviewed to meet these accessibility practices:

## Organizing Content

- Content is organized under headings and subheadings.
- Headings and subheadings are used sequentially (e.g., Heading 1, Heading 2).

## Images

- Images that convey information include alternative text (alt text) descriptions of the image's content or function.
- Graphs, charts, and maps also include contextual or supporting details in the text surrounding the image.
- Images do not rely on color to convey information.
- Images that are purely decorative do not have alt text descriptions. (Descriptive text is unnecessary if the image doesn't convey contextual content information).

## Links

- The link text describes the destination of the link and does not use generic text such as "click here" or "read more."
- If a link will open or download a file (like a PDF or Excel file), a textual reference is included in the link information (e.g., [PDF]).
- Links do not open in new windows or tabs.
- If a link must open in a new window or tab, a textual reference is included in the link information (e.g., [NewTab]).
- For citations and references, the title of the resource is hyperlinked, and the full URL is not hyperlinked.

## Tables

- Tables are used to structure information and not for layout.
- Tables include row and column headers.
- Row and column headers have the correct scope assigned.
- Tables include a caption.
- Tables avoid merged or split cells.
- Tables have adequate cell padding.

## Multimedia

- All audio content includes a transcript. The transcript includes all speech content and relevant descriptions of non-speech audio and speaker names/headings where necessary.
- Videos have captions of all speech content and relevant non-speech content that has been edited by a human for accuracy.
- All videos with contextual visuals (graphs, charts, etc.) are described audibly in the video.

## Formulas

- Equations written in plain text use proper symbols (i.e.,  $-$ ,  $\times$ ,  $\div$ ).<sup>1</sup>
- For complex equations, one of the following is true:
  - They were written using LaTeX and are rendered with MathJax (Pressbooks).
  - They were written using Microsoft Word's equation editor.
  - They are presented as images with alternative text descriptions.
- Written equations are properly interpreted by text-to-speech tools.<sup>2</sup>

## Font Size

- Font size is 12 points or higher for body text in Word and PDF documents.
- Font size is 9 points for footnotes or endnotes in Word and PDF documents.

---

1. For example, a hyphen (-) may look like a minus sign ( $-$ ), but it will not be read out correctly by text-to-speech tools.

2. Written equations should prioritize semantic markup over visual markup so text-to-speech tools will read out an equation in a way that makes sense to auditory learners. This applies to both equations written in LaTeX and equations written in Microsoft Word's equation editor.

- Font size can be enlarged by 200 percent in webbook or e-book formats without needing to scroll side to side.

Learn more about [Pressbooks' commitment to Accessibility](#).

“Checklist for Accessibility” by BCcampus is licensed under [CC BY 4.0](#).



# ACKNOWLEDGMENTS

OpenStax

---

[css dashed border animation](#)

A Pen By [yanjixiong](#)

*featured in chapters 12-17 around “Interactive Video Assignments”*

[18 Simple Styles for Horizontal Rules \(hr CSS Design\(Style 18\)\)](#)

A Pen By [Ibrahim Jabbari](#)

*Featured in the Horizontal Rule on the Table of Contents*