



openstax™

UConn

Chem- istry

2e.

Atoms First

Chemistry: Atoms First 2e

SENIOR CONTRIBUTING AUTHORS

PAUL FLOWERS, UNIVERSITY OF NORTH CAROLINA AT PEMBROKE

KLAUS THEOPOLD, UNIVERSITY OF DELAWARE

RICHARD LANGLEY, STEPHEN F. AUSTIN STATE UNIVERSITY

EDWARD J. NETH, UNIVERSITY OF CONNECTICUT

WILLIAM R. ROBINSON, PHD



OpenStax

Rice University
6100 Main Street MS-375
Houston, Texas 77005

To learn more about OpenStax, visit <https://openstax.org>.
Individual print copies and bulk orders can be purchased through our website.

©2019 Rice University. Textbook content produced by OpenStax is licensed under a Creative Commons Attribution 4.0 International License (CC BY 4.0). Under this license, any user of this textbook or the textbook contents herein must provide proper attribution as follows:

- If you redistribute this textbook in a digital format (including but not limited to PDF and HTML), then you must retain on every page the following attribution:
"Download for free at <https://openstax.org/details/books/chemistry-atoms-first-2e>."
- If you redistribute this textbook in a print format, then you must include on every physical page the following attribution:
"Download for free at <https://openstax.org/details/books/chemistry-atoms-first-2e>."
- If you redistribute part of this textbook, then you must retain in every digital format page view (including but not limited to PDF and HTML) and on every physical printed page the following attribution:
"Download for free at <https://openstax.org/details/books/chemistry-atoms-first-2e>."
- If you use this textbook as a bibliographic reference, please include <https://openstax.org/details/books/chemistry-atoms-first-2e> in your citation.

For questions regarding this licensing, please contact support@openstax.org.

Trademarks

The OpenStax name, OpenStax logo, OpenStax book covers, OpenStax CNX name, OpenStax CNX logo, OpenStax Tutor name, Openstax Tutor logo, Connexions name, Connexions logo, Rice University name, and Rice University logo are not subject to the license and may not be reproduced without the prior and express written consent of Rice University.

PRINT BOOK ISBN-10

1-947172-64-6

PRINT BOOK ISBN-13

978-1-947172-64-7

PDF VERSION ISBN-10

1-947172-63-8

PDF VERSION ISBN-13

978-1-947172-63-0

10 9 8 7 6 5 4 3 2 1

OPENSTAX

OpenStax provides free, peer-reviewed, openly licensed textbooks for introductory college and Advanced Placement® courses and low-cost, personalized courseware that helps students learn. A nonprofit ed tech initiative based at Rice University, we're committed to helping students access the tools they need to complete their courses and meet their educational goals.

RICE UNIVERSITY

OpenStax, OpenStax CNX, and OpenStax Tutor are initiatives of Rice University. As a leading research university with a distinctive commitment to undergraduate education, Rice University aspires to path-breaking research, unsurpassed teaching, and contributions to the betterment of our world. It seeks to fulfill this mission by cultivating a diverse community of learning and discovery that produces leaders across the spectrum of human endeavor.



PHILANTHROPIC SUPPORT

OpenStax is grateful for our generous philanthropic partners, who support our vision to improve educational opportunities for all learners.

Laura and John Arnold Foundation

Arthur and Carlyse Ciocca Charitable Foundation

Ann and John Doerr

Bill & Melinda Gates Foundation

Girard Foundation

Google Inc.

The William and Flora Hewlett Foundation

Rusty and John Jagers

The Calvin K. Kazanjian Economics Foundation

Charles Koch Foundation

Leon Lowenstein Foundation, Inc.

The Maxfield Foundation

Burt and Deedee McMurtry

Michelson 20MM Foundation

National Science Foundation

The Open Society Foundations

Jumee Yhu and David E. Park III

Brian D. Patterson USA-International Foundation

The Bill and Stephanie Sick Fund

Robin and Sandy Stuart Foundation

The Stuart Family Foundation

Tammy and Guillermo Treviño

new school year.

new classes.

new **free books.**

new **free app.**

OpenStax + SE

Get free textbooks for over 30 college courses in the free OpenStax + SE app.

Download it now on the App Store or get it on Google Play.

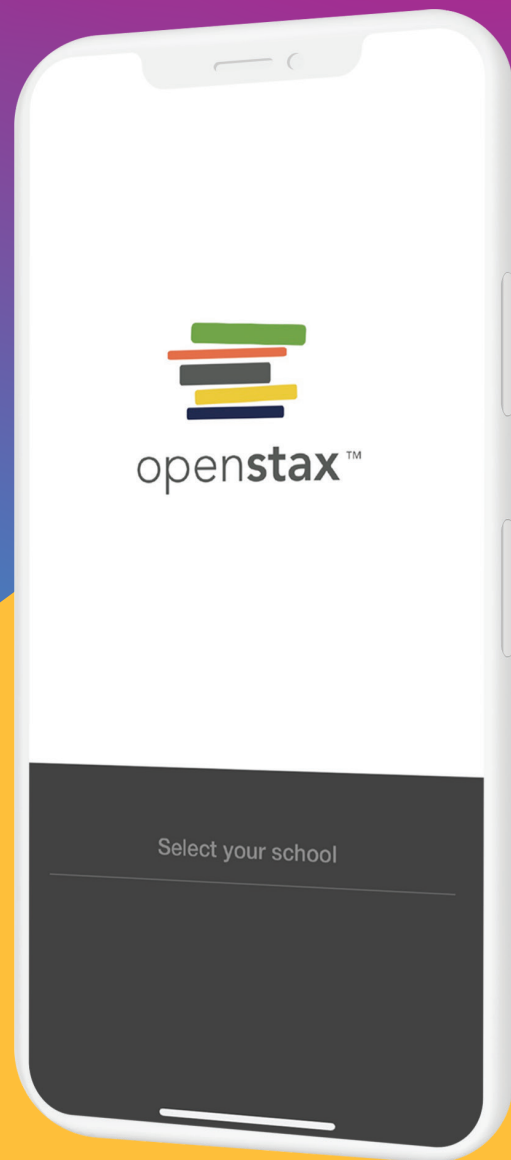


Table of Contents

Preface	1
Chapter 1: Essential Ideas	9
1.1 Chemistry in Context	10
1.2 Phases and Classification of Matter	14
1.3 Physical and Chemical Properties	25
1.4 Measurements	29
1.5 Measurement Uncertainty, Accuracy, and Precision	36
1.6 Mathematical Treatment of Measurement Results	44
Chapter 2: Atoms, Molecules, and Ions	67
2.1 Early Ideas in Atomic Theory	68
2.2 Evolution of Atomic Theory	73
2.3 Atomic Structure and Symbolism	79
2.4 Chemical Formulas	87
Chapter 3: Electronic Structure and Periodic Properties of Elements	115
3.1 Electromagnetic Energy	116
3.2 The Bohr Model	131
3.3 Development of Quantum Theory	135
3.4 Electronic Structure of Atoms (Electron Configurations)	148
3.5 Periodic Variations in Element Properties	158
3.6 The Periodic Table	165
3.7 Molecular and Ionic Compounds	169
Chapter 4: Chemical Bonding and Molecular Geometry	195
4.1 Ionic Bonding	196
4.2 Covalent Bonding	199
4.3 Chemical Nomenclature	205
4.4 Lewis Symbols and Structures	213
4.5 Formal Charges and Resonance	223
4.6 Molecular Structure and Polarity	227
Chapter 5: Advanced Theories of Bonding	263
5.1 Valence Bond Theory	264
5.2 Hybrid Atomic Orbitals	269
5.3 Multiple Bonds	281
5.4 Molecular Orbital Theory	284
Chapter 6: Composition of Substances and Solutions	309
6.1 Formula Mass	310
6.2 Determining Empirical and Molecular Formulas	312
6.3 Molarity	320
6.4 Other Units for Solution Concentrations	327
Chapter 7: Stoichiometry of Chemical Reactions	341
7.1 Writing and Balancing Chemical Equations	342
7.2 Classifying Chemical Reactions	348
7.3 Reaction Stoichiometry	363
7.4 Reaction Yields	368
7.5 Quantitative Chemical Analysis	373
Chapter 8: Gases	397
8.1 Gas Pressure	398
8.2 Relating Pressure, Volume, Amount, and Temperature: The Ideal Gas Law	407
8.3 Stoichiometry of Gaseous Substances, Mixtures, and Reactions	420
8.4 Effusion and Diffusion of Gases	433
8.5 The Kinetic-Molecular Theory	438

8.6 Non-Ideal Gas Behavior	443
Chapter 9: Thermochemistry	461
9.1 Energy Basics	462
9.2 Calorimetry	472
9.3 Enthalpy	485
9.4 Strengths of Ionic and Covalent Bonds	499
Chapter 10: Liquids and Solids	521
10.1 Intermolecular Forces	522
10.2 Properties of Liquids	534
10.3 Phase Transitions	540
10.4 Phase Diagrams	551
10.5 The Solid State of Matter	558
10.6 Lattice Structures in Crystalline Solids	565
Chapter 11: Solutions and Colloids	599
11.1 The Dissolution Process	600
11.2 Electrolytes	604
11.3 Solubility	607
11.4 Colligative Properties	618
11.5 Colloids	638
Chapter 12: Thermodynamics	657
12.1 Spontaneity	657
12.2 Entropy	661
12.3 The Second and Third Laws of Thermodynamics	667
12.4 Free Energy	671
Chapter 13: Fundamental Equilibrium Concepts	685
13.1 Chemical Equilibria	686
13.2 Equilibrium Constants	689
13.3 Shifting Equilibria: Le Châtelier's Principle	698
13.4 Equilibrium Calculations	702
Chapter 14: Acid-Base Equilibria	729
14.1 Brønsted-Lowry Acids and Bases	730
14.2 pH and pOH	733
14.3 Relative Strengths of Acids and Bases	739
14.4 Hydrolysis of Salts	754
14.5 Polyprotic Acids	759
14.6 Buffers	762
14.7 Acid-Base Titrations	769
Chapter 15: Equilibria of Other Reaction Classes	789
15.1 Precipitation and Dissolution	789
15.2 Lewis Acids and Bases	805
15.3 Coupled Equilibria	808
Chapter 16: Electrochemistry	827
16.1 Review of Redox Chemistry	828
16.2 Galvanic Cells	831
16.3 Electrode and Cell Potentials	835
16.4 Potential, Free Energy, and Equilibrium	841
16.5 Batteries and Fuel Cells	845
16.6 Corrosion	852
16.7 Electrolysis	855
Chapter 17: Kinetics	871
17.1 Chemical Reaction Rates	872
17.2 Factors Affecting Reaction Rates	877

17.3 Rate Laws	880
17.4 Integrated Rate Laws	887
17.5 Collision Theory	898
17.6 Reaction Mechanisms	904
17.7 Catalysis	908
Chapter 18: Representative Metals, Metalloids, and Nonmetals	939
18.1 Periodicity	940
18.2 Occurrence and Preparation of the Representative Metals	950
18.3 Structure and General Properties of the Metalloids	953
18.4 Structure and General Properties of the Nonmetals	962
18.5 Occurrence, Preparation, and Compounds of Hydrogen	970
18.6 Occurrence, Preparation, and Properties of Carbonates	977
18.7 Occurrence, Preparation, and Properties of Nitrogen	979
18.8 Occurrence, Preparation, and Properties of Phosphorus	984
18.9 Occurrence, Preparation, and Compounds of Oxygen	986
18.10 Occurrence, Preparation, and Properties of Sulfur	1001
18.11 Occurrence, Preparation, and Properties of Halogens	1003
18.12 Occurrence, Preparation, and Properties of the Noble Gases	1009
Chapter 19: Transition Metals and Coordination Chemistry	1027
19.1 Occurrence, Preparation, and Properties of Transition Metals and Their Compounds	1027
19.2 Coordination Chemistry of Transition Metals	1042
19.3 Spectroscopic and Magnetic Properties of Coordination Compounds	1057
Chapter 20: Nuclear Chemistry	1075
20.1 Nuclear Structure and Stability	1076
20.2 Nuclear Equations	1083
20.3 Radioactive Decay	1086
20.4 Transmutation and Nuclear Energy	1097
20.5 Uses of Radioisotopes	1112
20.6 Biological Effects of Radiation	1117
Chapter 21: Organic Chemistry	1137
21.1 Hydrocarbons	1138
21.2 Alcohols and Ethers	1156
21.3 Aldehydes, Ketones, Carboxylic Acids, and Esters	1160
21.4 Amines and Amides	1166
Appendix A: The Periodic Table	1187
Appendix B: Essential Mathematics	1189
Appendix C: Units and Conversion Factors	1197
Appendix D: Fundamental Physical Constants	1199
Appendix E: Water Properties	1201
Appendix F: Composition of Commercial Acids and Bases	1207
Appendix G: Standard Thermodynamic Properties for Selected Substances	1209
Appendix H: Ionization Constants of Weak Acids	1223
Appendix I: Ionization Constants of Weak Bases	1227
Appendix J: Solubility Products	1229
Appendix K: Formation Constants for Complex Ions	1233
Appendix L: Standard Electrode (Half-Cell) Potentials	1235
Appendix M: Half-Lives for Several Radioactive Isotopes	1241
Index	1311

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.

About OpenStax

OpenStax is a nonprofit based at Rice University, and it's our mission to improve student access to education. Our first openly licensed college textbook was published in 2012, and our library has since scaled to over 30 books for college and AP[®] courses used by hundreds of thousands of students. OpenStax Tutor, our low-cost personalized learning tool, is being used in college courses throughout the country. Through our partnerships with philanthropic foundations and our alliance with other educational resource organizations, OpenStax is breaking down the most common barriers to learning and empowering students and instructors to succeed.

About OpenStax resources

Customization

Chemistry: Atoms First 2e is licensed under a Creative Commons Attribution 4.0 International (CC BY) license, which means that you can distribute, remix, and build upon the content, as long as you provide attribution to OpenStax and its content contributors.

Because our books are openly licensed, you are free to use the entire book or pick and choose the sections that are most relevant to the needs of your course. Feel free to remix the content by assigning your students certain chapters and sections in your syllabus, in the order that you prefer. You can even provide a direct link in your syllabus to the sections in the web view of your book.

Instructors also have the option of creating a customized version of their OpenStax book. The custom version can be made available to students in low-cost print or digital form through their campus bookstore. Visit the Instructor Resources section of your book page on openstax.org for more information.

Errata

All OpenStax textbooks undergo a rigorous review process. However, like any professional-grade textbook, errors sometimes occur. Since our books are web based, we can make updates periodically when deemed pedagogically necessary. If you have a correction to suggest, submit it through the link on your book page on openstax.org. Subject matter experts review all errata suggestions. OpenStax is committed to remaining transparent about all updates, so you will also find a list of past errata changes on your book page on openstax.org.

Format

You can access this textbook for free in web view or PDF through openstax.org, and for a low cost in print.

About *Chemistry: Atoms First 2e*

This text is an atoms-first adaptation of OpenStax *Chemistry 2e*. The intention of “atoms-first” involves a few basic principles: first, it introduces atomic and molecular structure much earlier than the traditional approach, and it threads these themes through subsequent chapters. This approach may be chosen as a way to delay the introduction of material such as stoichiometry that students traditionally find abstract and difficult, thereby allowing students time to acclimate their study skills to chemistry. Additionally, it gives students a basis for understanding the application of quantitative principles to the chemistry that underlies the entire course. It also aims to center the study of chemistry on the atomic foundation that many will expand upon in a later course covering organic chemistry, easing that transition when the time arrives.

The second edition has been revised to incorporate clearer, more current, and more dynamic explanations, while maintaining the same organization as the first edition. Substantial improvements have been made in the figures,

illustrations, and example exercises that support the text narrative.

Coverage and scope

In *Chemistry: Atoms First 2e*, we strive to make chemistry, as a discipline, interesting and accessible to students. With this objective in mind, the content of this textbook has been developed and arranged to provide a logical progression from fundamental to more advanced concepts of chemical science. All of the material included in a traditional general chemistry course is here. It has been reorganized in an atoms-first approach and, where necessary, new material has been added to allow for continuity and to improve the flow of topics. The text can be used for a traditional two-semester introduction to chemistry or for a three-semester introduction, an approach becoming more common at many institutions. The goal is to provide a progressive, graduated introduction to chemistry that focuses on the fundamentally atom-focused nature of the subject. Topics are introduced within the context of familiar experiences whenever possible, treated with an appropriate rigor to satisfy the intellect of the learner, and reinforced in subsequent discussions of related content. The organization and pedagogical features were developed and vetted with feedback from chemistry educators dedicated to the project.

Changes to the second edition

OpenStax only undertakes second editions when significant modifications to the text are necessary. In the case of *Chemistry: Atoms First 2e*, user feedback indicated that we needed to focus on a few key areas, which we have done in the following ways:

Content revisions for clarity and accuracy. The revision plan varied by chapter based on need. About five chapters were extensively rewritten and another twelve chapters were substantially revised to improve the readability and clarity of the narrative.

Example and end-of-chapter exercises. The example and end-of-chapter exercises in several chapters were subjected to a rigorous accuracy check and revised to correct any errors, and additional exercises were added to several chapters to more fully support chapter content.

Art and illustrations. Under the guidance of the authors and expert scientific illustrators, especially those well-versed in creating accessible art, the OpenStax team made changes to much of the art in the first edition of *Chemistry: Atoms First*. The revisions included correcting errors, redesigning illustrations to improve understanding, and recoloring for overall consistency.

Accessibility improvements. As with all OpenStax books, the first edition of *Chemistry: Atoms First* was created with a focus on accessibility. We have emphasized and improved that approach in the second edition. To accommodate users of specific assistive technologies, all alternative text was reviewed and revised for comprehensiveness and clarity. Many illustrations were revised to improve the color contrast, which is important for some visually impaired students. Overall, the OpenStax platform has been continually upgraded to improve accessibility.

Partnership with University of Connecticut and UConn Undergraduate Student Government

Chemistry: Atoms First 2e is a peer-reviewed, openly licensed introductory textbook produced through a collaborative publishing partnership between OpenStax and the University of Connecticut and UConn Undergraduate Student Government Association.

Pedagogical foundation

Throughout *Chemistry: Atoms First 2e*, you will find features that draw the students into scientific inquiry by taking selected topics a step further. Students and educators alike will appreciate discussions in these feature boxes.

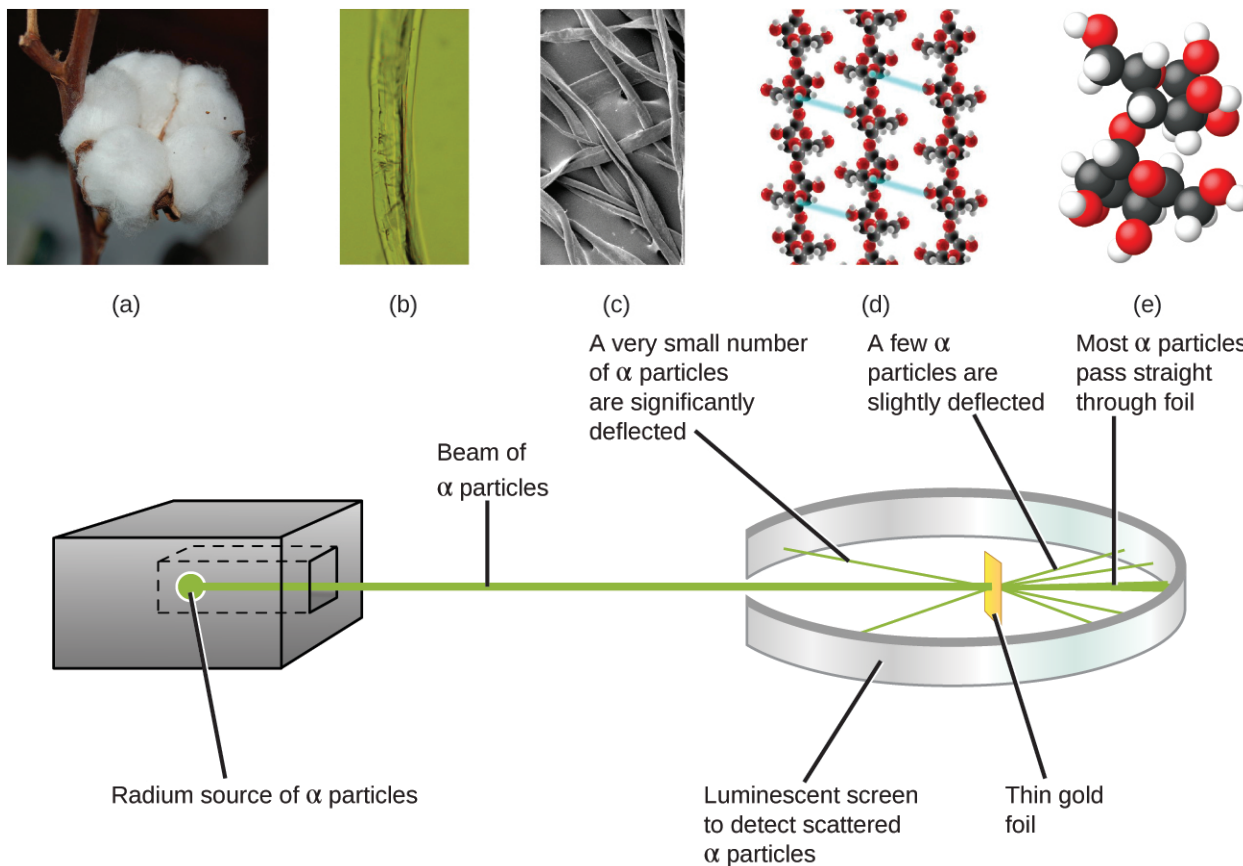
Chemistry in Everyday Life ties chemistry concepts to everyday issues and real-world applications of science that students encounter in their lives. Topics include cell phones, solar thermal energy power plants, plastics recycling, and measuring blood pressure.

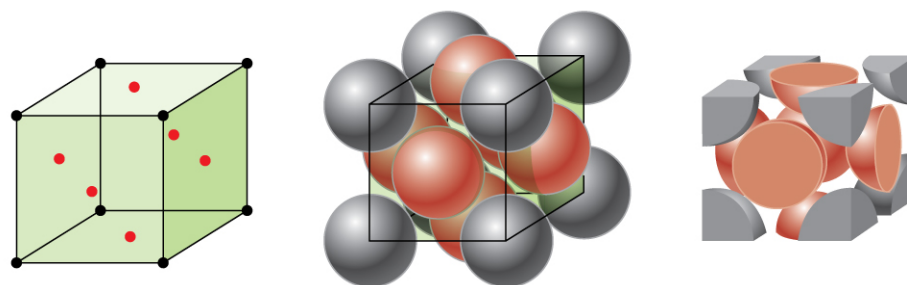
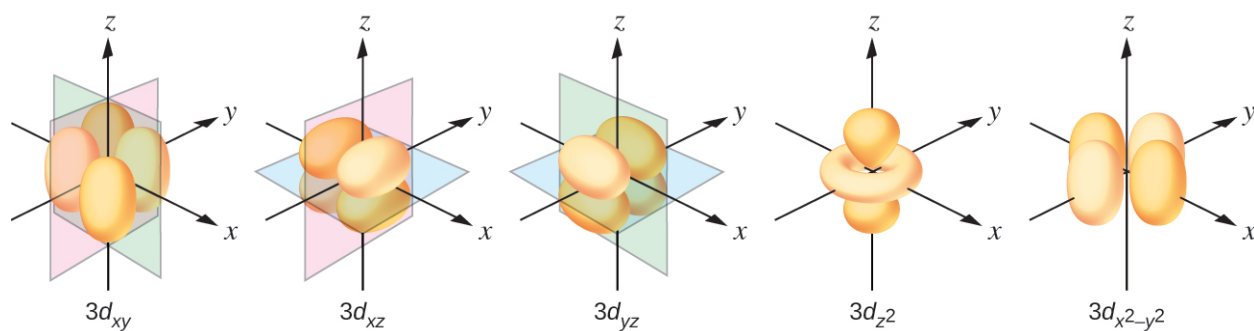
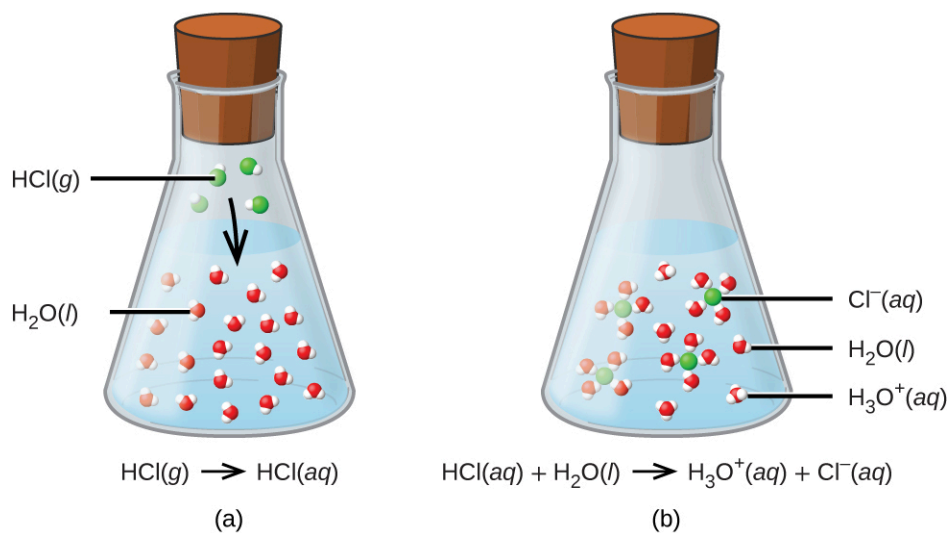
How Sciences Interconnect feature boxes discuss chemistry in context of its interconnectedness with other scientific disciplines. Topics include neurotransmitters, greenhouse gases and climate change, and proteins and enzymes.

Portrait of a Chemist features present a short bio and an introduction to the work of prominent figures from history and present day so that students can see the “faces” of contributors in this field as well as science in action.

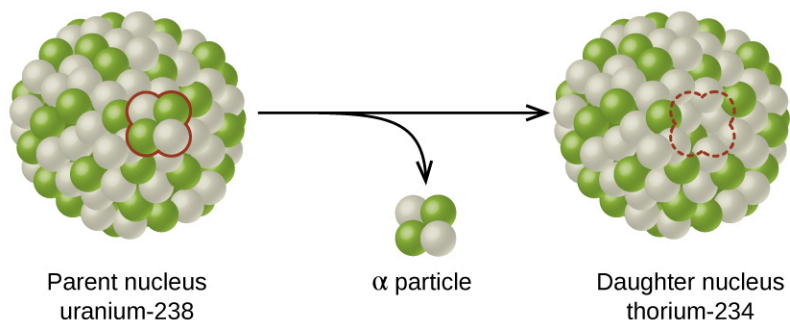
Comprehensive art program

Our art program is designed to enhance students’ understanding of concepts through clear, effective illustrations, diagrams, and photographs.





Face-centered cubic structure



Interactives that engage

Chemistry: Atoms First 2e incorporates links to relevant interactive exercises and animations that help bring topics to life through our **Link to Learning** feature. Examples include:

PhET simulations

IUPAC data and interactives

TED talks

Assessments that reinforce key concepts

In-chapter **Examples** walk students through problems by posing a question, stepping out a solution, and then asking students to practice the skill with a “Check Your Learning” component. The book also includes assessments at the end of each chapter so students can apply what they’ve learned through practice problems.

Additional resources

Student and instructor resources

We’ve compiled additional resources for both students and instructors, including Getting Started Guides, PowerPoint slides, and an instructor answer guide. Instructor resources require a verified instructor account, which you can apply for when you log in or create your account on openstax.org. Take advantage of these resources to supplement your OpenStax book.

Community Hubs

OpenStax partners with the Institute for the Study of Knowledge Management in Education (ISKME) to offer Community Hubs on OER Commons—a platform for instructors to share community-created resources that support OpenStax books, free of charge. Through our Community Hubs, instructors can upload their own materials or download resources to use in their own courses, including additional ancillaries, teaching material, multimedia, and relevant course content. We encourage instructors to join the hubs for the subjects most relevant to your teaching and research as an opportunity both to enrich your courses and to engage with other faculty.

To reach the Community Hubs, visit www.oercommons.org/hubs/OpenStax.

Technology partners

As allies in making high-quality learning materials accessible, our technology partners offer optional low-cost tools that are integrated with OpenStax books. To access the technology options for your text, visit your book page on openstax.org.

About the University of Connecticut

The University of Connecticut is one of the top public research universities in the nation, with more than 30,000 students pursuing answers to critical questions in labs, lecture halls, and the community. Knowledge exploration throughout the University’s network of campuses is united by a culture of innovation. An unprecedented commitment from the state of Connecticut ensures UConn attracts internationally renowned faculty and the world’s brightest students. A tradition of coaching winning athletes makes UConn a standout in Division I sports and fuels our academic spirit. As a vibrant, progressive leader, UConn fosters a diverse and dynamic culture that meets the challenges of a changing global society.

About our team

Senior contributing authors

Paul Flowers, University of North Carolina–Pembroke

Dr. Paul Flowers earned a BS in Chemistry from St. Andrews Presbyterian College in 1983 and a PhD in Analytical Chemistry from the University of Tennessee in 1988. After a one-year postdoctoral appointment at Los Alamos National Laboratory, he joined the University of North Carolina–Pembroke in the fall of 1989. Dr. Flowers teaches courses in general and analytical chemistry, and conducts experimental research involving the development of new devices and methods for microscale chemical analysis.

Klaus Theopold, University of Delaware

Dr. Klaus Theopold (born in Berlin, Germany) received his Vordiplom from the Universität Hamburg in 1977. He then decided to pursue his graduate studies in the United States, where he received his PhD in inorganic chemistry from UC Berkeley in 1982. After a year of postdoctoral research at MIT, he joined the faculty at Cornell University. In 1990, he moved to the University of Delaware, where he is a Professor in the Department of Chemistry and Biochemistry and serves as an Associate Director of the University's Center for Catalytic Science and Technology. Dr. Theopold regularly teaches graduate courses in inorganic and organometallic chemistry as well as General Chemistry.

Richard Langley, Stephen F. Austin State University

Dr. Richard Langley earned BS degrees in Chemistry and Mineralogy from Miami University of Ohio in the early 1970s and went on to receive his PhD in Chemistry from the University of Nebraska in 1977. After a postdoctoral fellowship at the Arizona State University Center for Solid State Studies, Dr. Langley taught in the University of Wisconsin system and participated in research at Argonne National Laboratory. Moving to Stephen F. Austin State University in 1982, Dr. Langley today serves as Professor of Chemistry. His areas of specialization are solid state chemistry, synthetic inorganic chemistry, fluorine chemistry, and chemical education.

Edward J. Neth, University of Connecticut (*Chemistry: Atoms First*)

Dr. Edward J. Neth earned his BS in Chemistry (minor in Politics) at Fairfield University in 1985 and his MS (1988) and PhD (1995; Inorganic/Materials Chemistry) at the University of Connecticut. He joined the University of Connecticut in 2004 as a lecturer and currently teaches general and inorganic chemistry; his background includes having worked as a network engineer in both corporate and university settings, and he has served as Director of Academic Computing at New Haven University. He currently teaches a three-semester, introductory chemistry sequence at UConn and is involved with training and coordinating teaching assistants.

William R. Robinson, PhD

Contributing authors

Mark Blaser, Shasta College
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
Jennifer Look, Mercer University
George Kaminski, Worcester Polytechnic Institute
Carol Martinez, Central New Mexico Community College
Troy Milliken, Jackson State University
Vicki Moravec, Trine University
Jason Powell, Ferrum College
Thomas Sorensen, University of Wisconsin–Milwaukee
Allison Soult, University of Kentucky

Reviewers

Casey Akin, College Station Independent School District
Lara AL-Hariri, University of Massachusetts–Amherst
Sahar Atwa, University of Louisiana at Monroe
Todd Austell, University of North Carolina–Chapel Hill
Bobby Bailey, University of Maryland–University College
Robert Baker, Trinity College
Jeffrey Bartz, Kalamazoo College
Greg Baxley, Cuesta College
Ashley Beasley Green, National Institute of Standards and Technology

Patricia Bianconi, University of Massachusetts
Lisa Blank, Lyme Central School District
Daniel Branan, Colorado Community College System
Dorian Canelas, Duke University
Emmanuel Chang, York College
Carolyn Collins, College of Southern Nevada
Colleen Craig, University of Washington
Yasmine Daniels, Montgomery College–Germantown
Patricia Dockham, Grand Rapids Community College
Erick Fuoco, Richard J. Daley College
Andrea Geyer, University of Saint Francis
Daniel Goebbert, University of Alabama
John Goodwin, Coastal Carolina University
Stephanie Gould, Austin College
Patrick Holt, Bellarmine University
Kevin Kolack, Queensborough Community College
Amy Kovach, Roberts Wesleyan College
Judit Kovacs Beagle, University of Dayton
Krzysztof Kuczera, University of Kansas
Marcus Lay, University of Georgia
Pamela Lord, University of Saint Francis
Oleg Maksimov, Excelsior College
John Matson, Virginia Tech
Katrina Miranda, University of Arizona
Douglas Mulford, Emory University
Mark Ott, Jackson College
Adrienne Oxley, Columbia College
Richard Pennington, Georgia Gwinnett College
Rodney Powell, Coastal Carolina Community College
Jeanita Pritchett, Montgomery College–Rockville
Aheda Saber, University of Illinois at Chicago
Raymond Sadeghi, University of Texas at San Antonio
Nirmala Shankar, Rutgers University
Jonathan Smith, Temple University
Bryan Spiegelberg, Rider University
Ron Sternfels, Roane State Community College
Cynthia Strong, Cornell College
Kris Varazo, Francis Marion University
Victor Vilchiz, Virginia State University
Alex Waterson, Vanderbilt University
Juchao Yan, Eastern New Mexico University
Mustafa Yatin, Salem State University
Kazushige Yokoyama, State University of New York at Geneseo
Curtis Zaleski, Shippensburg University
Wei Zhang, University of Colorado–Boulder

Chapter 1

Essential Ideas



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. (credit “left”: modification of work by “vxla”/Flickr; credit “left middle”: modification of work by “the Italian voice”/Flickr; credit “right middle”: modification of work by Jason Trim; credit “right”: modification of work by “gosheshe”/Flickr)

Chapter Outline

- 1.1 Chemistry in Context
- 1.2 Phases and Classification of Matter
- 1.3 Physical and Chemical Properties
- 1.4 Measurements
- 1.5 Measurement Uncertainty, Accuracy, and Precision
- 1.6 Mathematical Treatment of Measurement Results

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.

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

From alchemy came the historical progressions that led to modern chemistry: the isolation of drugs from natural sources, metallurgy, and the dye industry. Today, chemistry continues to deepen our understanding and improve our ability to harness and control the behavior of matter.

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.

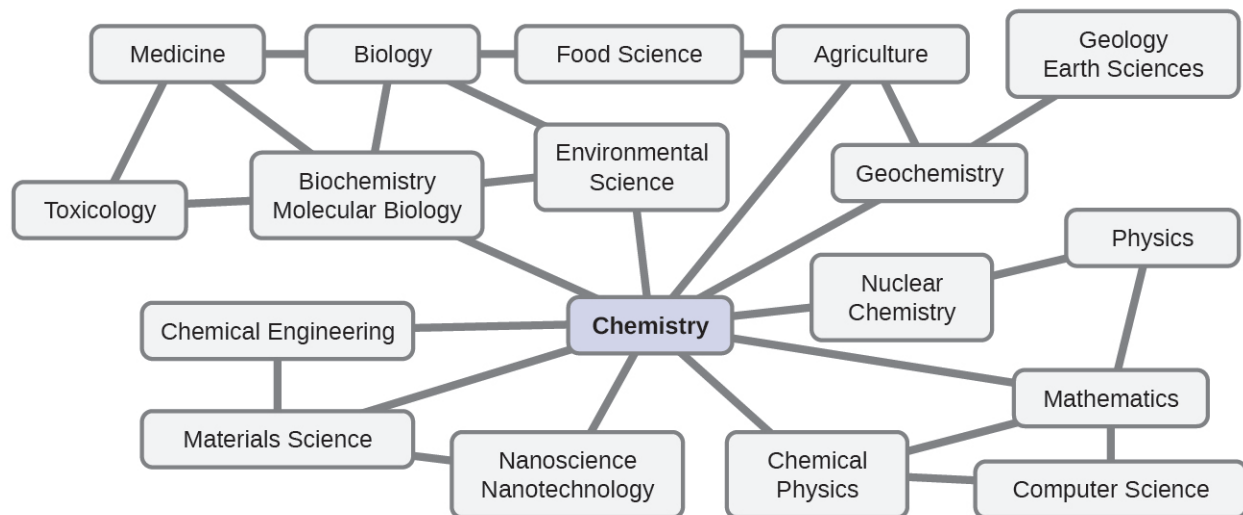


Figure 1.3 Knowledge of chemistry is central to understanding a wide range of scientific disciplines. This diagram shows just some of the interrelationships between chemistry and other fields.

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).

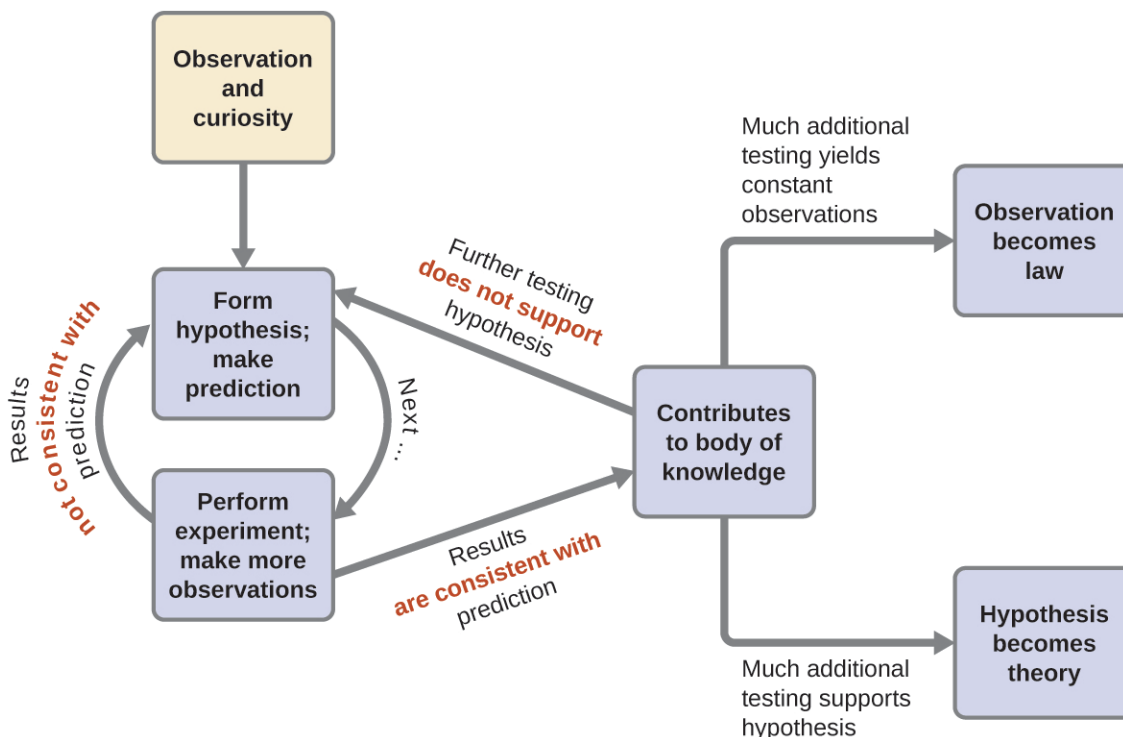


Figure 1.4 The scientific method follows a process similar to the one shown in this diagram. All the key components are shown, in roughly the right order. Scientific progress is seldom neat and clean: It requires open inquiry and the reworking of questions and ideas in response to findings.

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 H_2O , which can describe water at either the macroscopic or microscopic levels, is an example of the symbolic domain. The abbreviations (*g*) for gas, (*s*) for solid, and (*l*) for liquid are also symbolic.

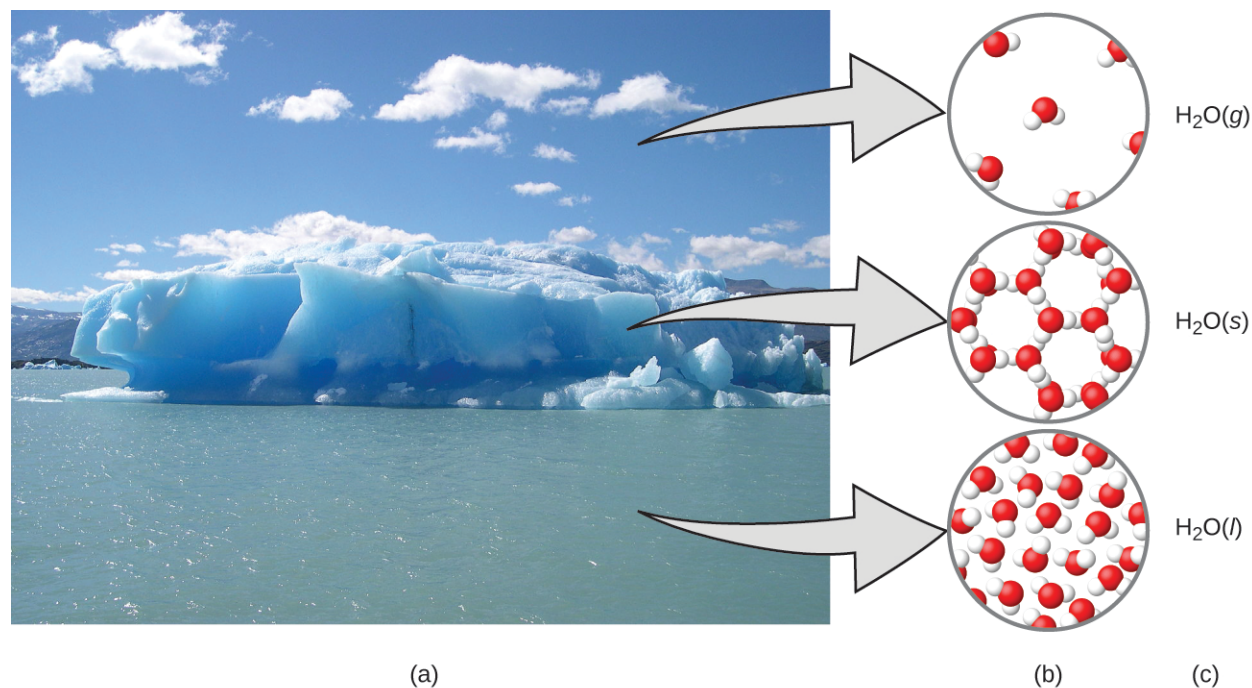


Figure 1.5 (a) Moisture in the air, icebergs, and the ocean represent water in the macroscopic domain. (b) At the molecular level (microscopic domain), gas molecules are far apart and disorganized, solid water molecules are close together and organized, and liquid molecules are close together and disorganized. (c) The formula H_2O 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. (credit a: modification of work by “Gorkaazk”/Wikimedia Commons)

1.2 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.

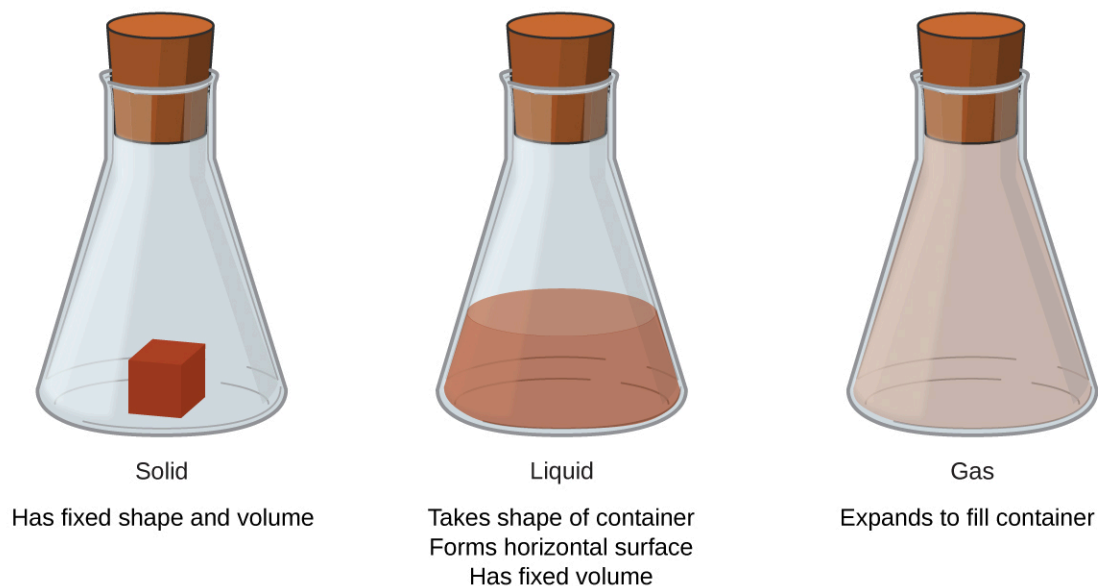


Figure 1.6 The three most common states or phases of matter are solid, liquid, and gas.

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 A plasma torch can be used to cut metal. (credit: "Hypertherm"/Wikimedia Commons)

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 \(http://openstaxcollege.org//16plasma\)](http://openstaxcollege.org//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.

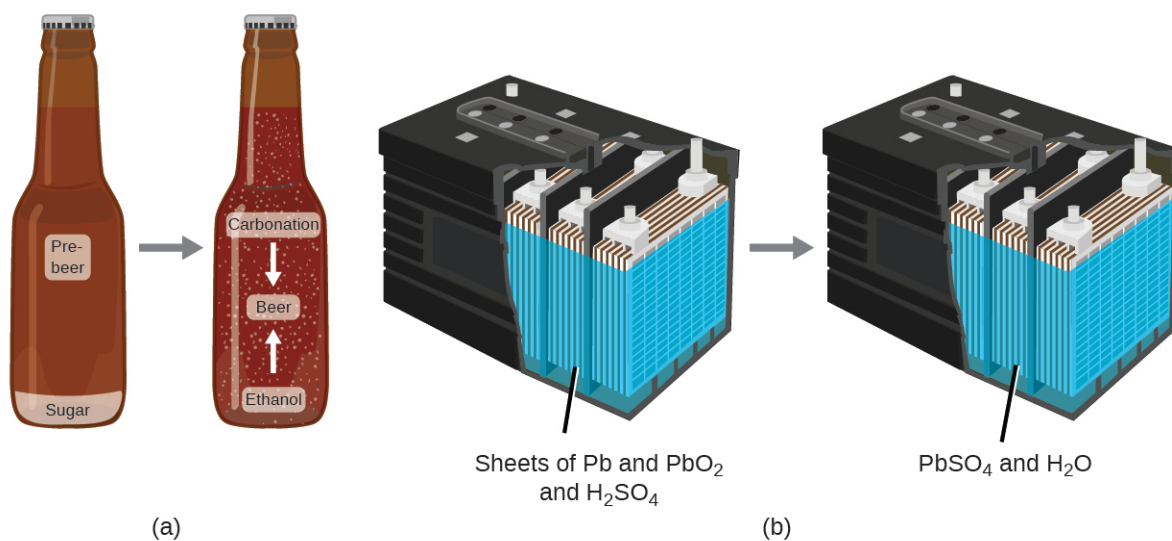


Figure 1.8 (a) The mass of beer precursor materials is the same as the mass of beer produced: Sugar has become alcohol and carbon dioxide. (b) The mass of the lead, lead oxide, and sulfuric acid consumed by the production of electricity is exactly equal to the mass of lead sulfate and water that is formed.

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).

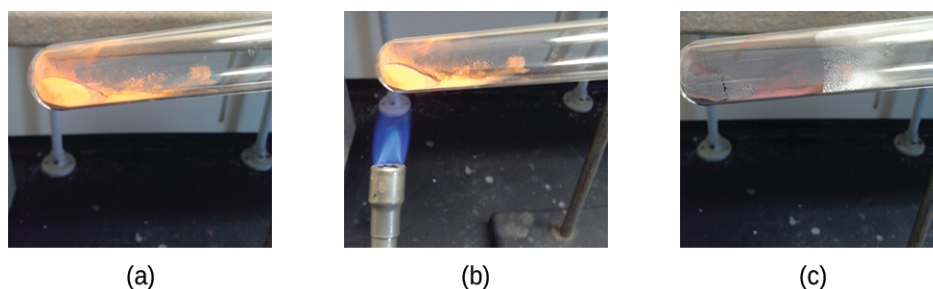


Figure 1.9 (a) The compound mercury(II) oxide, (b) when heated, (c) decomposes into silvery droplets of liquid mercury and invisible oxygen gas. (credit: modification of work by Paul Flowers)

Link to Learning

Many compounds break down when heated. This [site \(http://openstaxcollege.org//16mercury\)](http://openstaxcollege.org//16mercury) shows the breakdown of mercury oxide, HgO . You can also view an example of the **photochemical decomposition of silver chloride** (<http://openstaxcollege.org//16silvchloride>) (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.

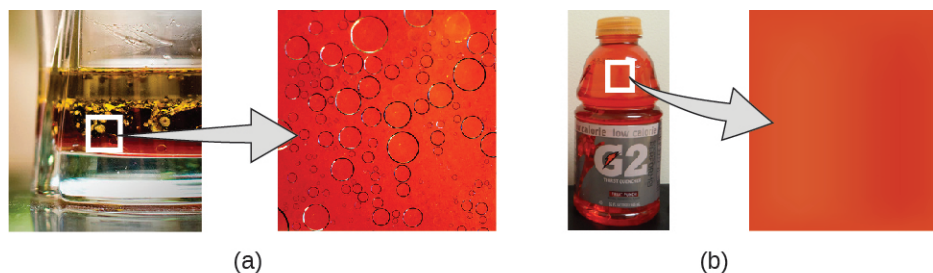


Figure 1.10 (a) Oil and vinegar salad dressing is a heterogeneous mixture because its composition is not uniform throughout. (b) A commercial sports drink is a homogeneous mixture because its composition is uniform throughout. (credit a “left”: modification of work by John Mayer; credit a “right”: modification of work by Umberto Salvagnin; credit b “left: modification of work by Jeff Bedford)

Although there are just over 100 elements, tens of millions of chemical compounds result from different combinations of these elements. Each compound has a specific composition and possesses definite chemical and physical properties 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).

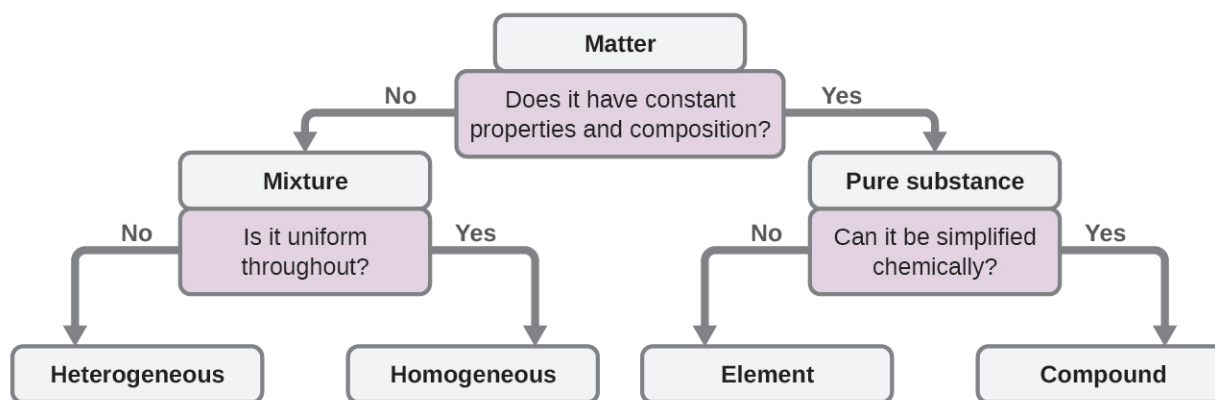


Figure 1.11 Depending on its properties, a given substance can be classified as a homogeneous mixture, a heterogeneous mixture, a compound, or an element.

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.

Elemental Composition of Earth

Element	Symbol	Percent Mass	Element	Symbol	Percent Mass
oxygen	O	49.20	chlorine	Cl	0.19
silicon	Si	25.67	phosphorus	P	0.11
aluminum	Al	7.50	manganese	Mn	0.09

Table 1.1

Elemental Composition of Earth

Element	Symbol	Percent Mass	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

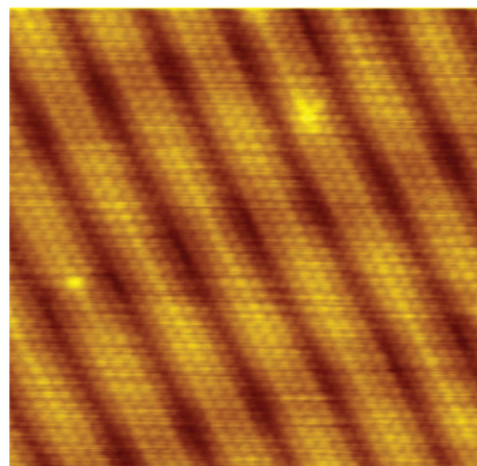
Table 1.1

Atoms and Molecules

An **atom** is the smallest particle of an element that has the properties of that element and can enter into a chemical combination. Consider the element gold, for example. Imagine cutting a gold nugget in half, then cutting one of the halves in half, and repeating this process until a piece of gold remained that was so small that it could not be cut in half (regardless of how tiny your knife may be). This minimally sized piece of gold is an atom (from the Greek *atomos*, meaning “indivisible”) (Figure 1.12). 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. (credit a: modification of work by United States Geological Survey; credit b: modification of work by “Erwinrossen”/Wikimedia Commons)

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

An atom is so small that its size is difficult to imagine. One of the smallest things we can see with our unaided eye is a single thread of a spider web: These strands are about $1/10,000$ of a centimeter (0.0001 cm) in diameter. Although the cross-section of one strand is almost impossible to see without a microscope, it is huge on an atomic scale. A single carbon atom in the web has a diameter of about 0.000000015 centimeter, and it would take about 7000 carbon atoms to span the diameter of the strand. To put this in perspective, if a carbon atom were the size of a dime, the cross-section of one strand would be larger than a football field, which would require about 150 million carbon atom “dimes” to cover it. (Figure 1.13) shows increasingly close microscopic and atomic-level views of ordinary cotton.

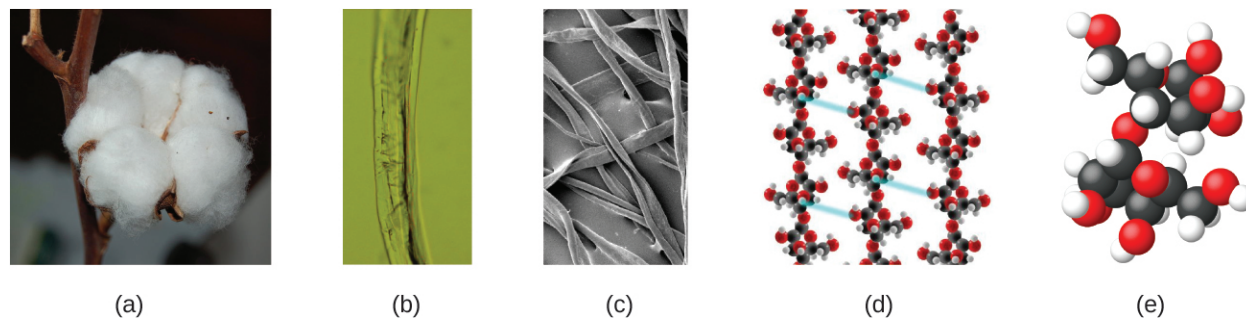


Figure 1.13 These images provide an increasingly closer view: (a) a cotton boll, (b) a single cotton fiber viewed under an optical microscope (magnified 40 times), (c) an image of a cotton fiber obtained with an electron microscope (much higher magnification than with the optical microscope); and (d and e) atomic-level models of the fiber (spheres of different colors represent atoms of different elements). (credit c: modification of work by “Featheredtar”/Wikimedia Commons)

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

It is rare to find collections of individual atoms. Only a few elements, such as the gases helium, neon, and argon, consist of a collection of individual atoms that move about independently of one another. Other elements, such as the gases hydrogen, nitrogen, oxygen, and chlorine, are composed of units that consist of pairs of atoms (Figure 1.14). 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.

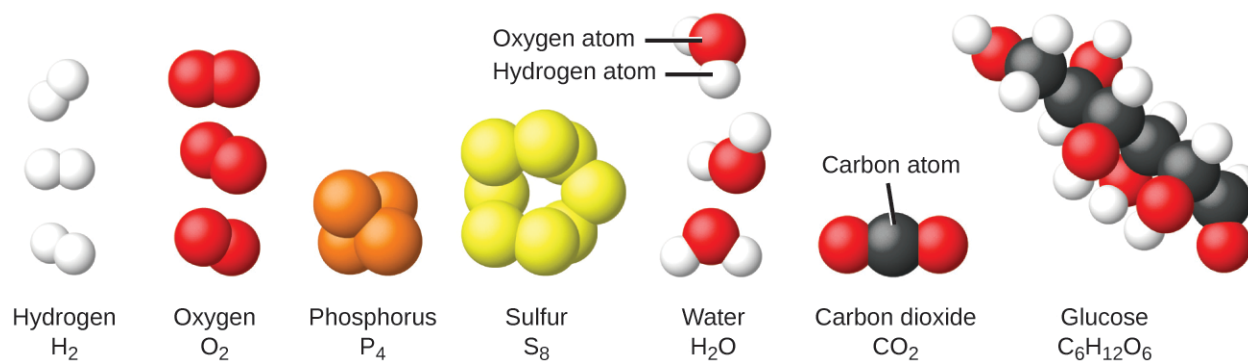


Figure 1.14 The elements hydrogen, oxygen, phosphorus, and sulfur form molecules consisting of two or more atoms of the same element. The compounds water, carbon dioxide, and glucose consist of combinations of atoms of different elements.

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).

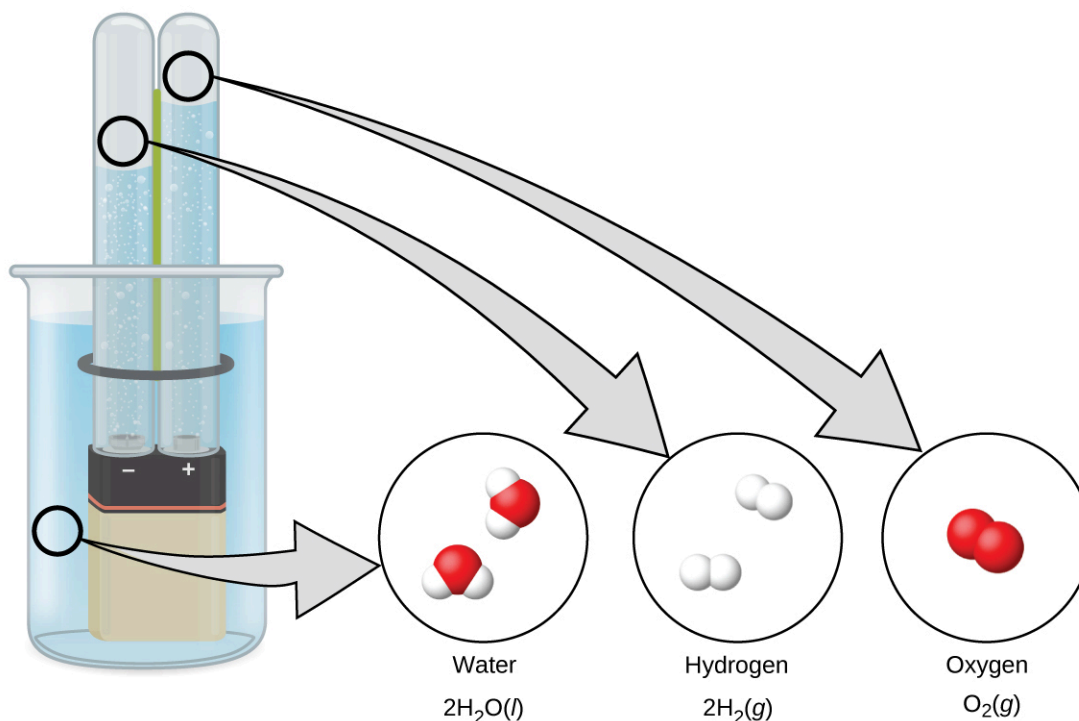


Figure 1.15 The decomposition of water is shown at the macroscopic, microscopic, and symbolic levels. The battery provides an electric current (microscopic) that decomposes water. At the macroscopic level, the liquid separates into the gases hydrogen (on the left) and oxygen (on the right). Symbolically, this change is presented by showing how liquid H_2O separates into H_2 and O_2 gases.

The breakdown of water involves a rearrangement of the atoms in water molecules into different molecules, each composed of two hydrogen atoms and two oxygen atoms, respectively. Two water molecules form one oxygen molecule and two hydrogen molecules. The representation for what occurs, $2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2(g) + \text{O}_2(g)$, 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 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.

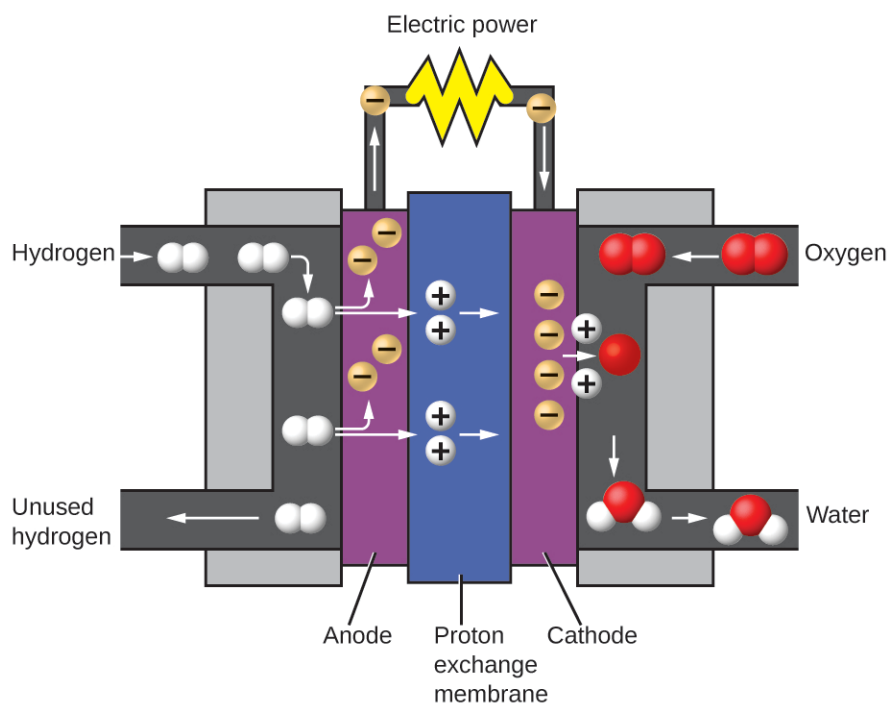
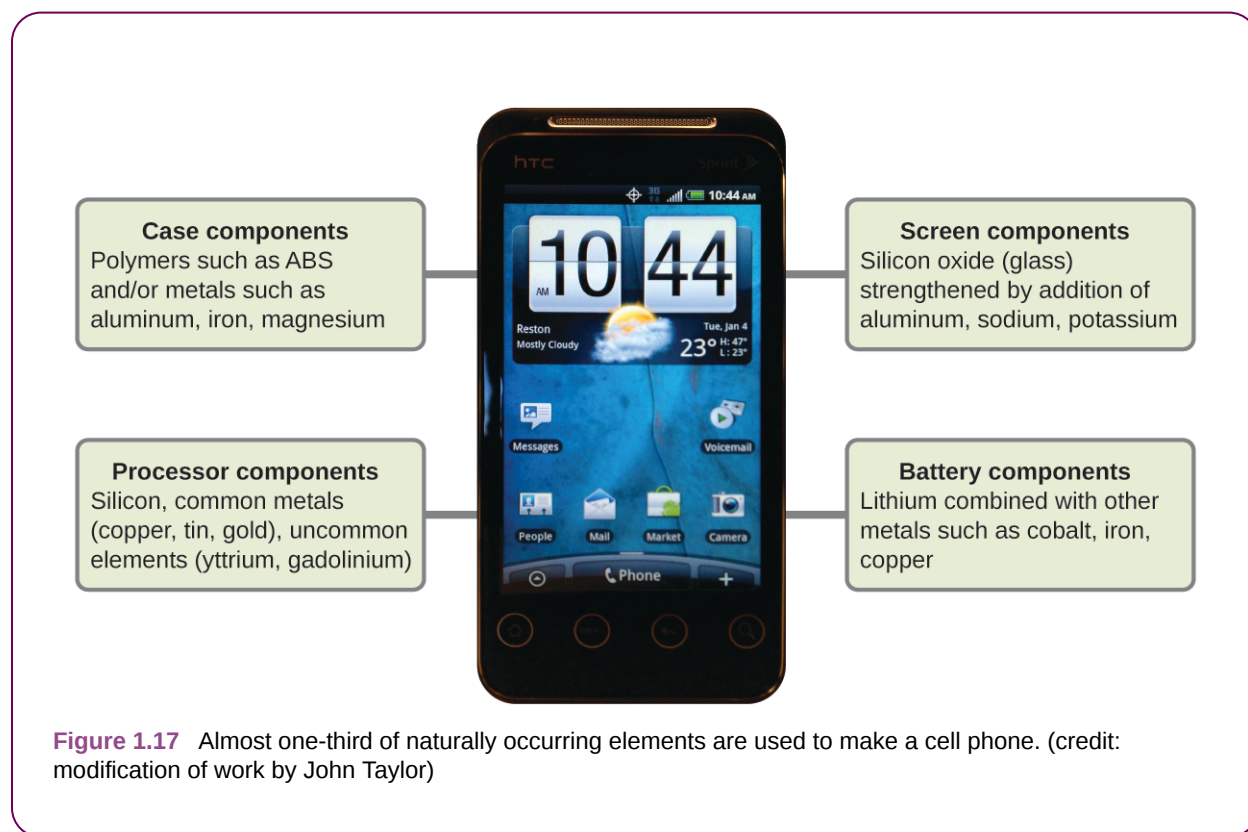


Figure 1.16 A fuel cell generates electrical energy from hydrogen and oxygen via an electrochemical process and produces only water as the waste product.

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.



1.3 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.



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. (credit a: modification of work by "95jb14"/Wikimedia Commons; credit b: modification of work by "mjneuby"/Flickr)

The change of one type of matter into another type (or the inability to change) is a **chemical property**. Examples of chemical properties include flammability, toxicity, acidity, 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.

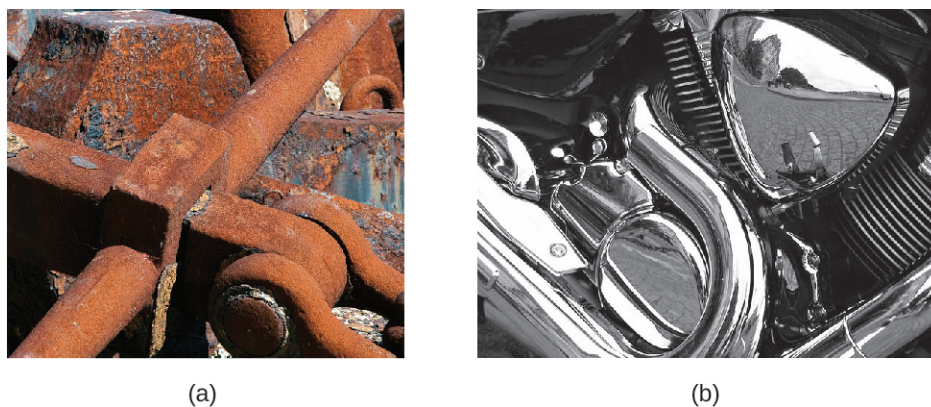


Figure 1.19 (a) One of the chemical properties of iron is that it rusts; (b) one of the chemical properties of chromium is that it does not. (credit a: modification of work by Tony Hisgett; credit b: modification of work by "Atoma"/Wikimedia Commons)

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**).

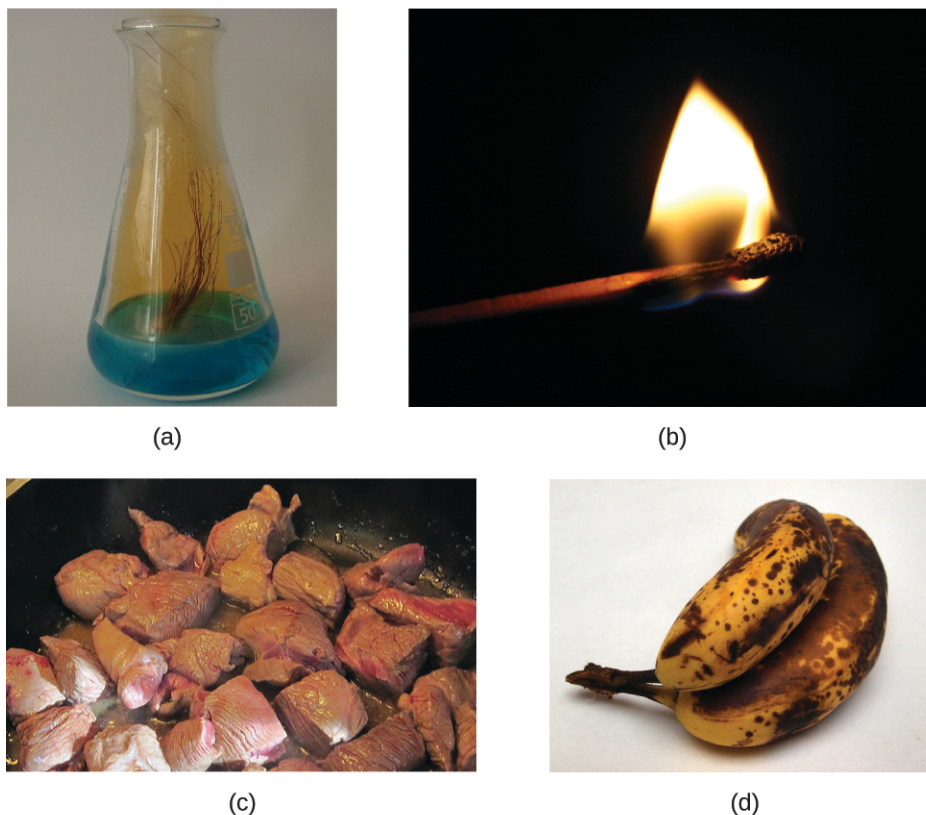


Figure 1.20 (a) Copper and nitric acid undergo a chemical change to form copper nitrate and brown, gaseous nitrogen dioxide. (b) During the combustion of a match, cellulose in the match and oxygen from the air undergo a chemical change to form carbon dioxide and water vapor. (c) Cooking red meat causes 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. (credit b: modification of work by Jeff Turner; credit c: modification of work by Gloria Cabada-Leman; credit d: modification of work by Roberto Verzo)

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

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.

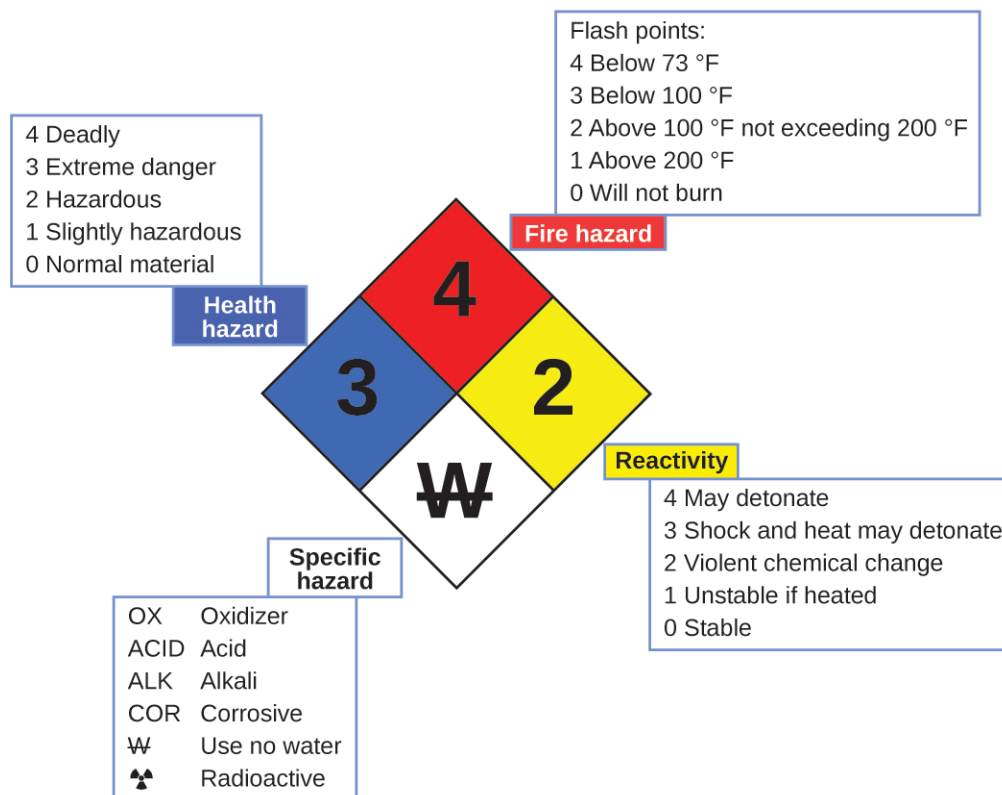


Figure 1.21 The National Fire Protection Agency (NFPA) hazard diamond summarizes the major hazards of a chemical substance.

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

The periodic table is organized into 7 periods (rows) and 18 groups (columns). Elements are color-coded based on their physical and chemical properties:

- Yellow:** Metal (Solid)
- Purple:** Metalloid (Liquid)
- Light Blue:** Nonmetal (Gas)

Callout for Hydrogen (H):

- Atomic number: 1
- Symbol: H
- Atomic mass: 1.008
- Name: hydrogen

Color Code Legend:

- Metal (Solid)
- Metalloid (Liquid)
- Nonmetal (Gas)

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.

1.4 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 2.98×10^5 kg. The mass of the average mosquito is about 0.0000025 kilograms, which can be written as 2.5×10^{-6} kg.

Units, such as liters, pounds, and centimeters, are standards of comparison for measurements. 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 1.2](#). 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.

Base Units of the SI System

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

Table 1.2

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 one 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 1.3](#).

Common Unit Prefixes

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

Table 1.3

Common Unit Prefixes

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

Table 1.3

Link to Learning

Need a refresher or more practice with scientific notation? Visit this [site \(http://openstaxcollege.org//16notation\)](http://openstaxcollege.org//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 39.37 inches longer than a yard (**Figure 1.23**); one meter is about 39.37 inches or 1.094 yards. Longer distances are often reported in kilometers ($1 \text{ km} = 1000 \text{ m} = 10^3 \text{ m}$), whereas shorter distances can be reported in centimeters ($1 \text{ cm} = 0.01 \text{ m} = 10^{-2} \text{ m}$) or millimeters ($1 \text{ mm} = 0.001 \text{ m} = 10^{-3} \text{ m}$).

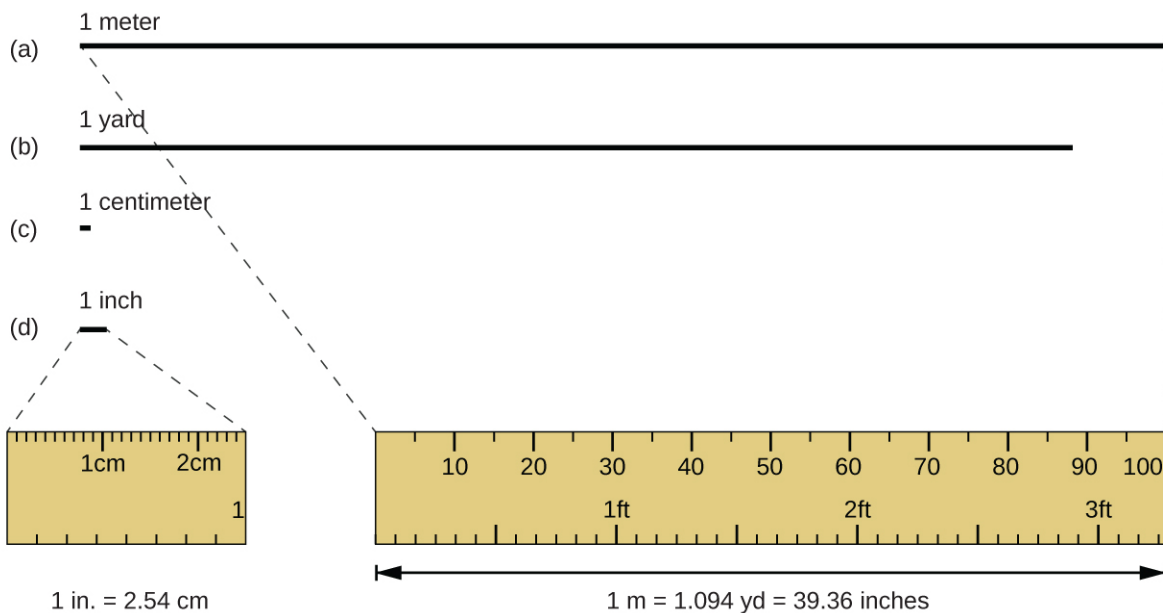


Figure 1.23 The relative lengths of 1 m, 1 yd, 1 cm, and 1 in. are shown (not actual size), as well as comparisons of 2.54 cm and 1 in., and of 1 m and 1.094 yd.

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)

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°C) and boils at 373.15 K (100°C) by definition, and normal human body temperature is approximately 310 K (37°C). The conversion between these two units and the Fahrenheit scale will be discussed later in this chapter.

Time

The SI base unit of time is the **second (s)**. Small and large time intervals can be expressed with the appropriate prefixes; for example, 3 microseconds = $0.000003\text{ s} = 3 \times 10^{-6}$ 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^3)**, a cube with an edge length of exactly one meter. To dispense a cubic meter of water, we could build a cubic box with edge lengths of exactly one meter. This box would hold a cubic meter of water or any other substance.

A more commonly used unit of volume is derived from the decimeter (0.1 m, or 10 cm). A cube with edge lengths of exactly one decimeter contains a volume of one cubic decimeter (dm^3). A **liter (L)** is the more common name for the cubic decimeter. One liter is about 1.06 quarts.

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

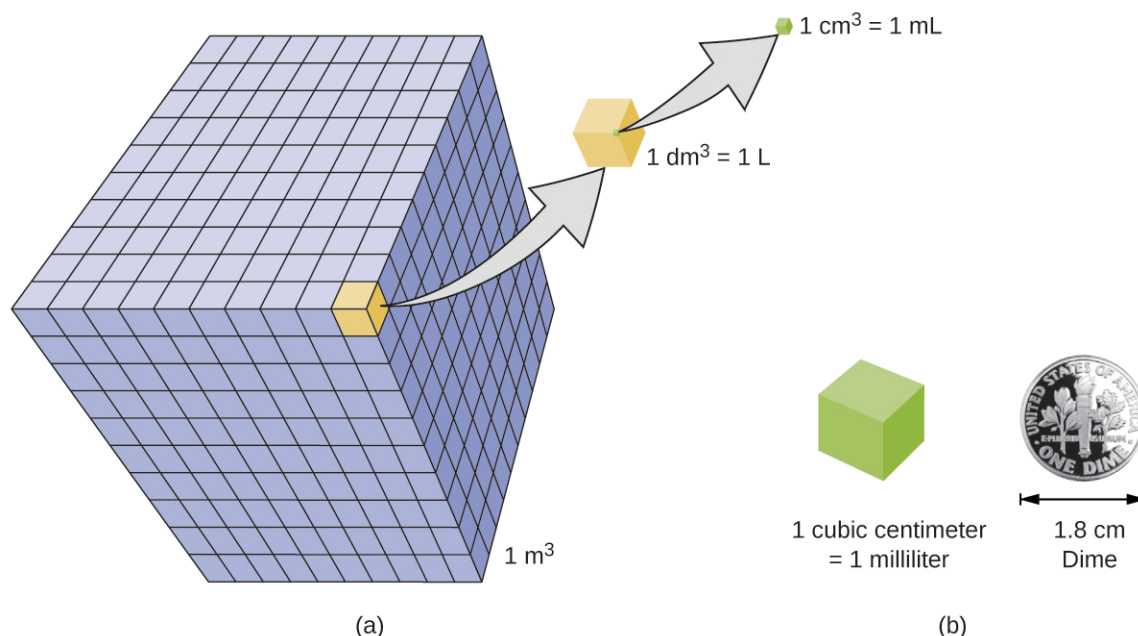


Figure 1.25 (a) The relative volumes are shown for cubes of 1 m^3 , 1 dm^3 (1 L), and 1 cm^3 (1 mL) (not to scale). (b) The diameter of a dime is compared relative to the edge length of a 1-cm^3 (1-mL) cube.

Density

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

The **density** of a substance is the ratio of the mass of a sample of the substance to its volume. The SI unit for density is the kilogram per cubic meter (kg/m^3). For many situations, however, this is an inconvenient unit, and we often use grams per cubic centimeter (g/cm^3) for the densities of solids and liquids, and grams per liter (g/L) for gases. Although there are exceptions, most liquids and solids have densities that range from about $0.7 \text{ g}/\text{cm}^3$ (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 1.4** shows the densities of some common substances.

Densities of Common Substances

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

Table 1.4

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^3 . What is the density of lead if a cube of lead has an edge length of 2.00 cm and a mass of 90.7 g?

Solution

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

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

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

Answer: (a) 0.599 cm^3 ; (b) 8.91 g/cm^3

Link to Learning

To learn more about the relationship between mass, volume, and density, use this [interactive simulator \(http://openstaxcollege.org/l/16phetmasvolden\)](http://openstaxcollege.org/l/16phetmasvolden) 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 \(http://openstaxcollege.org/l/16phetmasvolden\)](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 more dense than water, which has density = 1.00 kg/L), and the water level rises to 101.25 L.

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

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

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

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

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

1.5 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.

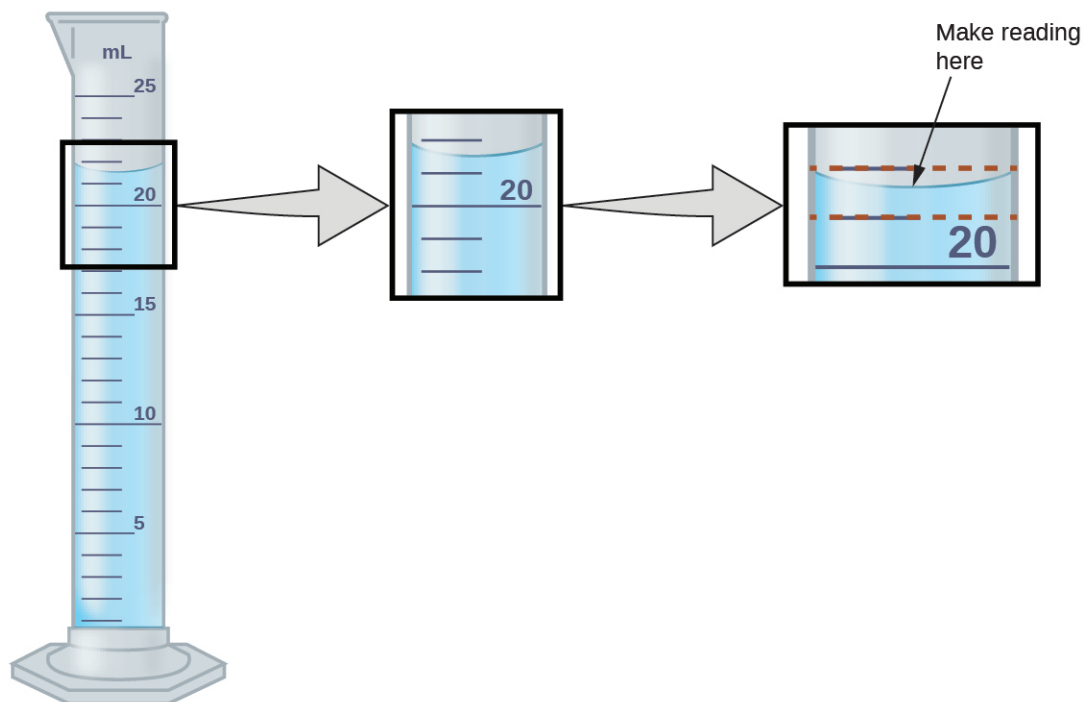


Figure 1.26 To measure the volume of liquid in this graduated cylinder, you must mentally subdivide the distance between the 21 and 22 mL marks into tenths of a milliliter, and then make a reading (estimate) at the bottom of the meniscus.

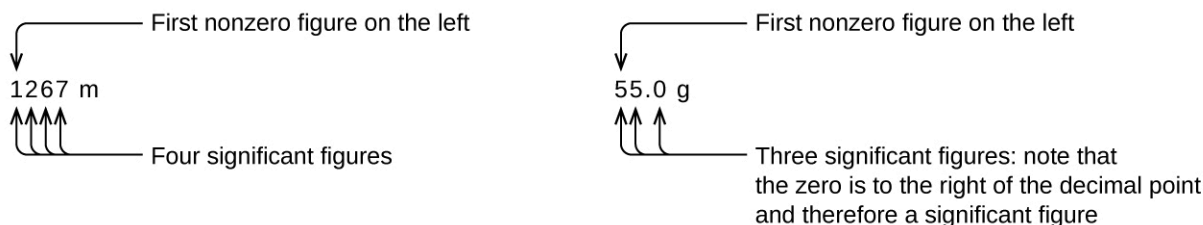
Refer to the illustration in **Figure 1.26**. The bottom of the meniscus in this case clearly lies between the 21 and 22 markings, meaning the liquid volume is *certainly* greater than 21 mL but less than 22 mL. The meniscus appears to be a bit closer to the 22-mL mark than to the 21-mL mark, and so 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 ± 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.

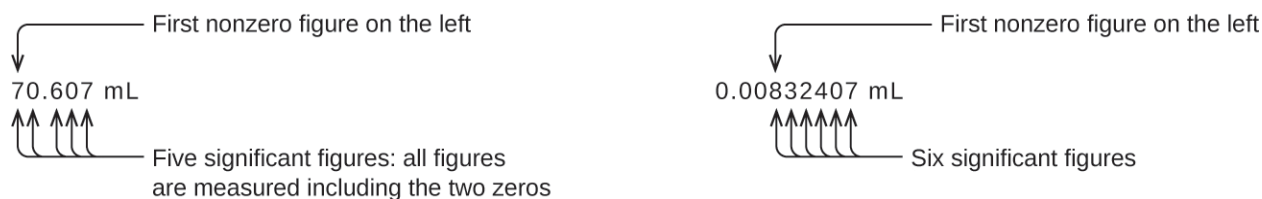
A measurement result is properly reported when its significant digits accurately represent the certainty of the measurement process. But what if you were analyzing a reported value and trying to determine what is significant and what is not? Well, for starters, all nonzero digits are significant, and 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.



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

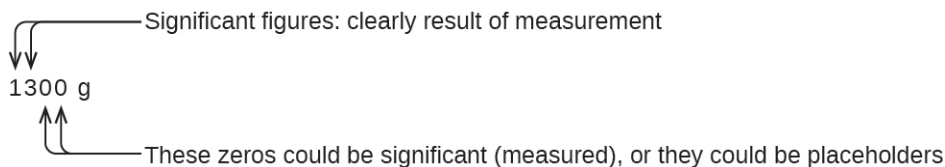


Captive zeros result from measurement and are therefore always significant. Leading zeros, however, are never significant—they merely tell us where the decimal point is located.



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

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



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 3.17×10^8 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:

1. 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).
2. 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).
3. 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:

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

Solution

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

Check Your Learning

Round the following to the indicated number of significant figures:

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

Answer: (a) 0.42; (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

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

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

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

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

$$\begin{array}{r}
 1.0023 \leftarrow \text{Ten thousandths place} \\
 + 4.383 \leftarrow \text{Thousandths place: least precise} \\
 \hline
 5.385\cancel{3} \\
 \uparrow \\
 \text{Round to thousandths}
 \end{array}$$

(a)

$$\begin{array}{r}
 486 \text{ g} \\
 - 421.23 \text{ g} \\
 \hline
 64.7\cancel{7} \text{ g} \longrightarrow \text{Answer is 65 g} \\
 \uparrow \\
 \text{Round to ones}
 \end{array}$$

(b)

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

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

- (b) $\frac{421.23 \text{ g}}{486 \text{ mL}} = 0.86728\dots \text{ g/mL} \rightarrow$ result is 0.867 g/mL (round to three significant figures)
 five significant figures
 three significant figures \rightarrow 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 cm^2 (b) 0.9884 m/s

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.

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

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

Check Your Learning

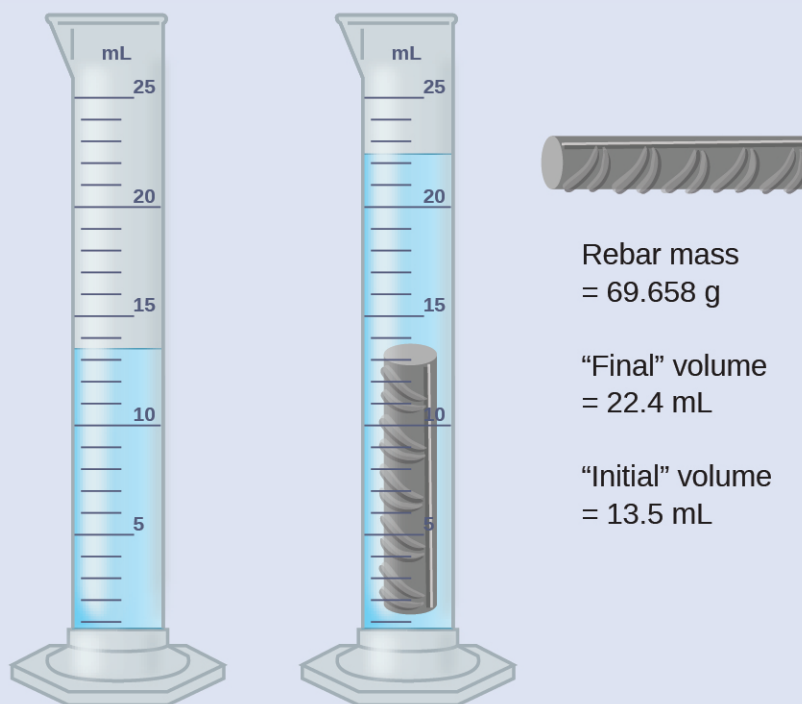
What is the density of a liquid with a mass of 31.1415 g and a volume of 30.13 cm³?

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.



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

Solution

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

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

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

The density is the mass-to-volume ratio:

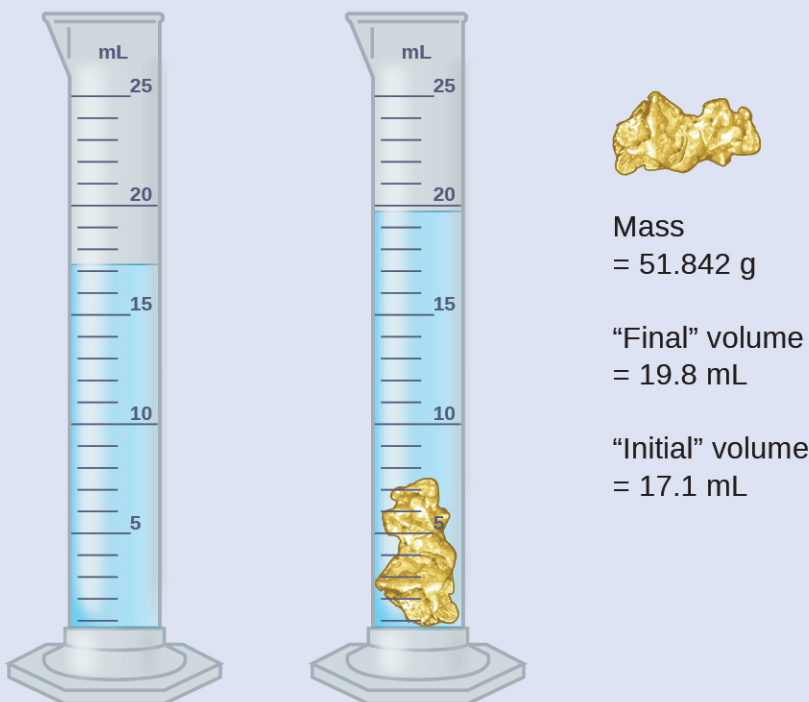
$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{69.658 \text{ g}}{8.9 \text{ cm}^3} = 7.8 \text{ g/cm}^3$$

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

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

Check Your Learning

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



(a) Use these values to determine the density of this material.

(b) Do you have any reasonable guesses as to the identity of this material? Explain your reasoning.

Answer: (a) 19 g/cm^3 ; (b) It is likely gold; the right appearance for gold and very close to the density given for gold in **Table 1.4**.

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 1.27**).

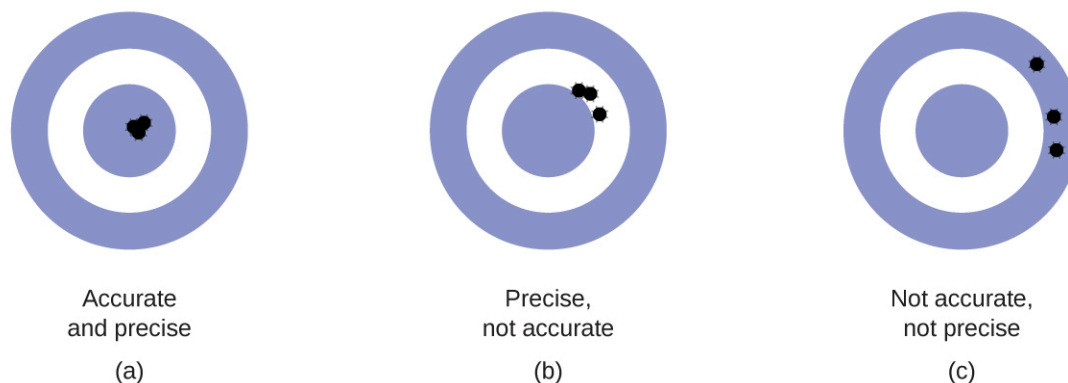


Figure 1.27 (a) These arrows are close to both the bull's eye and one another, so they are both accurate and precise. (b) These arrows are close to one another but not on target, so they are precise but not accurate. (c) These arrows are neither on target nor close to one another, so they are neither accurate nor precise.

Suppose a quality control chemist at a pharmaceutical company is tasked with checking the accuracy and precision of three different machines that are meant to dispense 10 ounces (296 mL) of cough syrup into storage bottles. She proceeds to use each machine to fill five bottles and then carefully determines the actual volume dispensed, obtaining the results tabulated in **Table 1.5**.

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

Dispenser #1	Dispenser #2	Dispenser #3
283.3	298.3	296.1
284.1	294.2	295.9
283.9	296.0	296.1
284.0	297.8	296.0
284.1	293.9	296.1

Table 1.5

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

1.6 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 ($\text{m/m/s} = \text{s}$) 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, m/m), the result is “1”—or, as commonly phrased, the units “cancel.”

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

Conversion Factors and Dimensional Analysis

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

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

Several other commonly used conversion factors are given in **Table 1.6**.

Common Conversion Factors

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

Table 1.6

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 $\frac{\text{in.} \times \text{cm}}{\text{in.}}$. Just as for numbers, a ratio of identical units is also numerically equal to one, $\frac{\text{in.}}{\text{in.}} = 1$, and the unit product thus simplifies to *cm*. (When identical units divide to yield a factor of 1, they are said to “cancel.”) 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 1.6).

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.

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

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 $\text{density} = \frac{\text{mass}}{\text{volume}}$, we need to divide the mass in grams by the volume in milliliters. In general: the number of units of B = the number of units of A \times unit conversion factor. The necessary conversion factors are given in **Table 1.6**: 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.

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

Then,

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

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

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

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.

(a) What (average) fuel economy, in miles per gallon, did the Roadster get during this trip?

(b) If gasoline costs \$3.80 per gallon, what was the fuel cost for this trip?

Solution

(a) First convert distance from kilometers to miles:

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

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:

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

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

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

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) \$62

Conversion of Temperature Units

We use the word **temperature** to refer to the hotness or coldness of a substance. One way we measure a change in temperature is to use the fact that most substances expand when their temperature increases and contract when their temperature decreases. The mercury or alcohol in a common glass thermometer changes its volume as the temperature changes, 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:

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

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

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

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

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

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

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

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

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

As mentioned earlier in this chapter, the SI unit of temperature is the kelvin (K). Unlike the Celsius and Fahrenheit scales, the kelvin scale is an absolute temperature scale in which 0 (zero) K corresponds to the lowest temperature that can theoretically be achieved. Since the kelvin temperature scale is absolute, a degree symbol is not included in the unit abbreviation, K. The early 19th-century discovery of the relationship between a gas's volume and temperature suggested that the volume of a gas would be zero at $-273.15\text{ }^{\circ}\text{C}$. 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 $1\frac{\text{K}}{\text{ }^{\circ}\text{C}}$. Following the same approach, the equations for converting between the kelvin and Celsius temperature scales are derived to be:

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

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

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.

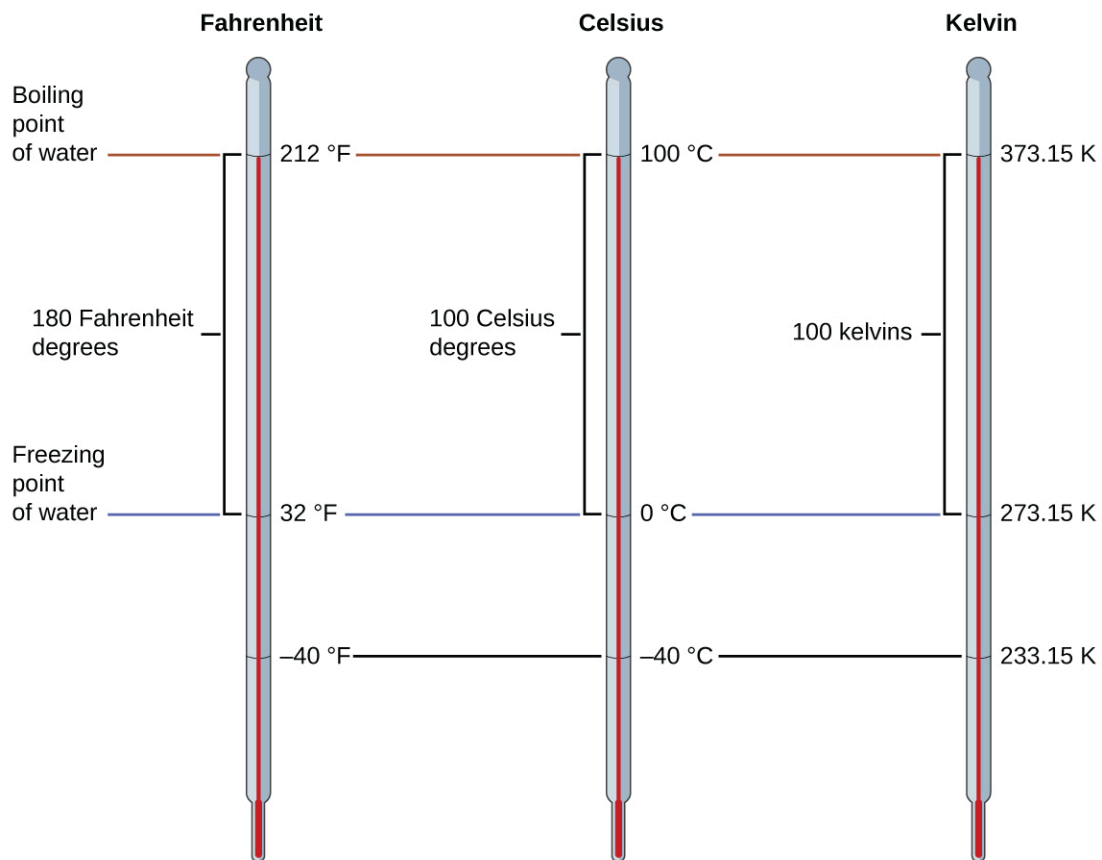


Figure 1.28 The Fahrenheit, Celsius, and kelvin temperature scales are compared.

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 $37.0\text{ }^{\circ}\text{C}$ (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

$$\begin{aligned} \text{K} &= \text{ }^{\circ}\text{C} + 273.15 = 37.0 + 273.2 = 310.2 \text{ K} \\ \text{ }^{\circ}\text{F} &= \frac{9}{5}\text{ }^{\circ}\text{C} + 32.0 = \left(\frac{9}{5} \times 37.0\right) + 32.0 = 66.6 + 32.0 = 98.6 \text{ }^{\circ}\text{F} \end{aligned}$$

Check Your Learning

Convert $80.92\text{ }^{\circ}\text{C}$ to K and $^{\circ}\text{F}$.

Answer: 354.07 K, 177.7 $^{\circ}\text{F}$

Example 1.12

Conversion from Fahrenheit

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

Solution

$$\begin{aligned} \text{ }^{\circ}\text{C} &= \frac{5}{9}(\text{ }^{\circ}\text{F} - 32) = \frac{5}{9}(450 - 32) = \frac{5}{9} \times 418 = 232 \text{ }^{\circ}\text{C} \longrightarrow \text{set oven to } 230 \text{ }^{\circ}\text{C} \quad (\text{two significant figures}) \\ \text{K} &= \text{ }^{\circ}\text{C} + 273.15 = 230 + 273 = 503 \text{ K} \longrightarrow 5.0 \times 10^2 \text{ K} \quad (\text{two significant figures}) \end{aligned}$$

Check Your Learning

Convert $50\text{ }^{\circ}\text{F}$ to $^{\circ}\text{C}$ and K.

Answer: $10\text{ }^{\circ}\text{C}$, 280 K

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 (cm³ or cc) volume of a cube with an edge length of exactly 1 cm

cubic meter (m³) 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 K = 0 °C

kilogram (kg) standard SI unit of mass; 1 kg = approximately 2.2 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; $1 \text{ m} =$ 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^3

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

- $\text{density} = \frac{\text{mass}}{\text{volume}}$
- $T_{\text{°C}} = \frac{5}{9} \times (T_{\text{°F}} - 32)$
- $T_{\text{°F}} = \left(\frac{9}{5} \times T_{\text{°C}}\right) + 32$
- $T_{\text{K}} = \text{°C} + 273.15$
- $T_{\text{°C}} = \text{K} - 273.15$

Summary

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 g/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 $0\text{ }^{\circ}\text{C}$ ($32\text{ }^{\circ}\text{F}$) 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 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 \longrightarrow 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 $-220\text{ }^{\circ}\text{C}$ and boils at $-188\text{ }^{\circ}\text{C}$. 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

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

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 \(http://openstaxcollege.org/l/16phetmasvolden\)](http://openstaxcollege.org/l/16phetmasvolden) 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 \(http://openstaxcollege.org/l/16phetmasvolden\)](http://openstaxcollege.org/l/16phetmasvolden) 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** (<http://openstaxcollege.org/l/16phetmasvolden>) 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) 2×10^{18} m
- (c) 3,486,002 kg
- (d) 9.74150×10^{-4} J
- (e) 0.0613 cm³
- (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) 2.05×10^8 m
- (c) 86,002 J
- (d) 9.740×10^4 m/s
- (e) 10.0613 m³
- (f) 0.17 g/mL
- (g) 0.88400 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) 1.497×10^{-3}
- (f) 0.445

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

(a) 517

(b) 86.3

(c) 6.382×10^3

(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) 628×342

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

(c) $\frac{28.0}{13.483}$

(d) 8119×0.000023

(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) 62.8×34

(b) $0.147 + 0.0066 + 0.012$

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

(d) $15 - 0.15 - 0.6155$

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

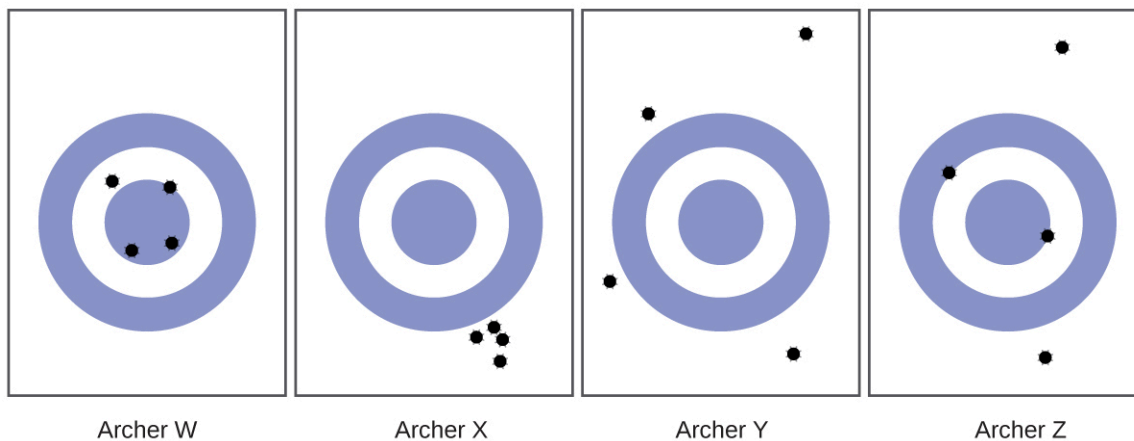
(f) $140 + 7.68 + 0.014$

(g) $28.7 - 0.0483$

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

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?



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 3×10^{-4} in. What is its diameter in centimeters?

66. The distance between the centers of the two oxygen atoms in an oxygen molecule is 1.21×10^{-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 μL 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 μm
 - (g) 1 Ts
 - (h) 27 ps
 - (i) 0.15 mK
72. Complete the following conversions between SI units.
- (a) 612 g = _____ mg
 - (b) 8.160 m = _____ cm
 - (c) 3779 μg = _____ g
 - (d) 781 mL = _____ L
 - (e) 4.18 kg = _____ g
 - (f) 27.8 m = _____ km
 - (g) 0.13 mL = _____ L
 - (h) 1738 km = _____ m
 - (i) 1.9 Gg = _____ 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^2 , 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^3 , 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^2
- (d) the displacement volume of an automobile engine, 161 in.^3 , to liters
- (e) the estimated mass of the atmosphere, 5.6×10^{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? ($1 \text{ \AA} = 1 \times 10^{-10} \text{ m}$)

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? ($1 \text{ \AA} = 1 \times 10^{-8} \text{ cm}$)

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 $\text{cm} \times \text{cm} \times \text{m}$?

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

87. Calculate the density of aluminum if 27.6 cm^3 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^3 ?

89. Calculate these masses.

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

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

90. Calculate these masses.

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

(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^3 ?

(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^3 ?

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

93. Convert the boiling temperature of gold, $2966 \text{ }^\circ\text{C}$, 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?

Chapter 2

Atoms, Molecules, and Ions

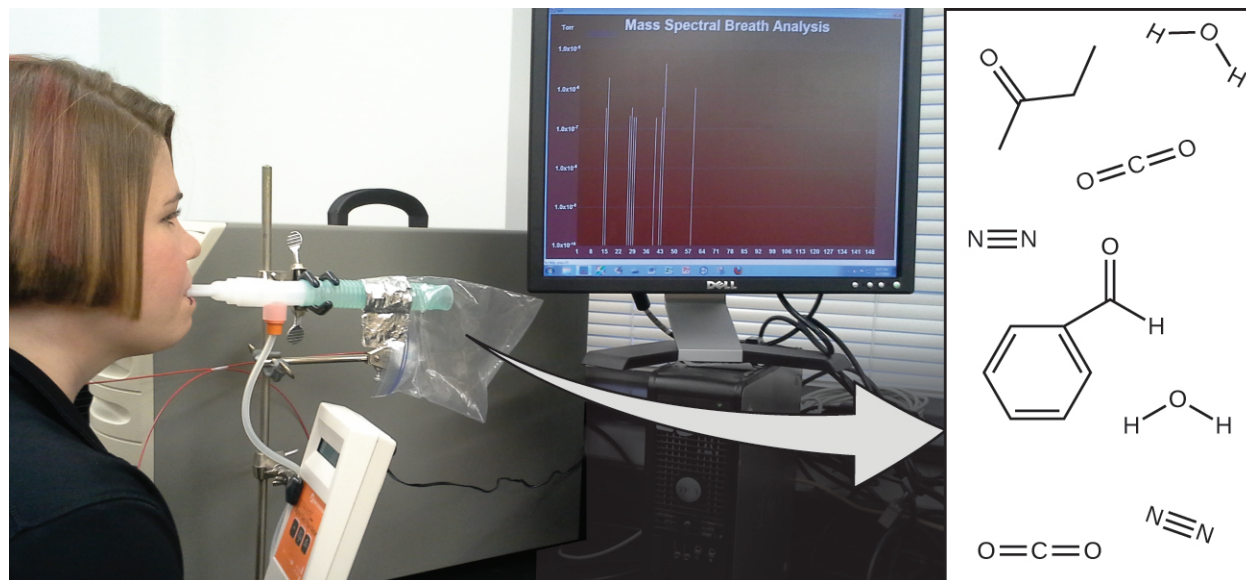


Figure 2.1 Analysis of molecules in an exhaled breath can provide valuable information, leading to early diagnosis of diseases or detection of environmental exposure to harmful substances. (credit: modification of work by Paul Flowers)

Chapter Outline

- 2.1 Early Ideas in Atomic Theory
- 2.2 Evolution of Atomic Theory
- 2.3 Atomic Structure and Symbolism
- 2.4 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.

2.1 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**.

1. Matter is composed of exceedingly small particles called atoms. An atom is the smallest unit of an element that can participate in a chemical change.
2. An element consists of only one type of atom, which has a mass that is characteristic of the element and is the same for all atoms of that element (**Figure 2.2**). A macroscopic sample of an element contains an incredibly large number of atoms, all of which have identical chemical properties.

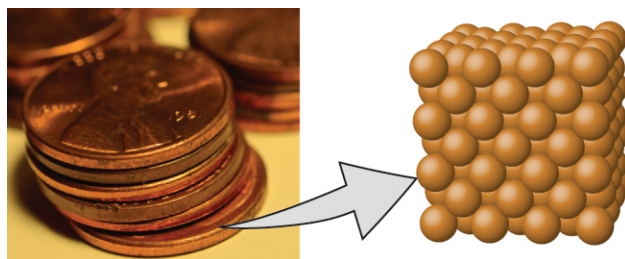


Figure 2.2 A pre-1982 copper penny (left) contains approximately 3×10^{22} copper atoms (several dozen are represented as brown spheres at the right), each of which has the same chemical properties. (credit: modification of work by “slgckgc”/Flickr)

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

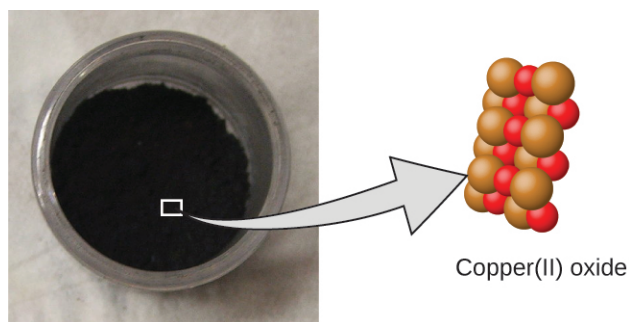


Figure 2.3 Copper(II) oxide, a powdery, black compound, results from the combination of two types of atoms—copper (brown spheres) and oxygen (red spheres)—in a 1:1 ratio. (credit: modification of work by “Chemicalinterest”/Wikimedia Commons)

5. Atoms are neither created nor destroyed during a chemical change, but are instead rearranged to yield substances that are different from those present before the change (**Figure 2.4**).

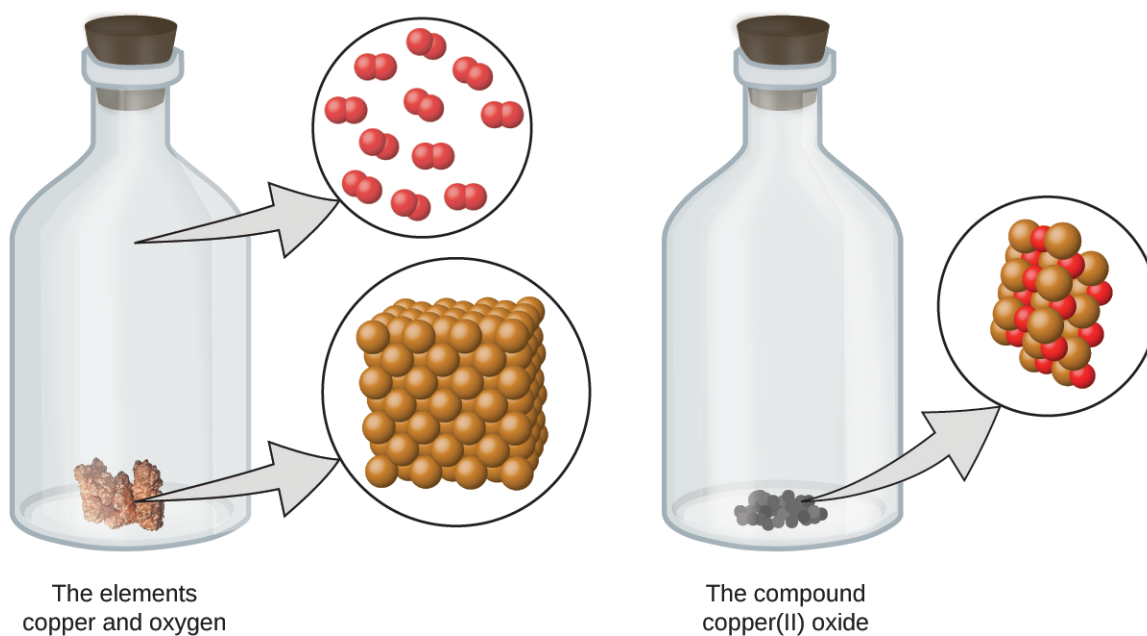


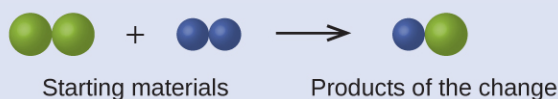
Figure 2.4 When the elements copper (a shiny, red-brown solid, shown here as brown spheres) and oxygen (a clear and colorless gas, shown here as red spheres) react, their atoms rearrange to form a compound containing copper and oxygen (a powdery, black solid). (credit copper: modification of work by <http://images-of-elements.com/copper.php>)

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

Example 2.1

Testing Dalton's Atomic Theory

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

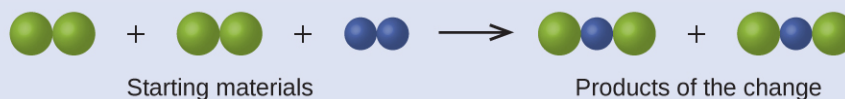


Solution

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

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?



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**.

Constant Composition of Isooctane

Sample	Carbon	Hydrogen	Mass Ratio
A	14.82 g	2.78 g	$\frac{14.82 \text{ g carbon}}{2.78 \text{ g hydrogen}} = \frac{5.33 \text{ g carbon}}{1.00 \text{ g hydrogen}}$

Table 2.1

Constant Composition of Isooctane

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

Table 2.1

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

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

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

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

This can be explained by atomic theory if the copper-to-chlorine ratio in the brown compound is 1 copper atom to 2 chlorine atoms, and the ratio in the green compound is 1 copper atom to 1 chlorine atom. The ratio of chlorine atoms (and thus the ratio of their masses) is therefore 2 to 1 (**Figure 2.5**).

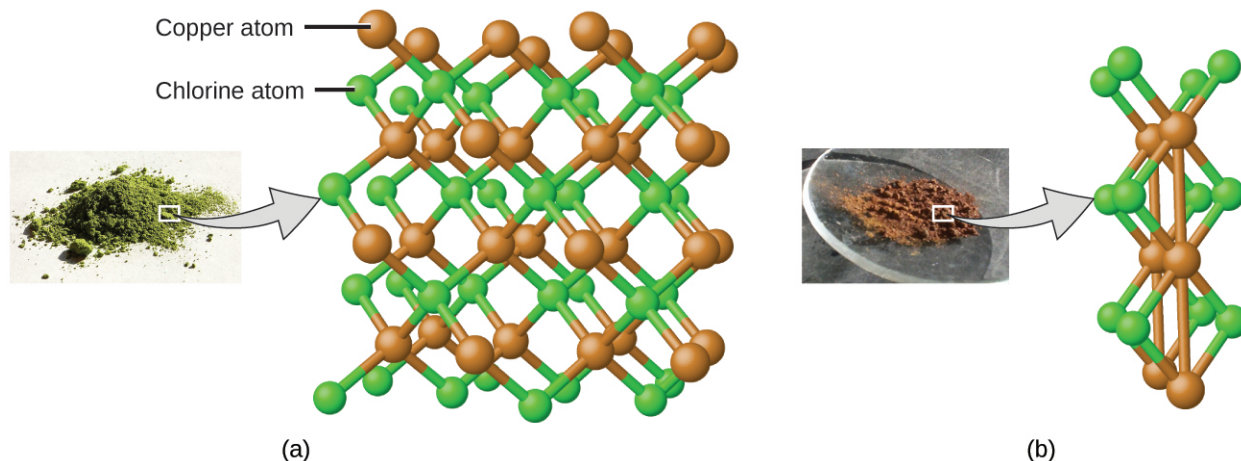


Figure 2.5 Compared to the copper chlorine compound in (a), where copper is represented by brown spheres and chlorine by green spheres, the copper chlorine compound in (b) has twice as many chlorine atoms per copper atom. (credit a: modification of work by “Benjah-bmm27”/Wikimedia Commons; credit b: modification of work by “Walkerma”/Wikimedia Commons)

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 an example of the law of definite proportions, the law of multiple proportions, or neither? What do these data tell you about substances A and B?

Solution

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

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

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

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

The ratio of these ratios is:

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

This supports the law of multiple proportions. This means that A and B are different compounds, with A having one-half as much carbon per amount of oxygen (or twice as much carbon per amount of oxygen) as B. A possible pair of compounds that would fit this relationship would be A = CO and B = CO₂.

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 $\frac{14.13 \text{ g C}}{2.96 \text{ g H}}$. In compound Y, the mass ratio of carbon to oxygen is $\frac{19.91 \text{ g C}}{3.34 \text{ g H}}$. The ratio of these ratios is

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

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

2.2 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 2.6**).

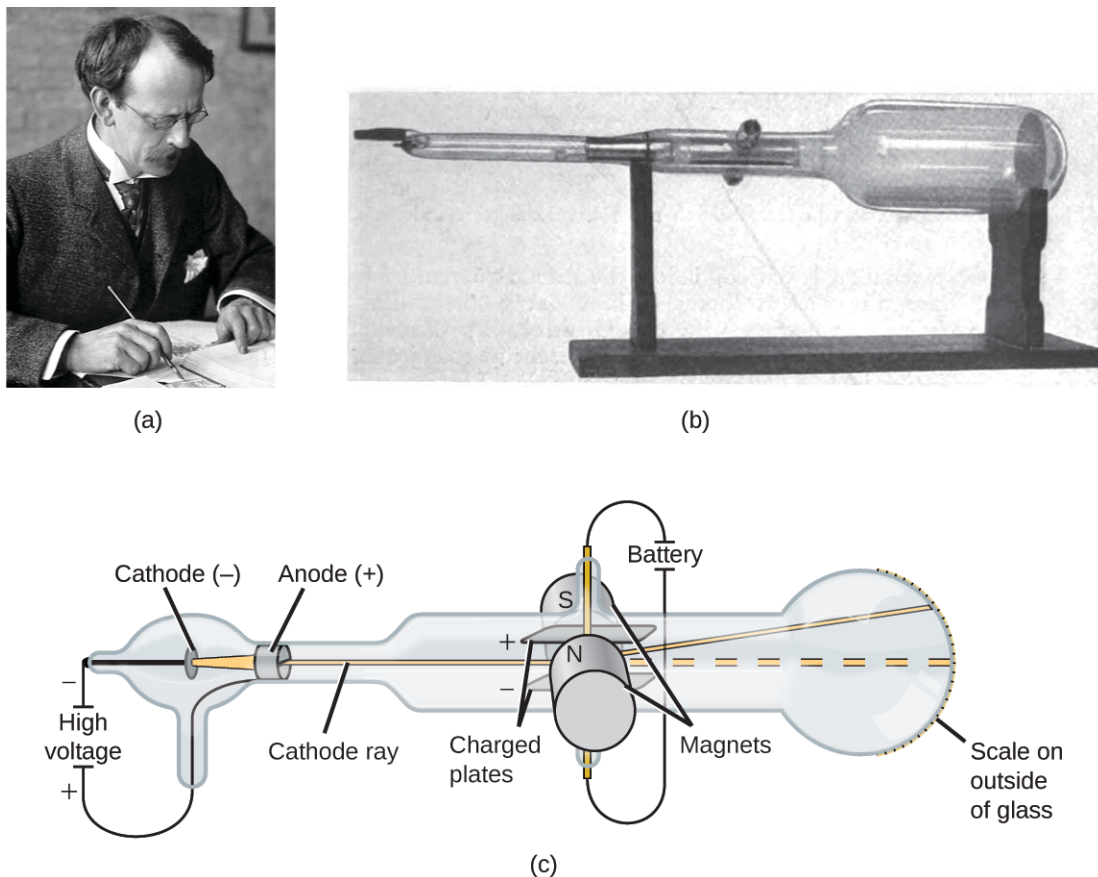


Figure 2.6 (a) J. J. Thomson produced a visible beam in a cathode ray tube. (b) This is an early cathode ray tube, invented in 1897 by Ferdinand Braun. (c) In the cathode ray, the beam (shown in yellow) comes from the cathode and is accelerated past the anode toward a fluorescent scale at the end of the tube. Simultaneous deflections by applied electric and magnetic fields permitted Thomson to calculate the mass-to-charge ratio of the particles composing the cathode ray. (credit a: modification of work by Nobel Foundation; credit b: modification of work by Eugen Nesper; credit c: modification of work by “Kurzon”/Wikimedia Commons)

Based on his observations, here is what Thomson proposed and why: The particles are attracted by positive (+) charges and repelled by negative (-) charges, so they must be negatively charged (like charges repel and unlike charges attract); they are less massive than atoms and indistinguishable, regardless of the source material, so they must be fundamental, subatomic constituents of all atoms. Although controversial at the time, Thomson’s idea was gradually accepted, and his cathode ray particle is what we now call an **electron**, a negatively charged, subatomic particle with a mass more than one thousand-times less that of an atom. The term “electron” was coined in 1891 by Irish physicist George Stoney, from “*electric ion*.”

Link to Learning

Click [here \(http://openstax.org//16JJThomson\)](http://openstax.org//16JJThomson) 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 2.7**).

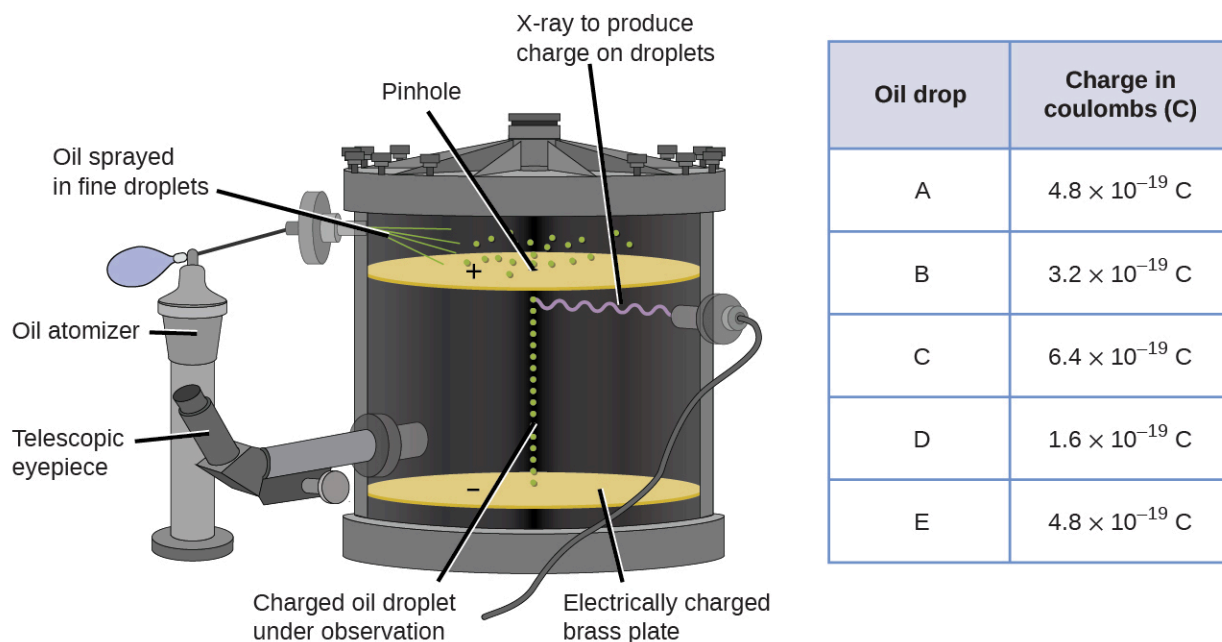


Figure 2.7 Millikan's experiment measured the charge of individual oil drops. The tabulated data are examples of a few possible values.

Looking at the charge data that Millikan gathered, you may have recognized that the charge of an oil droplet is always a multiple of a specific charge, $1.6 \times 10^{-19} \text{ C}$. 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 2.8**).

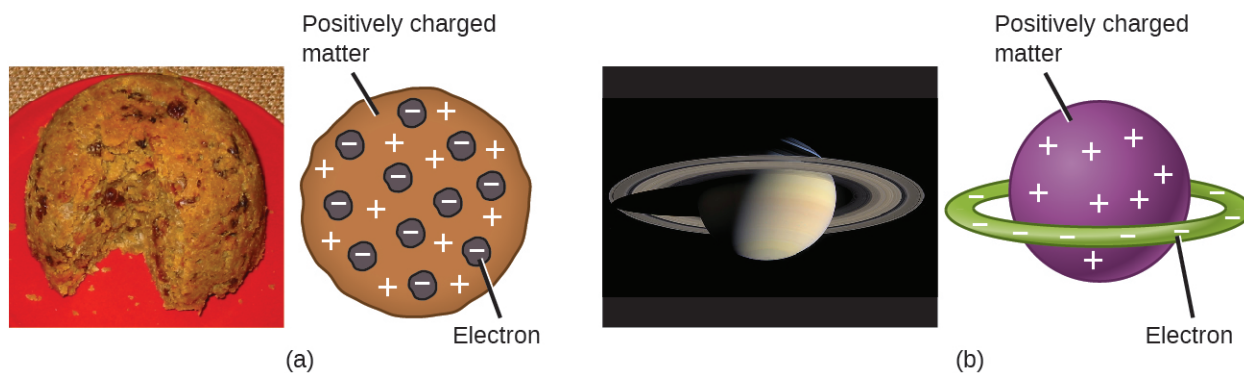


Figure 2.8 (a) Thomson suggested that atoms resembled plum pudding, an English dessert consisting of moist cake with embedded raisins (“plums”). (b) Nagaoka proposed that atoms resembled the planet Saturn, with a ring of electrons surrounding a positive “planet.” (credit a: modification of work by “Man vyi”/Wikimedia Commons; credit b: modification of work by “NASA”/Wikimedia Commons)

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

What did they discover? Most particles passed right through the foil without being deflected at all. However, some were diverted slightly, and a very small number were deflected almost straight back toward the source (**Figure 2.9**). Rutherford described finding these results: “It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you.”^[1]

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>.

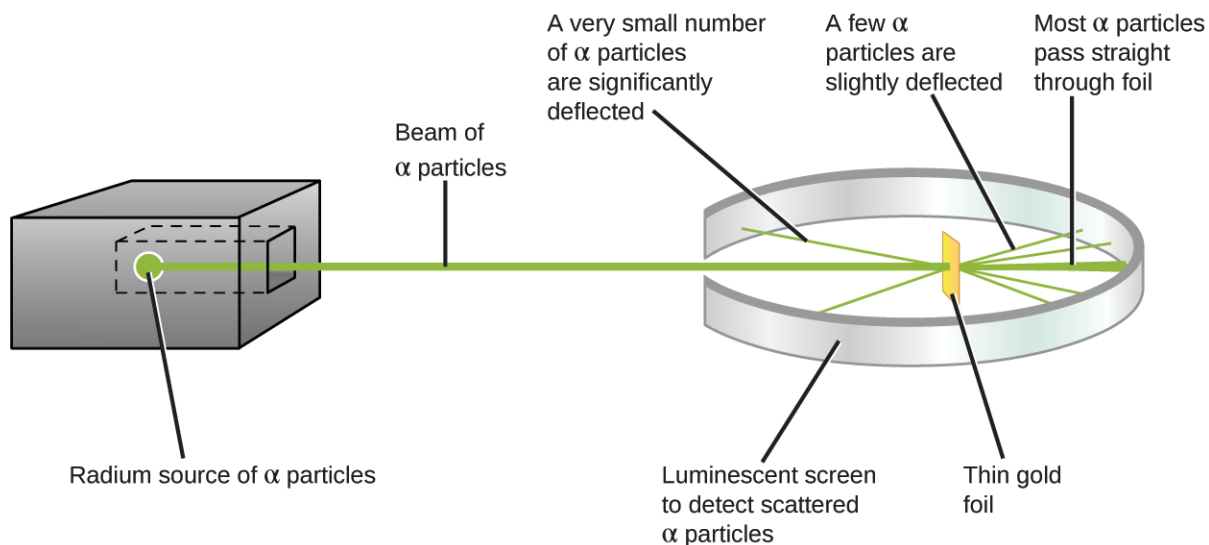


Figure 2.9 Geiger and Rutherford fired α particles at a piece of gold foil and detected where those particles went, as shown in this schematic diagram of their experiment. Most of the particles passed straight through the foil, but a few were deflected slightly and a very small number were significantly deflected.

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

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

Link to Learning

View this [simulation \(http://openstax.org//16Rutherford\)](http://openstax.org//16Rutherford) of the Rutherford gold foil experiment. Adjust the slit width to produce a narrower or broader beam of α 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 2.10**). 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.

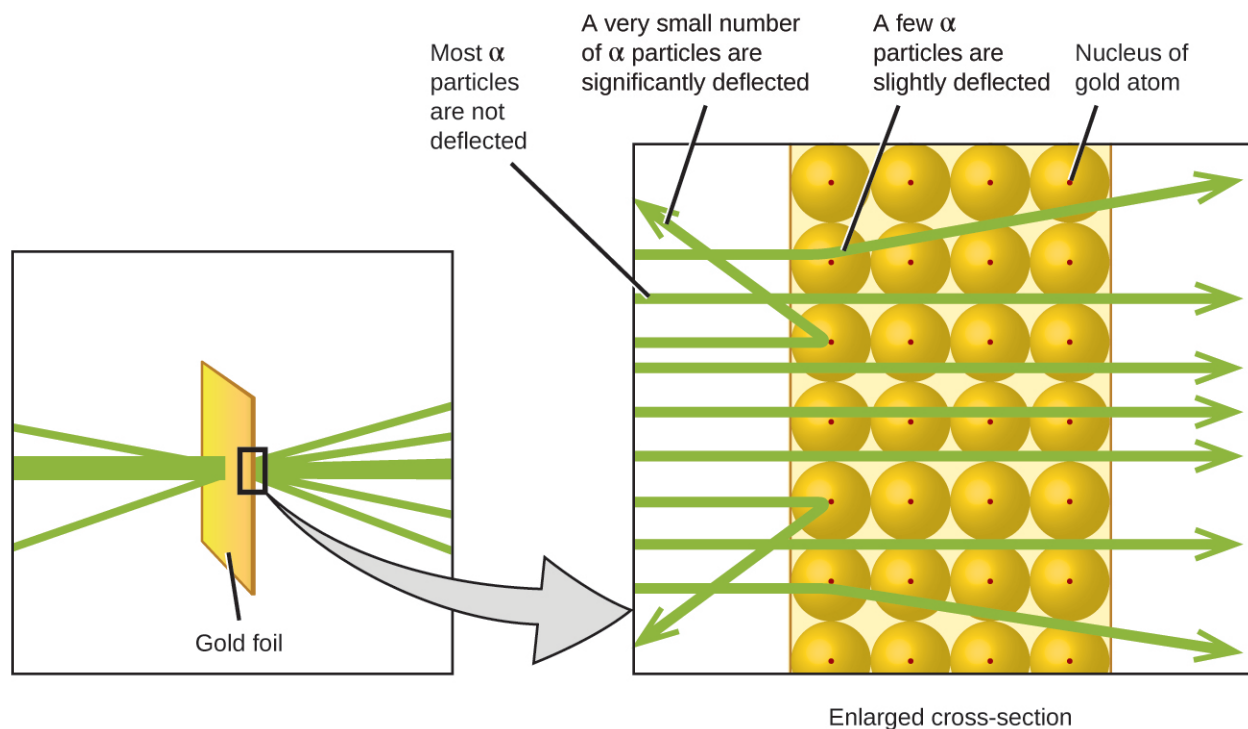


Figure 2.10 The α particles are deflected only when they collide with or pass close to the much heavier, positively charged gold nucleus. Because the nucleus is very small compared to the size of an atom, very few α particles are deflected. Most pass through the relatively large region occupied by electrons, which are too light to deflect the rapidly moving particles.

Link to Learning

The **Rutherford Scattering simulation** (<http://openstax.org//16PhetScatter>) allows you to investigate the differences between a “plum pudding” atom and a Rutherford atom by firing α 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.

2.3 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 2.11).

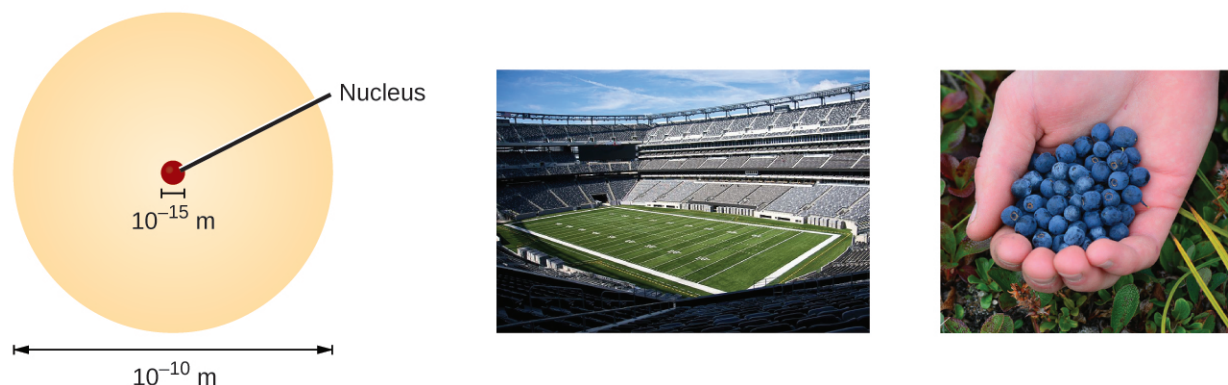


Figure 2.11 If an atom could be expanded to the size of a football stadium, the nucleus would be the size of a single blueberry. (credit middle: modification of work by “babyknight”/Wikimedia Commons; credit right: modification of work by Paxson Woelber)

Atoms—and the protons, neutrons, and electrons that compose them—are extremely small. For example, a carbon atom weighs less than 2×10^{-23} g, and an electron has a charge of less than 2×10^{-19} C (coulomb). When describing the properties of tiny objects such as atoms, we use appropriately small units of measure, such as the **atomic mass unit (amu)** and the **fundamental unit of charge (e)**. The 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 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.)

Properties of Subatomic Particles

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

Table 2.2

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:

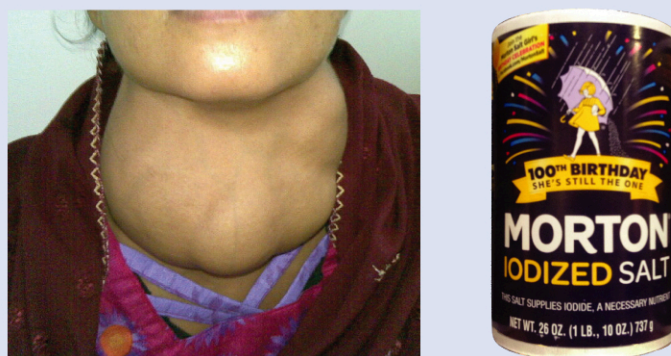
$$\text{Atomic charge} = \text{number of protons} - \text{number of electrons}$$

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 thyroid hormone. Insufficient iodine in the diet can lead to the development of a goiter, an enlargement of the thyroid gland (**Figure 2.12**).



(a)

(b)

Figure 2.12 (a) Insufficient iodine in the diet can cause an enlargement of the thyroid gland called a goiter. (b) The addition of small amounts of iodine to salt, which prevents the formation of goiters, has helped eliminate this concern in the US where salt consumption is high. (credit a: modification of work by “Almazi”/Wikimedia Commons; credit b: modification of work by Mike Mozart)

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

Solution

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

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 2.13**). 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 2.13 The symbol Hg represents the element mercury regardless of the amount; it could represent one atom of mercury or a large amount of mercury.

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**).

Some Common Elements and Their Symbols

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

Table 2.3

Nuclear Compositions of Atoms of the Very Light Elements

Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (amu)	% Natural Abundance
	${}^2_1\text{H}$ (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	${}^{12}_6\text{C}$	6	6	6	12.0000	98.89
	${}^{13}_6\text{C}$	6	6	7	13.0034	1.11
	${}^{14}_6\text{C}$	6	6	8	14.0032	— (trace)
nitrogen	${}^{14}_7\text{N}$	7	7	7	14.0031	99.63
	${}^{15}_7\text{N}$	7	7	8	15.0001	0.37
oxygen	${}^{16}_8\text{O}$	8	8	8	15.9949	99.757
	${}^{17}_8\text{O}$	8	8	9	16.9991	0.038
	${}^{18}_8\text{O}$	8	8	10	17.9992	0.205
fluorine	${}^{19}_9\text{F}$	9	9	10	18.9984	100
neon	${}^{20}_{10}\text{Ne}$	10	10	10	19.9924	90.48
	${}^{21}_{10}\text{Ne}$	10	10	11	20.9938	0.27
	${}^{22}_{10}\text{Ne}$	10	10	12	21.9914	9.25

Table 2.4

Link to Learning

Use this **Build an Atom simulator** (<http://openstax.org//16PhetAtomBld>) 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}B with a mass of 10.0129 amu, and the remaining 80.1% are ^{11}B with a mass of 11.0093 amu. The average atomic mass for boron is calculated to be:

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

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

Example 2.4

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}Ne (mass 19.9924 amu), 0.47% ^{21}Ne (mass 20.9940 amu), and 7.69% ^{22}Ne (mass 21.9914 amu). What is the average mass of the neon in the solar wind?

Solution

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

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

Check Your Learning

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

Answer: 24.31 amu

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

Example 2.5

Calculation of Percent Abundance

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

Solution

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

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

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

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

Substituting this into the average mass equation, we have:

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

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

Check Your Learning

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

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

Link to Learning

Visit this [site \(http://openstax.org//16PhetAtomMass\)](http://openstax.org//16PhetAtomMass) 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 2.15**), 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.

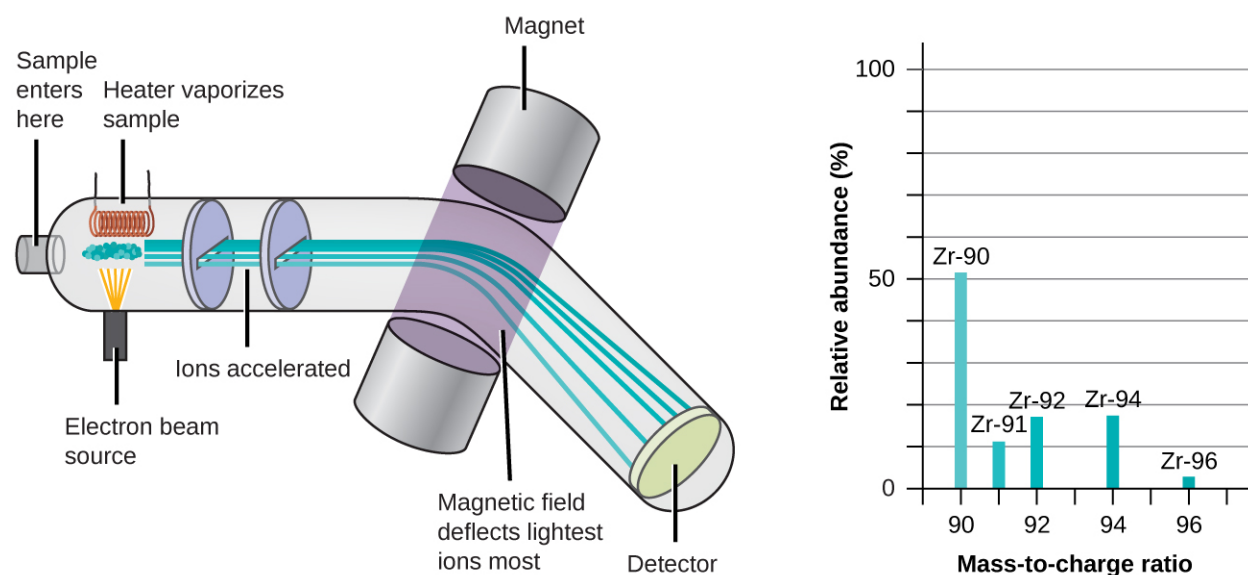


Figure 2.15 Analysis of zirconium in a mass spectrometer produces a mass spectrum with peaks showing the different isotopes of Zr.

Link to Learning

See an [animation \(http://openstax.org//16MassSpec\)](http://openstax.org//16MassSpec) that explains mass spectrometry. Watch this [video \(http://openstax.org//16RSCChemistry\)](http://openstax.org//16RSCChemistry) from the Royal Society for Chemistry for a brief description of the rudiments of mass spectrometry.

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 2.16**). 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.

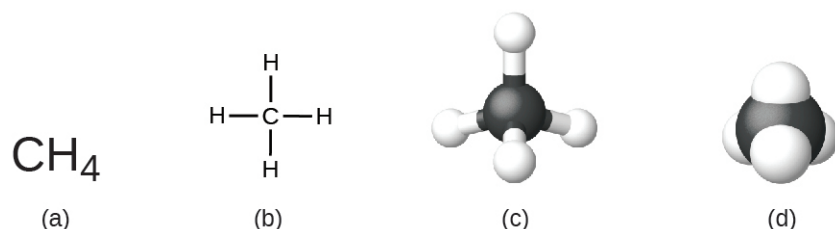


Figure 2.16 A methane molecule can be represented as (a) a molecular formula, (b) a structural formula, (c) a ball-and-stick model, and (d) a space-filling model. Carbon and hydrogen atoms are represented by black and white spheres, respectively.

Although many elements consist of discrete, individual atoms, some exist as molecules made up of two or more atoms of the element chemically bonded together. For example, most samples of the elements hydrogen, oxygen, and nitrogen are composed of molecules that contain two atoms each (called diatomic molecules) and thus have the molecular formulas H_2 , O_2 , and N_2 , respectively. Other elements commonly found as diatomic molecules are fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2). The most common form of the element sulfur is composed of molecules that consist of eight atoms of sulfur; its molecular formula is S_8 (**Figure 2.17**).

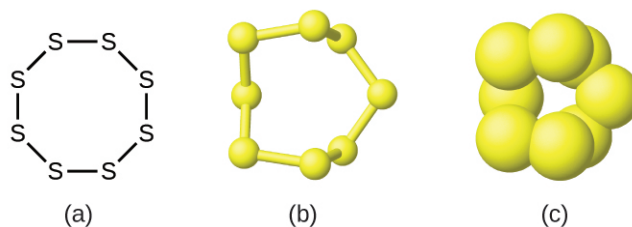


Figure 2.17 A molecule of sulfur is composed of eight sulfur atoms and is therefore written as S_8 . It can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. Sulfur atoms are represented by yellow spheres.

It is important to note that a subscript following a symbol and a number in front of a symbol do not represent the same thing; for example, H_2 and 2H represent distinctly different species. H_2 is a molecular formula; it represents a diatomic molecule of hydrogen, consisting of two atoms of the element that are chemically bonded together. The expression 2H , on the other hand, indicates two separate hydrogen atoms that are not combined as a unit. The expression 2H_2 represents two molecules of diatomic hydrogen (**Figure 2.18**).

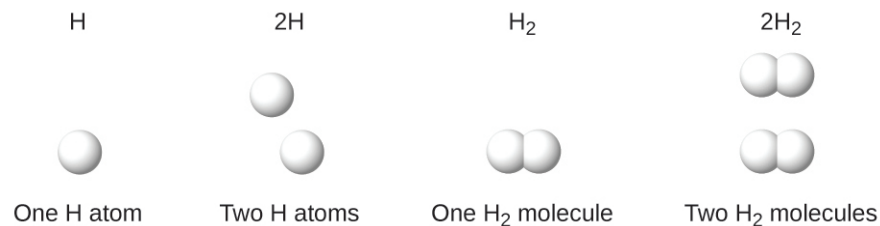


Figure 2.18 The symbols H, 2H, H₂, and 2H₂ represent very different entities.

Compounds are formed when two or more elements chemically combine, resulting in the formation of bonds. For example, hydrogen and oxygen can react to form water, and sodium and chlorine can react to form table salt. We sometimes describe the composition of these compounds with an **empirical formula**, which indicates the types of atoms present and *the simplest whole-number ratio of the number of atoms (or ions) in the compound*. For example, titanium dioxide (used as pigment in white paint and in the thick, white, blocking type of sunscreen) has an empirical formula of TiO₂. 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 2.19**).

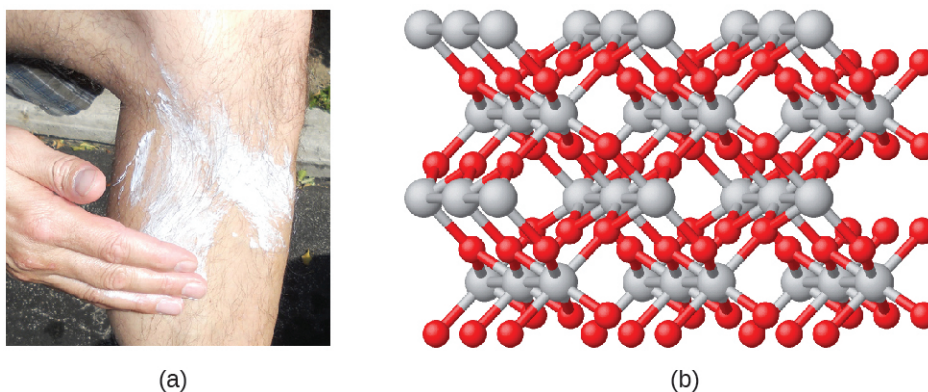


Figure 2.19 (a) The white compound titanium dioxide provides effective protection from the sun. (b) A crystal of titanium dioxide, TiO₂, contains titanium and oxygen in a ratio of 1 to 2. The titanium atoms are gray and the oxygen atoms are red. (credit a: modification of work by “osseous”/Flickr)

As discussed previously, we can describe a compound with a molecular formula, in which the subscripts indicate the *actual numbers of atoms* of each element in a molecule of the compound. In many cases, the molecular formula of a substance is derived from experimental determination of both its empirical formula and its molecular mass (the sum of atomic masses for all atoms composing the molecule). For example, it can be determined experimentally that benzene contains two elements, carbon (C) and hydrogen (H), and that for every carbon atom in benzene, there is one hydrogen atom. Thus, the empirical formula is CH. An experimental determination of the molecular mass reveals that a molecule of benzene contains six carbon atoms and six hydrogen atoms, so the molecular formula for benzene is C₆H₆ (**Figure 2.20**).

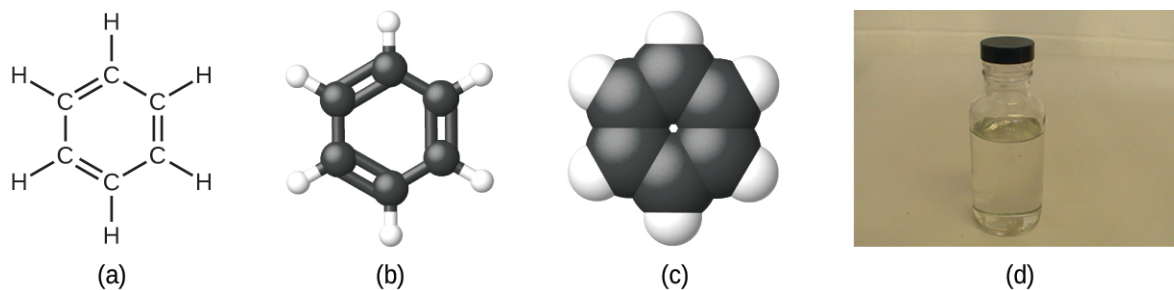


Figure 2.20 Benzene, C_6H_6 , is produced during oil refining and has many industrial uses. A benzene molecule can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. (d) Benzene is a clear liquid. (credit d: modification of work by Sahar Atwa)

If we know a compound's formula, we can easily determine the empirical formula. (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 2.21**) contains two carbon atoms, four hydrogen atoms, and two oxygen atoms. The ratio of atoms is 2:4:2. Dividing by the lowest common denominator (2) gives the simplest, whole-number ratio of atoms, 1:2:1, so the empirical formula is CH_2O . Note that a molecular formula is always a whole-number multiple of an empirical formula.

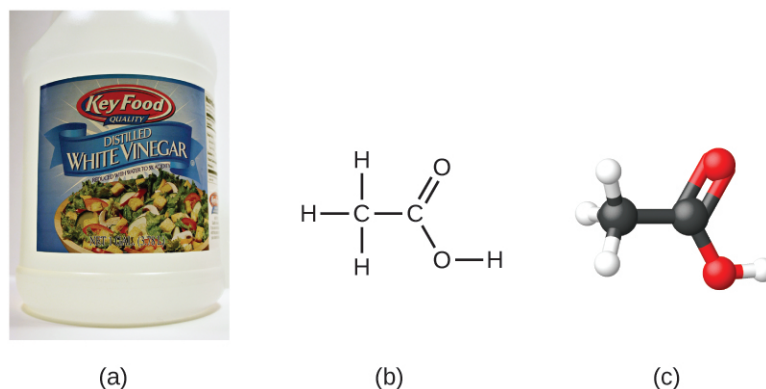


Figure 2.21 (a) Vinegar contains acetic acid, $C_2H_4O_2$, which has an empirical formula of CH_2O . It can be represented as (b) a structural formula and (c) as a ball-and-stick model. (credit a: modification of work by "HomeSpot HQ"/Flickr)

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

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

Link to Learning

You can explore **molecule building** (<http://openstax.org//16molbuilding>) 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.”^[2] View his **full talk** (<http://openstax.org//16LeeCronin>) at the TED website.

2. Lee Cronin, “Print Your Own Medicine,” Talk presented at TED Global 2012, Edinburgh, Scotland, June 2012.



Figure 2.22 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. (credit: image courtesy of Lee Cronin)

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

If you predict that another compound with the formula $C_2H_4O_2$ could exist, then you demonstrated good chemical insight and are correct. Two C atoms, four H atoms, and two O atoms can also be arranged to form 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 2.23**). 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.

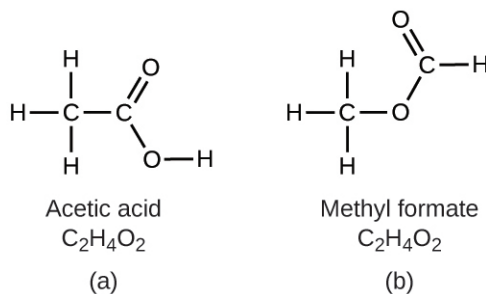


Figure 2.23 Molecules of (a) acetic acid and methyl formate (b) are structural isomers; they have the same formula ($C_2H_4O_2$) but different structures (and therefore different chemical properties).

Many types of isomers exist (**Figure 2.24**). 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.

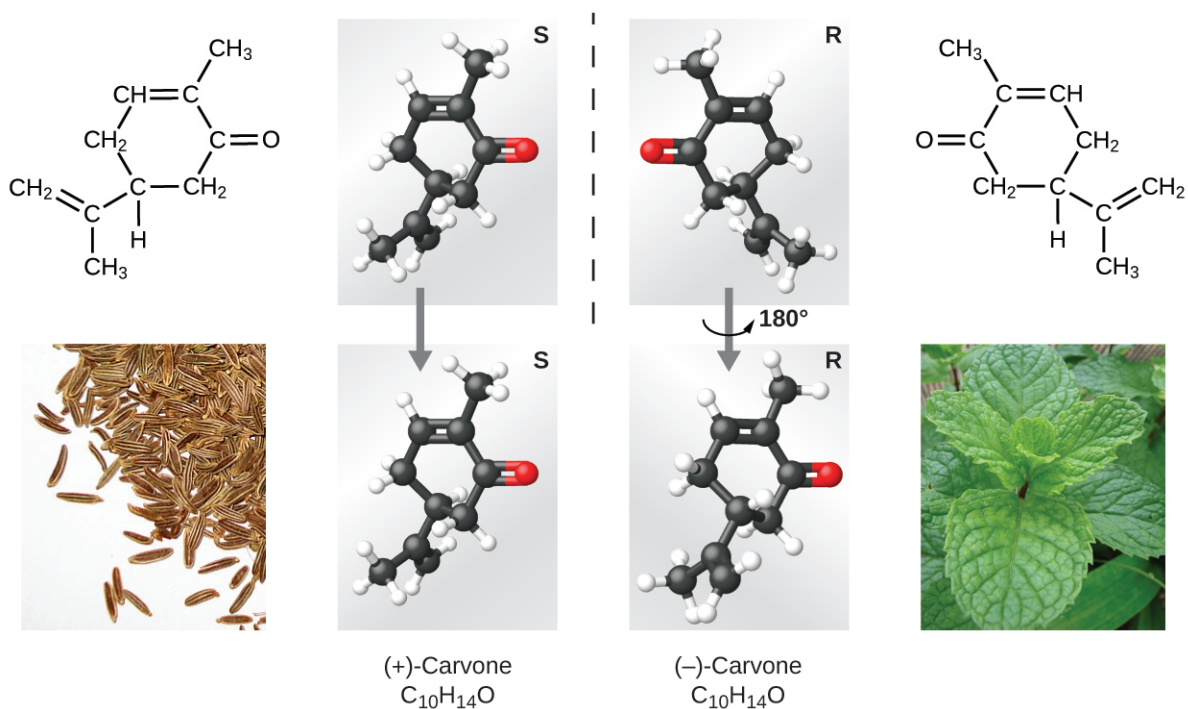


Figure 2.24 Molecules of carvone are spatial isomers; they only differ in the relative orientations of the atoms in space. (credit bottom left: modification of work by "Miansari66"/Wikimedia Commons; credit bottom right: modification of work by Forest & Kim Starr)

Link to Learning

Select this [link \(http://openstax.org//16isomers\)](http://openstax.org//16isomers) 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 amount of substances, the *mole*, which remains indispensable in modern chemical science.

The mole is an amount unit similar to familiar units like pair, dozen, gross, etc. It provides a specific measure of *the number* of atoms or molecules in a bulk sample of matter. A **mole** is defined as the amount of substance containing the same number of discrete entities (such as atoms, molecules, and ions) as the number of atoms in a sample of pure ^{12}C weighing exactly 12 g. One Latin connotation for the word “mole” is “large mass” or “bulk,” which is consistent with its use as the name for this unit. The mole provides a link between an easily measured macroscopic property, bulk mass, and an extremely important fundamental property, number of atoms, molecules, and so forth.

The number of entities composing a mole has been experimentally determined to be $6.02214179 \times 10^{23}$, 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 2.25**).

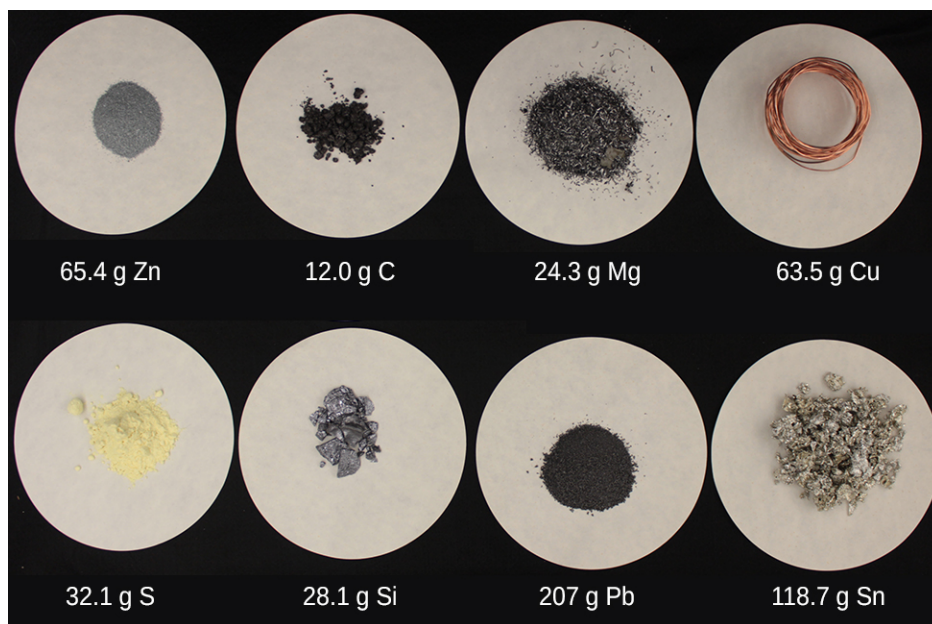


Figure 2.25 Each sample contains 6.022×10^{23} atoms—1.00 mol of atoms. From left to right (top row): 65.4 g zinc, 12.0 g carbon, 24.3 g magnesium, and 63.5 g copper. From left to right (bottom row): 32.1 g sulfur, 28.1 g silicon, 207 g lead, and 118.7 g tin. (credit: modification of work by Mark Ott)

Because the definitions of both the mole and the atomic mass unit are based on the same reference substance, ^{12}C , the molar mass of any substance is numerically equivalent to its atomic or formula weight in amu. Per the amu definition, a single ^{12}C atom weighs 12 amu (its atomic mass is 12 amu). According to the definition of the mole, 12 g of ^{12}C contains 1 mole of ^{12}C atoms (its molar mass is 12 g/mol). This relationship holds for all elements, since their atomic masses are measured relative to that of the amu-reference substance, ^{12}C . Extending this principle, the molar mass of a compound in grams is likewise numerically equivalent to its formula mass in amu (**Figure 2.26**).



Figure 2.26 Each sample contains 6.02×10^{23} molecules or formula units—1.00 mol of the compound or element. Clock-wise from the upper left: 130.2 g of $\text{C}_8\text{H}_{17}\text{OH}$ (1-octanol, formula mass 130.2 amu), 454.4 g of HgI_2 (mercury(II) iodide, formula mass 454.4 amu), 32.0 g of CH_3OH (methanol, formula mass 32.0 amu) and 256.5 g of S_8 (sulfur, formula mass 256.5 amu). (credit: Sahar Atwa)

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

While 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 2.27**). 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 2.27 The number of molecules in a single droplet of water is roughly 100 billion times greater than the number of people on earth. (credit: "tanakawho"/Wikimedia commons)

Link to Learning

The mole is used in chemistry to represent 6.022×10^{23} of something, but it can be difficult to conceptualize such a large number. Watch this [video \(http://openstax.org//16molevideo\)](http://openstax.org//16molevideo) and then complete the "Think" questions that follow. Explore more about the mole by reviewing the information under "Dig Deeper."

The relationships between formula mass, the mole, and Avogadro's number can be applied to compute various

quantities that describe the composition of substances and compounds. For example, if we know the mass and chemical composition of a substance, we can determine the number of moles and calculate number of atoms or molecules in the sample. Likewise, if we know the number of moles of a substance, we can derive the number of atoms or molecules and calculate the substance's mass.

Example 2.7

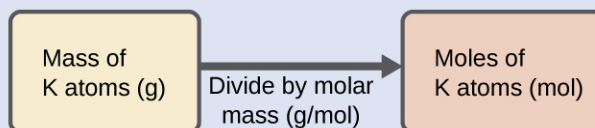
Deriving Moles from Grams for an Element

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):



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

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

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

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

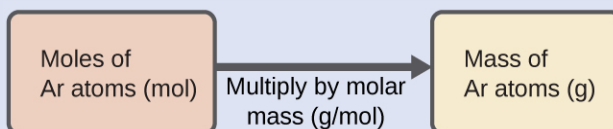
Example 2.8

Deriving Grams from Moles for an Element

A liter of air contains 9.2×10^{-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 (~ 0.04 g):



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

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

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 Number of Atoms from Mass for an Element

Copper is commonly used to fabricate electrical wire (**Figure 2.28**). How many copper atoms are in 5.00 g of copper wire?

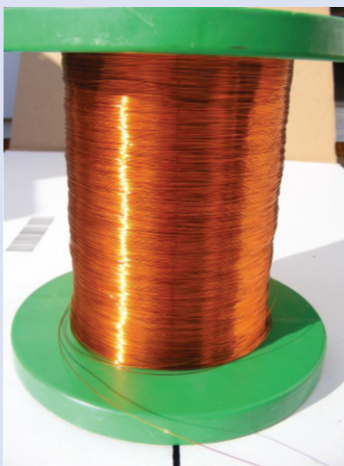
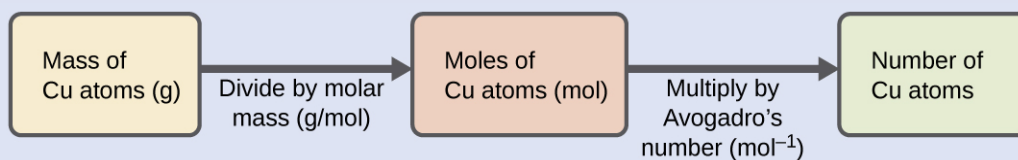


Figure 2.28 Copper wire is composed of many, many atoms of Cu. (credit: Emilian Robert Vicoli)

Solution

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



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

$$5.00 \text{ g Cu} \left(\frac{\text{mol Cu}}{63.55 \text{ g}} \right) \left(\frac{6.022 \times 10^{23} \text{ atoms}}{\text{mol}} \right) = 4.74 \times 10^{22} \text{ atoms of copper}$$

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: 4.586×10^{22} Au atoms

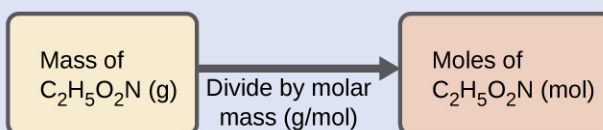
Example 2.10

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?

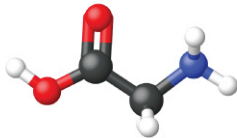
Solution

We can derive the number of moles of a compound from its mass following the same procedure we used for an element in **Example 2.7**:



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



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:

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

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

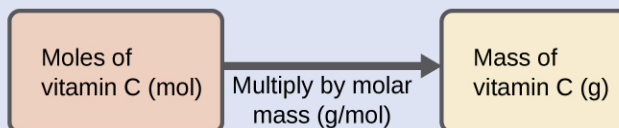
Example 2.11

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 1.42×10^{-4} mol. What is the mass of this allowance in grams?

Solution

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



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

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

This is consistent with the anticipated result.

Check Your Learning

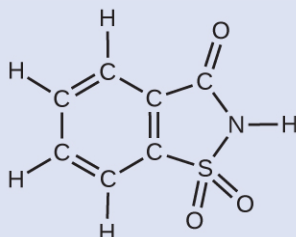
What is the mass of 0.443 mol of hydrazine, N_2H_4 ?

Answer: 14.2 g

Example 2.12

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

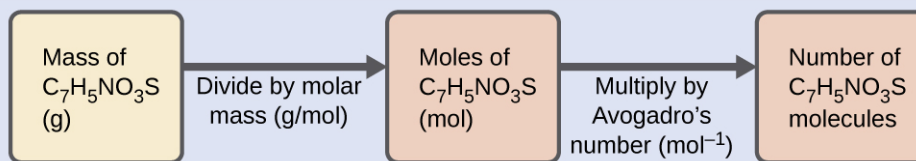
A packet of an artificial sweetener contains 40.0 mg of saccharin ($\text{C}_7\text{H}_5\text{NO}_3\text{S}$), which has the structural formula:



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

Solution

The number of molecules in a given mass of compound is computed by first deriving the number of moles, as demonstrated in **Example 2.10**, and then multiplying by Avogadro's number:



Using the provided mass and molar mass for saccharin yields:

$$0.0400 \text{ g C}_7\text{H}_5\text{NO}_3\text{S} \left(\frac{1 \text{ mol C}_7\text{H}_5\text{NO}_3\text{S}}{183.18 \text{ g C}_7\text{H}_5\text{NO}_3\text{S}} \right) \left(\frac{6.022 \times 10^{23} \text{ C}_7\text{H}_5\text{NO}_3\text{S molecules}}{1 \text{ mol C}_7\text{H}_5\text{NO}_3\text{S}} \right)$$

$$= 1.31 \times 10^{20} \text{ C}_7\text{H}_5\text{NO}_3\text{S molecules}$$

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

$$1.31 \times 10^{20} \text{ C}_7\text{H}_5\text{NO}_3\text{S molecules} \left(\frac{7 \text{ C atoms}}{1 \text{ C}_7\text{H}_5\text{NO}_3\text{S molecule}} \right) = 9.17 \times 10^{20} \text{ C atoms}$$

Check Your Learning

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

Answer: 9.545×10^{22} molecules C_4H_{10} ; 9.545×10^{23} atoms H

How Sciences Interconnect

Counting Neurotransmitter Molecules in the Brain

The brain is the control center of the central nervous system (**Figure 2.29**). 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 (more details available at www.whitehouse.gov/share/brain-initiative).

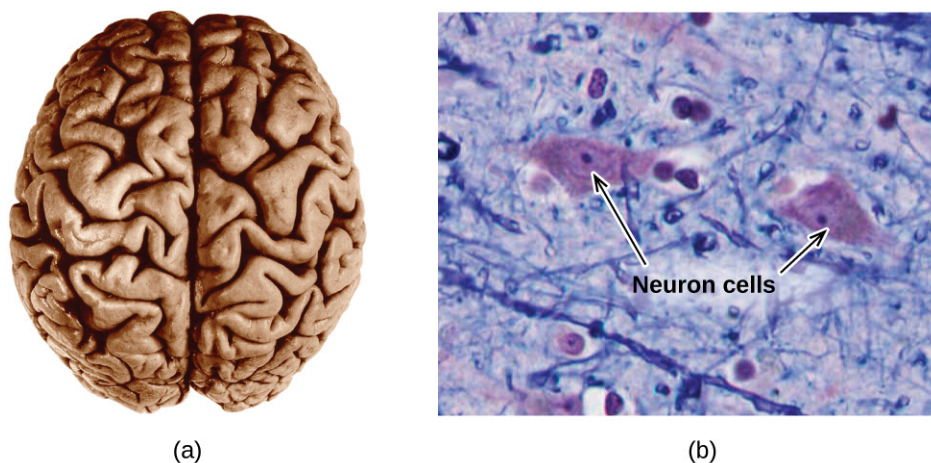


Figure 2.29 (a) A typical human brain weighs about 1.5 kg and occupies a volume of roughly 1.1 L. (b) Information is transmitted in brain tissue and throughout the central nervous system by specialized cells called neurons (micrograph shows cells at 1600× magnification).

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 2.30**). One neurotransmitter that has been very extensively studied is dopamine, $C_8H_{11}NO_2$. 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.

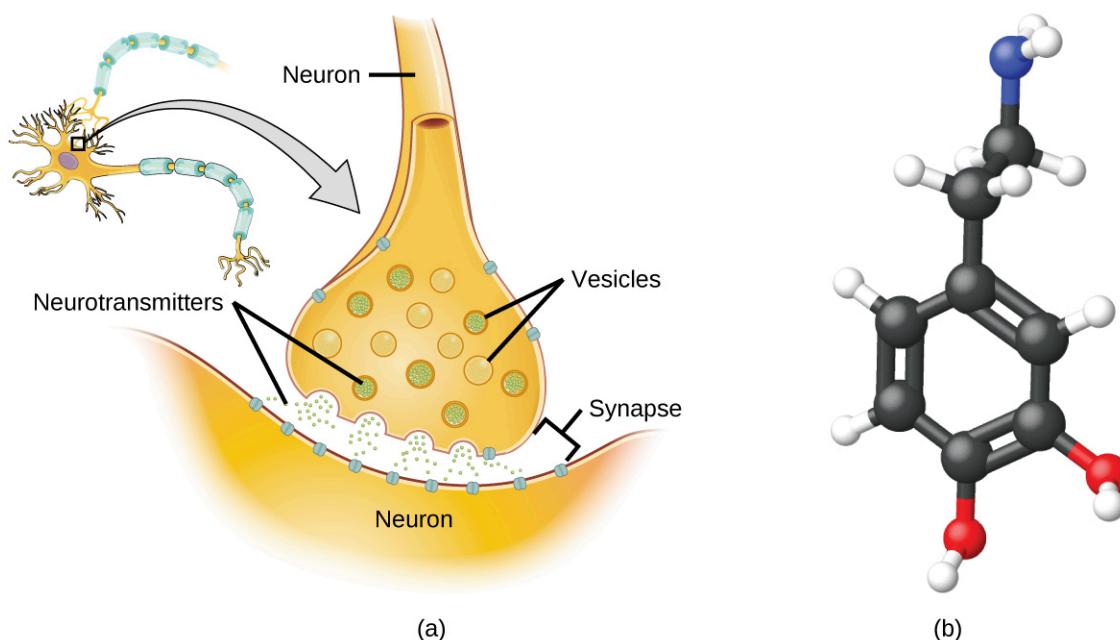


Figure 2.30 (a) Chemical signals are transmitted from neurons to other cells by the release of neurotransmitter molecules into the small gaps (synapses) between the cells. (b) Dopamine, $C_8H_{11}NO_2$, is a neurotransmitter involved in a number of neurological processes.

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 5×10^{-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.^[3]

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

Key Terms

alpha particle (α 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}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 Equations

- average mass = \sum_i (fractional abundance \times isotopic mass)_i

Summary

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 1.6605×10^{-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

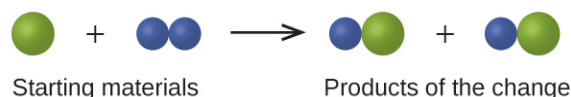
A molecular formula uses chemical symbols and subscripts to indicate the exact numbers of different atoms in a molecule or compound. An empirical formula gives the simplest, whole-number ratio of atoms in a compound. A structural formula indicates the bonding arrangement of the atoms in the molecule. 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 6.022×10^{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?



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 α particles fired at a "plum pudding" model atom.
- (a) Predict the paths taken by α particles that are fired at atoms with a Thomson's plum pudding model structure. Explain why you expect the α particles to take these paths.
- (b) If α particles of higher energy than those in (a) are fired at plum pudding atoms, predict how their paths will differ from the lower-energy α particle paths. Explain your reasoning.
- (c) Now test your predictions from (a) and (b). Open the **Rutherford Scattering simulation** (<http://openstax.org//16PhetScatter>) and select the "Plum Pudding Atom" tab. Set "Alpha Particles Energy" to "min," and select "show traces." Click on the gun to start firing α particles. Does this match your prediction from (a)? If not, explain why the actual path would be that shown in the simulation. Hit the pause button, or "Reset All." Set "Alpha Particles Energy" to "max," and start firing α particles. Does this match your prediction from (b)? If not, explain the effect of increased energy on the actual paths as shown in the simulation.

9. Predict and test the behavior of α particles fired at a Rutherford atom model.

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

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

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

(d) Now test your predictions from (a), (b), and (c). Open the **Rutherford Scattering simulation** (<http://openstax.org//16PhetScatter>) and select the “Rutherford Atom” tab. Due to the scale of the simulation, it is best to start with a small nucleus, so select “20” for both protons and neutrons, “min” for energy, show traces, and then start firing α particles. Does this match your prediction from (a)? If not, explain why the actual path would be that shown in the simulation. Pause or reset, set energy to “max,” and start firing α particles. Does this match your prediction from (b)? If not, explain the effect of increased energy on the actual path as shown in the simulation. Pause or reset, select “40” for both protons and neutrons, “min” for energy, show traces, and fire away. Does this match your prediction from (c)? If not, explain why the actual path would be that shown in the simulation. Repeat this with larger numbers of protons and neutrons. What generalization can you make regarding the type of atom and effect on the path of α particles? Be clear and specific.

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** (<http://openstax.org//16PhetAtomBld>) 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** (<http://openstax.org//16PhetAtomBld>)

(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** (<http://openstax.org//16PhetAtomBld>)

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

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

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

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

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

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

(a) ${}_{3}^{7}\text{Li}$

(b) ${}_{52}^{125}\text{Te}$

(c) ${}_{47}^{109}\text{Ag}$

(d) ${}_{7}^{15}\text{N}$

(e) ${}_{15}^{31}\text{P}$

20. Click on the [site \(http://openstax.org/l/16PhetAtomMass\)](http://openstax.org/l/16PhetAtomMass) 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}Br and ^{81}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% ^6Li and 92.5% ^7Li , 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% ^6Li (and the rest ^7Li). 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}B , 10.0129 amu and ^{11}B , 11.0931 amu). The actual atomic mass of boron can vary from 10.807 to 10.819, depending on whether the mineral source is from Turkey or the United States. Calculate the percent abundances leading to the two values of the average atomic masses of boron from these two countries.

26. The ^{18}O : ^{16}O abundance ratio in some meteorites is greater than that used to calculate the average atomic mass of oxygen on earth. Is the average mass of an oxygen atom in these meteorites greater than, less than, or equal to that of a terrestrial oxygen atom?

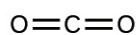
2.4 Chemical Formulas

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

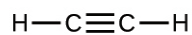
28. Explain why the symbol for the element sulfur and the formula for a molecule of sulfur differ.

29. Write the molecular and empirical formulas of the following compounds:

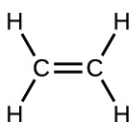
(a)



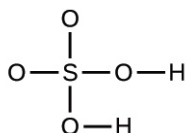
(b)



(c)

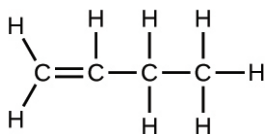


(d)

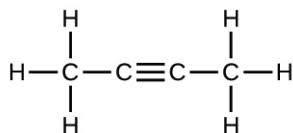


30. Write the molecular and empirical formulas of the following compounds:

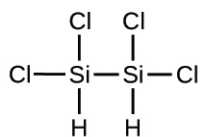
(a)



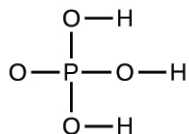
(b)



(c)



(d)



31. Determine the empirical formulas for the following compounds:

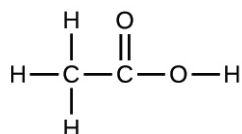
- (a) caffeine, $C_8H_{10}N_4O_2$
- (b) fructose, $C_{12}H_{22}O_{11}$
- (c) hydrogen peroxide, H_2O_2
- (d) glucose, $C_6H_{12}O_6$
- (e) ascorbic acid (vitamin C), $C_6H_8O_6$

32. Determine the empirical formulas for the following compounds:

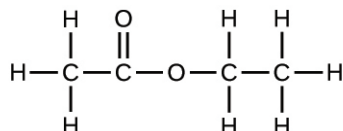
- (a) acetic acid, $C_2H_4O_2$
- (b) citric acid, $C_6H_8O_7$
- (c) hydrazine, N_2H_4
- (d) nicotine, $C_{10}H_{14}N_2$
- (e) butane, C_4H_{10}

33. Write the empirical formulas for the following compounds:

(a)



(b)



34. Open the **Build a Molecule simulation** (<http://openstax.org//16molbuilding>) 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** (<http://openstax.org//16molbuilding>) 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** (<http://openstax.org//16molbuilding>) 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 H_2 , 1 mole of O_2 , and 1 mole of 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 (HCO_2H), or 1.0 mol of water (H_2O)? 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 (HCO_2H), or 1 mol of water (H_2O)? 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, HF

(b) ammonia, NH_3

(c) nitric acid, HNO_3

(d) silver sulfate, Ag_2SO_4

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

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

(a) S_8

(b) C_5H_{12}

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

(d) CH_3COCH_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, CaCO_3

(b) halite, 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, $C_2HBrClF_3$

(b) the herbicide paraquat, $C_{12}H_{14}N_2Cl_2$

(c) caffeine, $C_8H_{10}N_4O_2$

(d) urea, $CO(NH_2)_2$

(e) a typical soap, $C_{17}H_{35}CO_2Na$

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, C_3H_6

(b) 3.06×10^{-3} g of the amino acid glycine, $C_2H_5NO_2$

(c) 25 lb of the herbicide Treflan, $C_{13}H_{16}N_2O_4F$ (1 lb = 454 g)

(d) 0.125 kg of the insecticide Paris Green, $Cu_4(AsO_3)_2(CH_3CO_2)_2$

(e) 325 mg of aspirin, $C_6H_4(CO_2H)(CO_2CH_3)$

47. Determine the mass of each of the following:

(a) 0.0146 mol KOH

(b) 10.2 mol ethane, C_2H_6

(c) 1.6×10^{-3} mol Na_2SO_4

(d) 6.854×10^3 mol glucose, $C_6H_{12}O_6$

(e) 2.86 mol $Co(NH_3)_6Cl_3$

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_3PO_4

(c) 23 kg of calcium carbonate, $CaCO_3$

(d) 78.452 g of aluminum sulfate, $Al_2(SO_4)_3$

(e) 0.1250 mg of caffeine, $C_8H_{10}N_4O_2$

49. Determine the mass of each of the following:

(a) 2.345 mol LiCl

(b) 0.0872 mol acetylene, C_2H_2

(c) 3.3×10^{-2} mol Na_2CO_3

(d) 1.23×10^3 mol fructose, $C_6H_{12}O_6$

(e) 0.5758 mol $FeSO_4(H_2O)_7$

50. The approximate minimum daily dietary requirement of the amino acid leucine, $C_6H_{13}NO_2$, 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, O_2

(c) 0.600 mol of ozone molecules, O_3

52. A 55-kg woman has 7.5×10^{-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, ZrSiO_4 , a semiprecious stone.
54. Determine which of the following contains the greatest mass of hydrogen: 1 mol of CH_4 , 0.6 mol of C_6H_6 , or 0.4 mol of C_3H_8 .
55. Determine which of the following contains the greatest mass of aluminum: 122 g of AlPO_4 , 266 g of Al_2C_16 , or 225 g of Al_2S_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, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$) 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 ($\text{Na}_2\text{PO}_3\text{F}$) 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)

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). (credit: modification of work by NASA and ESA)

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.

3.1 Electromagnetic Energy

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

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

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

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

Waves

A **wave** is an oscillation or periodic movement that can transport energy from one point in space to another. Common examples of waves are all around us. Shaking the end of a rope transfers energy from your hand to the other end of the rope, dropping a pebble into a pond causes waves to ripple outward along the water's surface, and the expansion of air that accompanies a lightning strike generates sound waves (thunder) that can travel outward for several miles. In each of these cases, kinetic energy is transferred through matter (the rope, water, or air) while the matter remains essentially in place. An insightful example of a wave occurs in sports stadiums when fans in a narrow region of seats rise simultaneously and stand with their arms raised up for a few seconds before sitting down again while the fans in neighboring sections likewise stand up and sit down in sequence. While this wave can quickly encircle a large stadium in a few seconds, none of the fans actually travel with the wave—they all stay in or above their seats.

Waves need not be restricted to travel through matter. As Maxwell showed, electromagnetic waves consist of an

electric field oscillating in step with a perpendicular magnetic field, both of which are perpendicular to the direction of travel. These waves can travel through a vacuum at a constant speed of 2.998×10^8 m/s, the speed of light (denoted by c).

All waves, including forms of electromagnetic radiation, are characterized by, a **wavelength** (denoted by λ , the lowercase Greek letter lambda), a **frequency** (denoted by ν , the lowercase Greek letter nu), and an **amplitude**. As can be seen in **Figure 3.2**, 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 (10^3 m) to picometers (10^{-12} m) have been observed. The frequency is the number of wave cycles that pass a specified point in space in a specified amount of time (in the SI system, this is measured in seconds). A cycle corresponds to one complete wavelength. The unit for frequency, expressed as cycles per second [s^{-1}], is the **hertz (Hz)**. Common multiples of this unit are megahertz, ($1 \text{ MHz} = 1 \times 10^6 \text{ Hz}$) and gigahertz ($1 \text{ GHz} = 1 \times 10^9 \text{ Hz}$). 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.

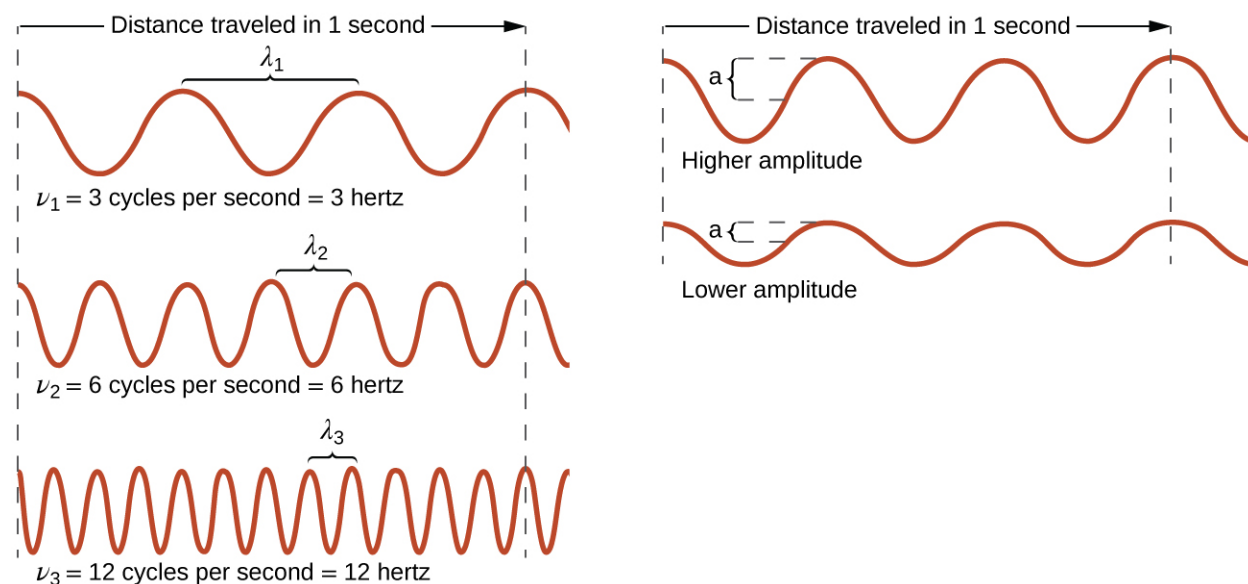


Figure 3.2 One-dimensional sinusoidal waves show the relationship among wavelength, frequency, and speed. The wave with the shortest wavelength has the highest frequency. Amplitude is one-half the height of the wave from peak to trough.

The product of a wave's wavelength (λ) and its frequency (ν), $\lambda\nu$, is the speed of the wave. Thus, for electromagnetic radiation in a vacuum, 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).

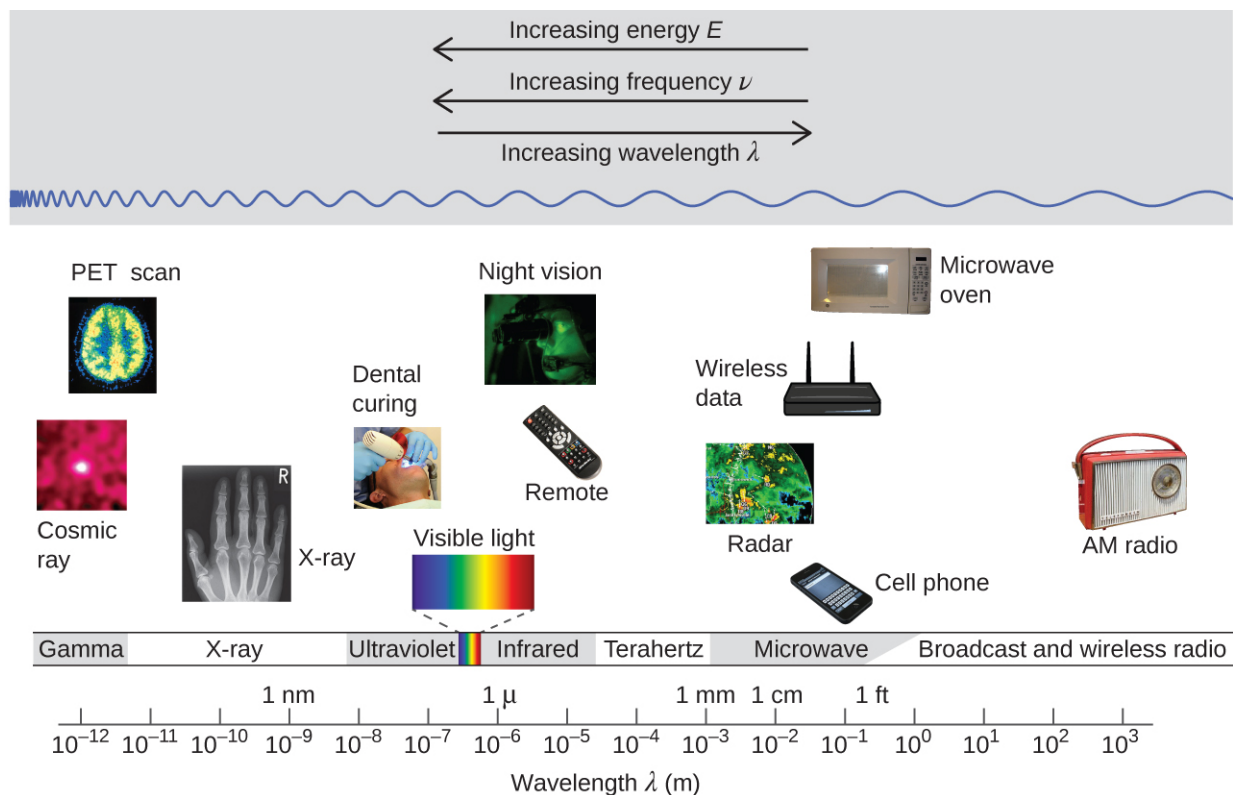


Figure 3.3 Portions of the electromagnetic spectrum are shown in order of decreasing frequency and increasing wavelength. (credit “Cosmic ray”: modification of work by NASA; credit “PET scan”: modification of work by the National Institute of Health; credit “X-ray”: modification of work by Dr. Jochen Lengerke; credit “Dental curing”: modification of work by the Department of the Navy; credit “Night vision”: modification of work by the Department of the Army; credit “Remote”: modification of work by Emilian Robert Vicol; credit “Cell phone”: modification of work by Brett Jordan; credit “Microwave oven”: modification of work by Billy Mabray; credit “Ultrasound”: modification of work by Jane Whitney; credit “AM radio”: modification of work by Dave Clausen)

Example 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.

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

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: $0.353 \text{ m} = 35.3 \text{ cm}$

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.

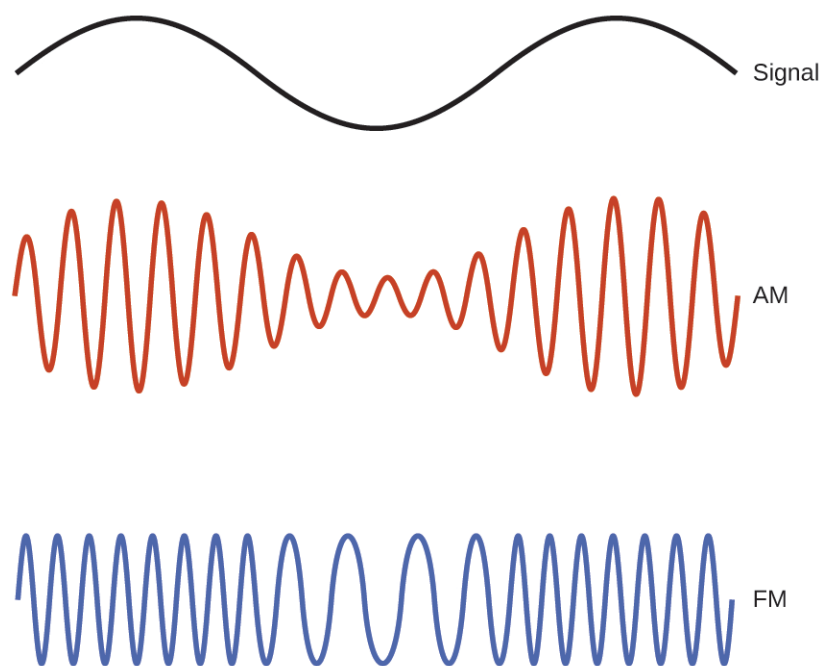


Figure 3.5 This schematic depicts how amplitude modulation (AM) and frequency modulation (FM) can be used to transmit a radio wave.

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.

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.

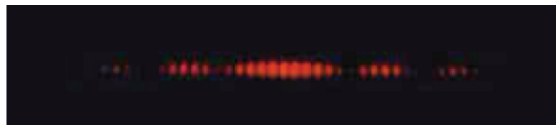


Figure 3.6 Interference fringe patterns are shown for light passing through two closely spaced, narrow slits. The spacing of the fringes depends on the wavelength, with the fringes being more closely spaced for the shorter-wavelength blue light. (credit: PASCO)

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 better understanding of the disease and treatment options.

Not all waves are travelling waves. **Standing waves** (also known as **stationary waves**) remain constrained within some region of space. As we shall see, standing waves play an important role in our understanding of the electronic structure of atoms and molecules. The simplest example of a standing wave is a one-dimensional wave associated with a vibrating string that is held fixed at its two end points. **Figure 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.

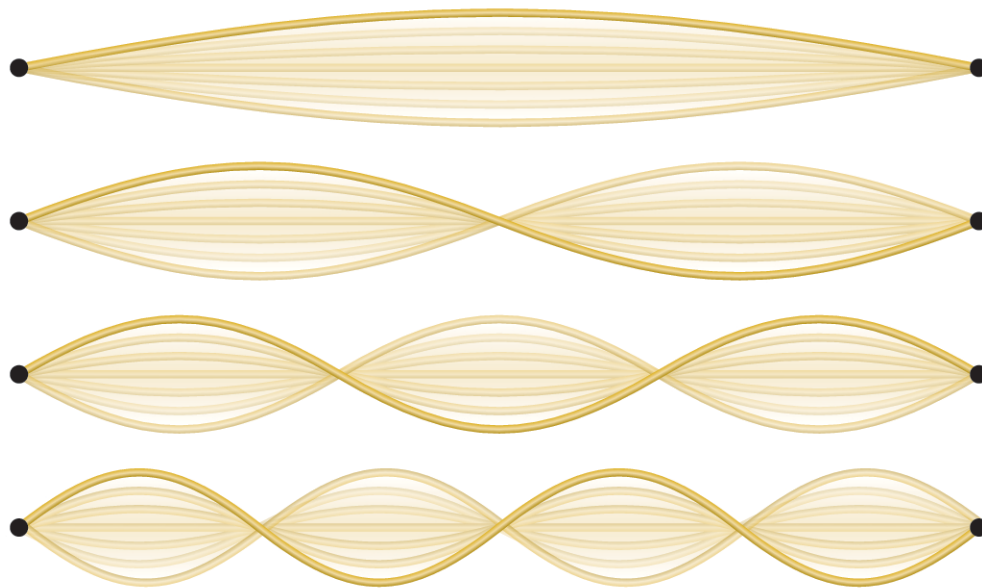


Figure 3.7 A vibrating string shows some one-dimensional standing waves. Since the two end points of the string are held fixed, only waves having an integer number of half-wavelengths can form. The points on the string between the end points that are not moving are called the nodes.

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).

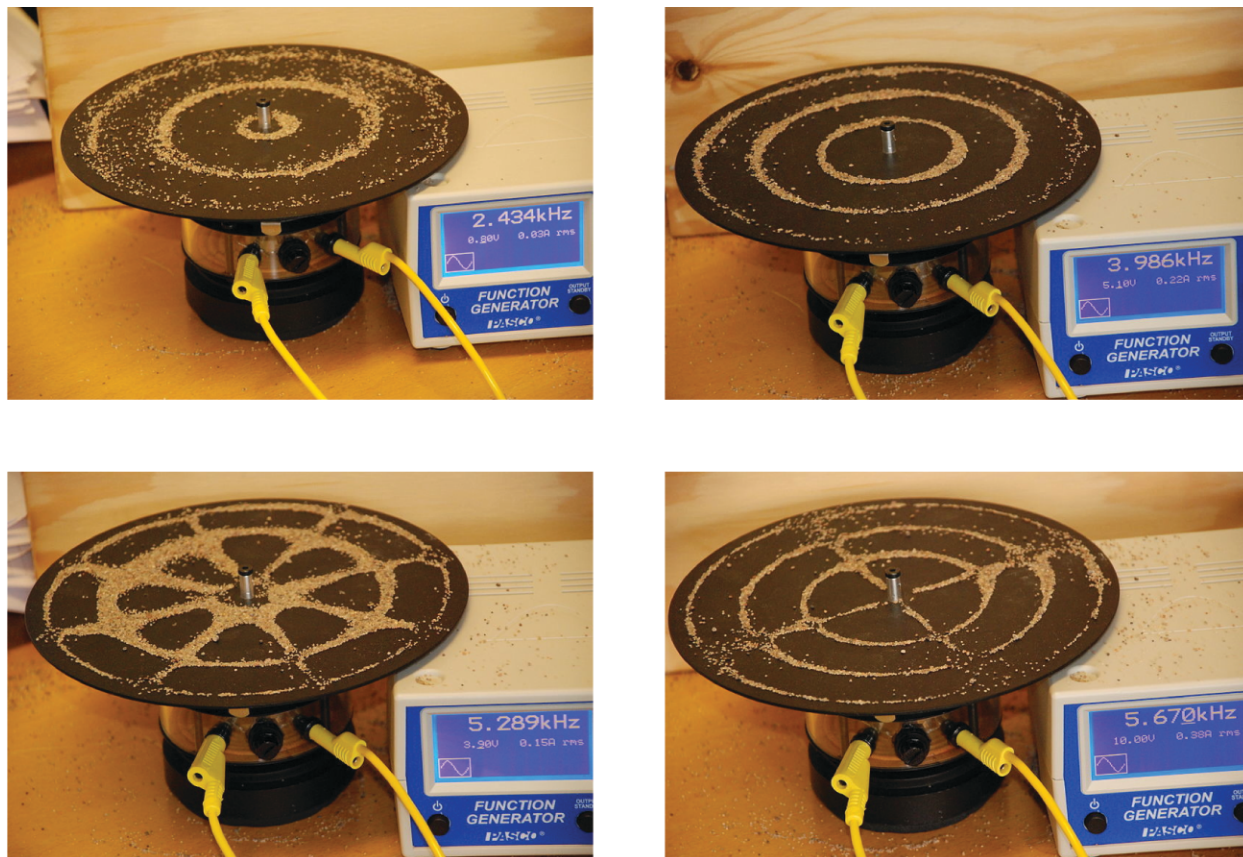


Figure 3.8 Two-dimensional standing waves can be visualized on a vibrating surface. The surface has been sprinkled with a powder that collects near the nodal lines. There are two types of nodes visible: radial nodes (circles) and angular nodes (radial lines).

Link to Learning

You can watch the formation of various radial nodes [here \(http://openstax.org//16radnodes\)](http://openstax.org//16radnodes) 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.

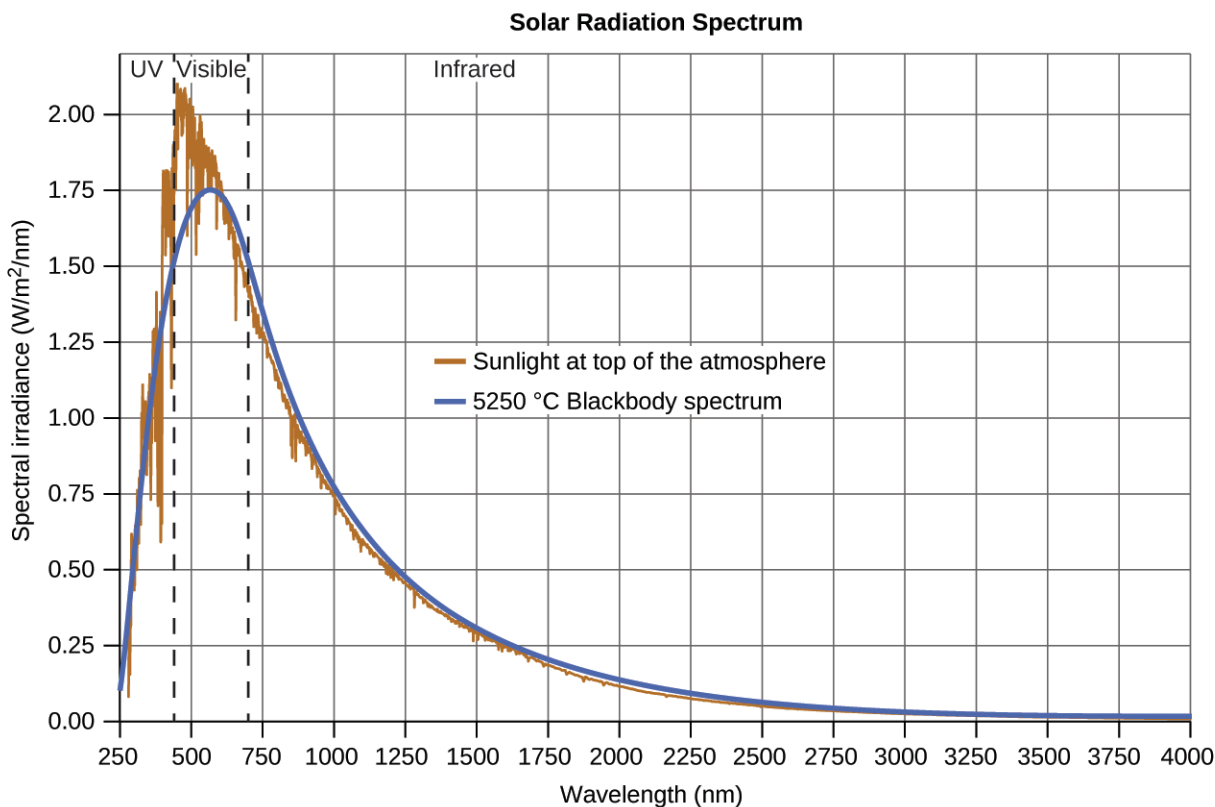


Figure 3.9 The spectral distribution (light intensity vs. wavelength) of sunlight reaches the Earth's atmosphere as UV light, visible light, and IR light. The unabsorbed sunlight at the top of the atmosphere has a distribution that approximately matches the theoretical distribution of a blackbody at 5250 °C, represented by the blue curve. (credit: modification of work by American Society for Testing and Materials (ASTM) Terrestrial Reference Spectra for Photovoltaic Performance Evaluation)

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, λ_{max} , shift to shorter wavelengths as the temperature increases, reflecting the observation that metals being heated to high temperatures begin to glow a darker red that becomes brighter as the temperature increases, eventually becoming white hot at very high temperatures as the intensities of all of the visible wavelengths become appreciable. This common observation was at the heart of the first paradox that showed the fundamental limitations of classical physics that we will examine.

Physicists derived mathematical expressions for the blackbody curves using well-accepted concepts from the theories of classical mechanics and classical electromagnetism. The theoretical expressions as functions of temperature fit the observed experimental blackbody curves well at longer wavelengths, but showed significant discrepancies at shorter wavelengths. Not only did the theoretical curves not show a peak, they absurdly showed the intensity becoming infinitely large as the wavelength became smaller, which would imply that everyday objects at room temperature should be emitting large amounts of UV light. This became known as the “ultraviolet catastrophe” because no one

could find any problems with the theoretical treatment that could lead to such unrealistic short-wavelength behavior. Finally, around 1900, Max Planck derived a theoretical expression for blackbody radiation that fit the experimental observations exactly (within experimental error). Planck developed his theoretical treatment by extending the earlier work that had been based on the premise that the atoms composing the oven vibrated at increasing frequencies (or decreasing wavelengths) as the temperature increased, with these vibrations being the source of the emitted electromagnetic radiation. But where the earlier treatments had allowed the vibrating atoms to have any energy values obtained from a continuous set of energies (perfectly reasonable, according to classical physics), Planck found that by restricting the vibrational energies to discrete values for each frequency, he could derive an expression for blackbody radiation that correctly had the intensity dropping rapidly for the short wavelengths in the UV region.

$$E = nh\nu, \quad n = 1, 2, 3, \dots$$

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, 6.626×10^{-34} joule seconds (J s), which helps explain why energy quantization had not been observed previously in macroscopic phenomena.

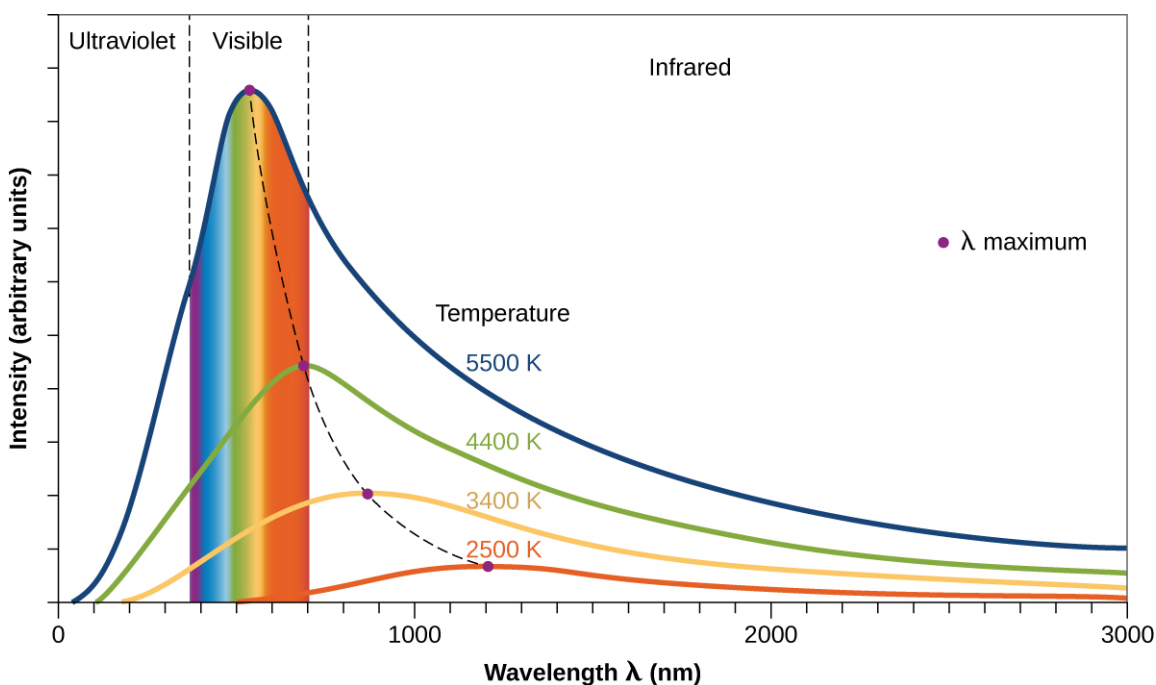


Figure 3.10 Blackbody spectral distribution curves are shown for some representative temperatures.

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 in a given time period was seen to increase as the brightness increased. In 1905, Albert Einstein was able to resolve the paradox by incorporating Planck's quantization findings into the discredited particle view of light (Einstein actually won his Nobel prize for this work, and not for his theories of relativity for which he is most famous).

Einstein argued that the quantized energies that Planck had postulated in his treatment of blackbody radiation could be applied to the light in the photoelectric effect so that the light striking the metal surface should not be viewed as a wave, but instead as a stream of particles (later called **photons**) whose energy depended on their frequency, according to Planck's formula, $E = h\nu$ (or, in terms of wavelength using $c = \nu\lambda$, $E = \frac{hc}{\lambda}$). Electrons were ejected when hit by photons having sufficient energy (a frequency greater than the threshold). The greater the frequency, the greater the kinetic energy imparted to the escaping electrons by the collisions. Processes that increase the energy of an atom involve the absorption of light and are called **endothermic**. Processes that decrease the energy involve 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**.

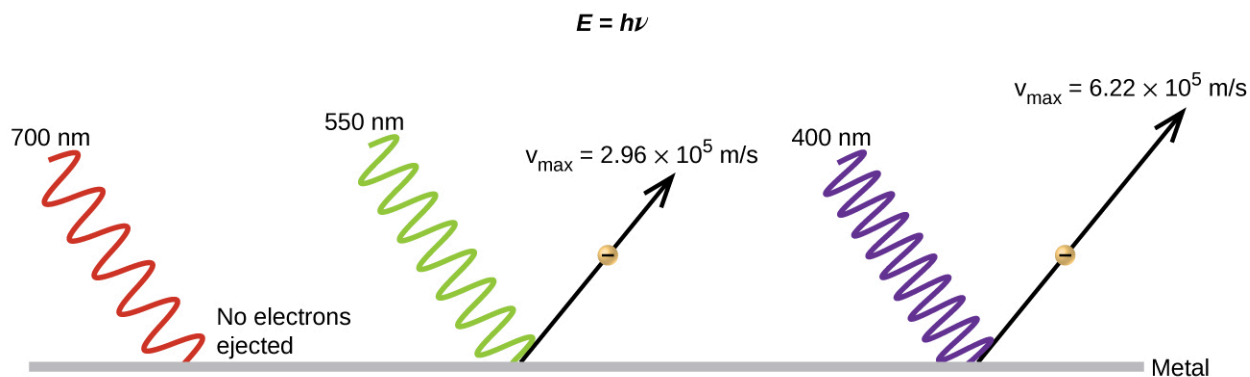


Figure 3.11 Photons with low frequencies do not have enough energy to cause electrons to be ejected via the photoelectric effect. For any frequency of light above the threshold frequency, the kinetic energy of an ejected electron will increase linearly with the energy of the incoming photon.

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, λ , and convert units of nanometers to meters so that the units of λ 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 3×10^9 Hz. What is the energy of one photon in these microwaves?

Answer: 2×10^{-24} J

Link to Learning

Use this [simulation program \(http://openstax.org//16photoelec\)](http://openstax.org//16photoelec) 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 9.87×10^{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. (credit: Dave Shaver)

Each emission line consists of a single wavelength of light, which implies that the light emitted by a gas consists of a set of discrete energies. For example, when an electric discharge passes through a tube containing hydrogen gas at low pressure, the H_2 molecules are broken apart into separate H atoms and we see a blue-pink color. Passing the light through a prism produces a line spectrum, indicating that this light is composed of photons of four visible wavelengths, as shown in **Figure 3.13**.

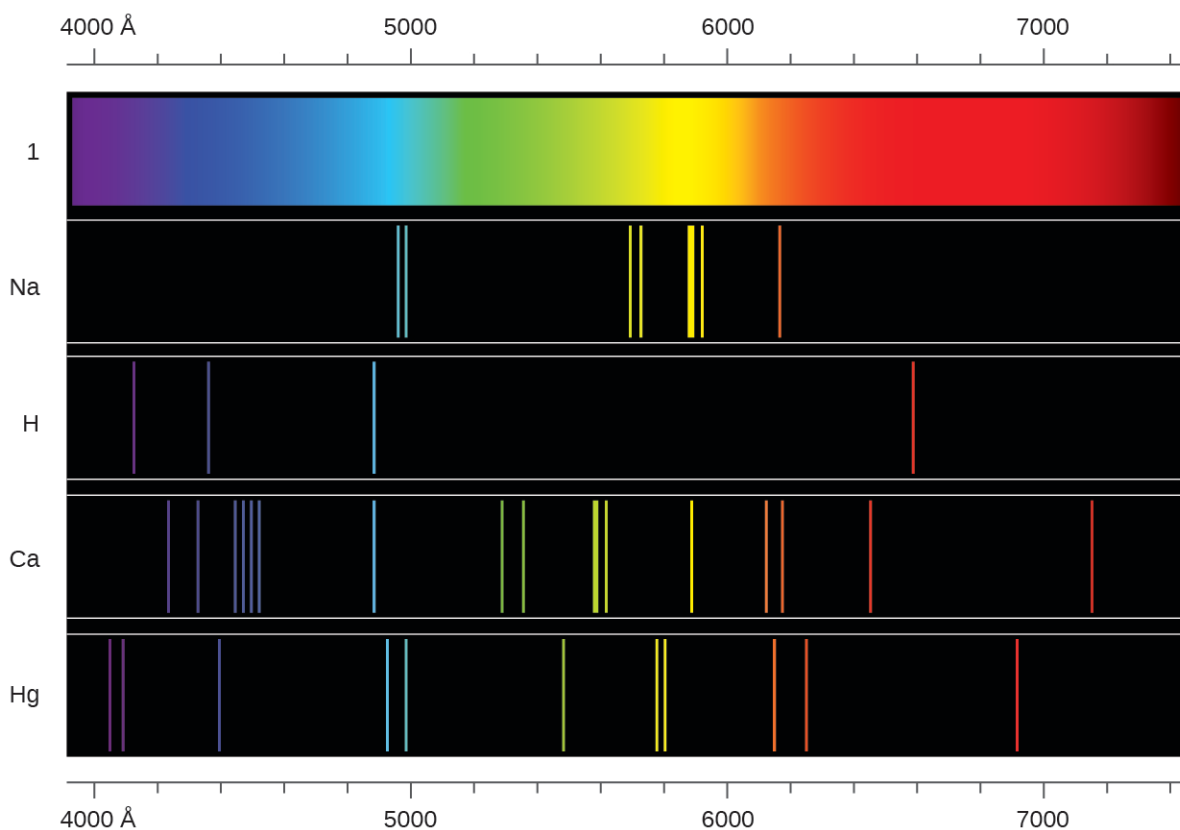


Figure 3.13 Compare the two types of emission spectra: continuous spectrum of white light (top) and the line spectra of the light from excited sodium, hydrogen, calcium, and mercury atoms.

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:

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

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

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

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

3.2 The Bohr Model

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 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:

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

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 ΔE 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_∞ , and compared it with the experimentally accepted value, he got 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 He^+ , Li^{2+} , 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 2.179×10^{-18} 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 5.292×10^{-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.

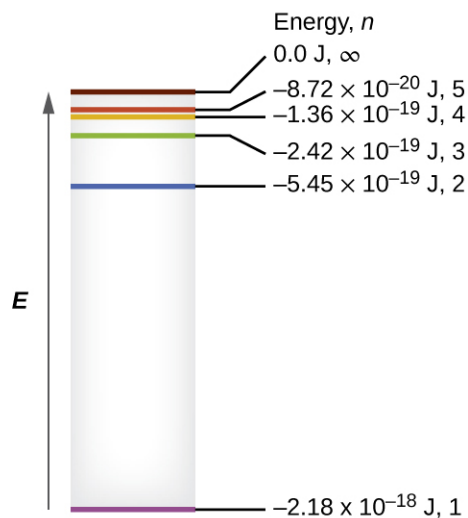


Figure 3.14 Quantum numbers and energy levels in a hydrogen atom. The more negative the calculated value, the lower the energy.

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; $k = 2.179 \times 10^{-18}$ 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: -6.053×10^{-20} J

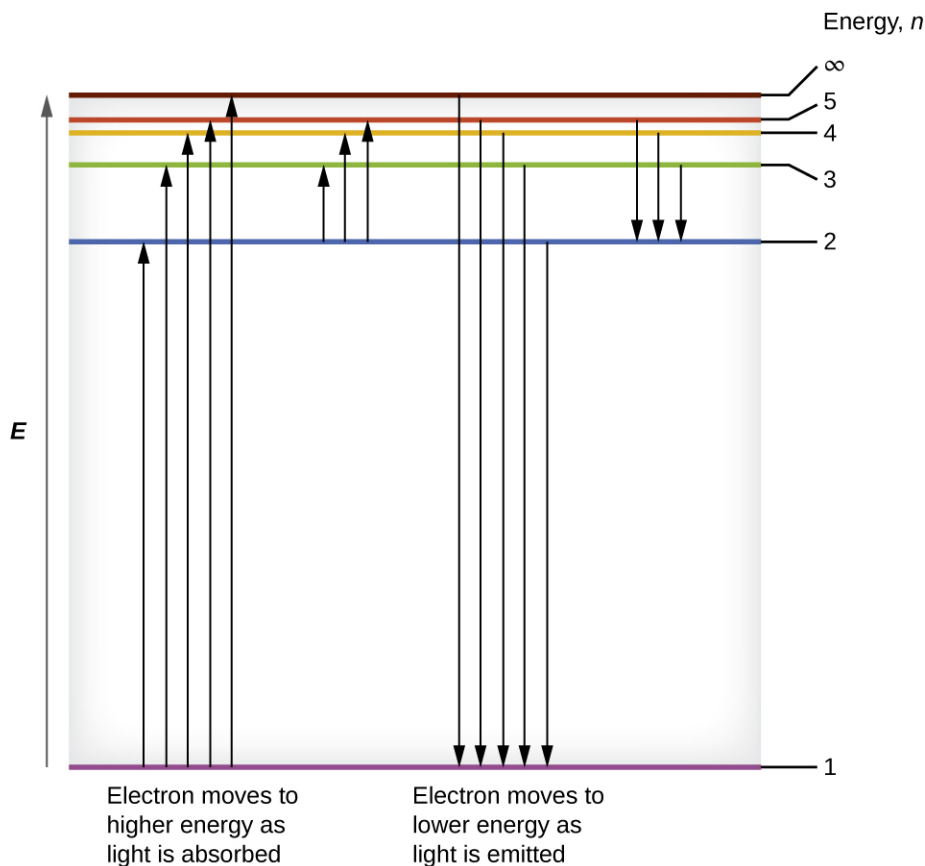


Figure 3.15 The horizontal lines show the relative energy of orbits in the Bohr model of the hydrogen atom, and the vertical arrows depict the energy of photons absorbed (left) or emitted (right) as electrons move between these orbits.

Example 3.5

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

What is the energy (in joules) and the wavelength (in meters) of the line in the spectrum of hydrogen that represents the movement of an electron from Bohr orbit with $n = 4$ to the orbit with $n = 6$? In what part of the electromagnetic spectrum do we find this radiation?

Solution

In this case, the electron starts out with $n = 4$, so $n_1 = 4$. It comes to rest in the $n = 6$ orbit, so $n_2 = 6$. The difference in energy between the two states is given by this expression:

$$\begin{aligned}\Delta E &= E_1 - E_2 = 2.179 \times 10^{-18} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \\ \Delta E &= 2.179 \times 10^{-18} \left(\frac{1}{4^2} - \frac{1}{6^2} \right) \text{J} \\ \Delta E &= 2.179 \times 10^{-18} \left(\frac{1}{16} - \frac{1}{36} \right) \text{J} \\ \Delta E &= 7.566 \times 10^{-20} \text{ J}\end{aligned}$$

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:

$$\begin{aligned}\lambda &= \frac{hc}{E} \\ &= (6.626 \times 10^{-34} \text{ J}\cdot\text{s}) \times \frac{2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1}}{7.566 \times 10^{-20} \text{ J}} \\ &= 2.626 \times 10^{-6} \text{ m}\end{aligned}$$

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 He^+ ion ($Z = 2$ for 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.

3.3 Development of Quantum Theory

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 on **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.

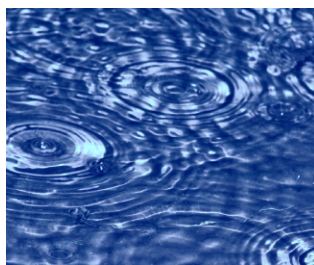


Figure 3.16 An interference pattern on the water surface is formed by interacting waves. The waves are caused by reflection of water from the rocks. (credit: modification of work by Sukanto Debnath)

As technological improvements allowed scientists to probe the microscopic world in greater detail, it became increasingly clear by the 1920s that very small pieces of matter follow a different set of rules from those we observe for large objects. The unquestionable separation of waves and particles was no longer the case for the microscopic world.

One of the first people to pay attention to the special behavior of the microscopic world was Louis de Broglie. He asked the question: If electromagnetic radiation can have particle-like character, can electrons and other submicroscopic particles exhibit wavelike character? In his 1925 doctoral dissertation, de Broglie extended the wave–particle duality of light that Einstein used to resolve the photoelectric-effect paradox to material particles. He predicted that a particle with mass m and velocity v (that is, with linear momentum p) should also exhibit the behavior of a wave with a wavelength value λ , given by this expression in which h is the familiar Planck’s constant:

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

This is called the *de Broglie wavelength*. Unlike the other values of λ discussed in this chapter, the de Broglie wavelength is a characteristic of particles and other bodies, not electromagnetic radiation (note that this equation involves velocity [v , m/s], not frequency [ν , 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**).

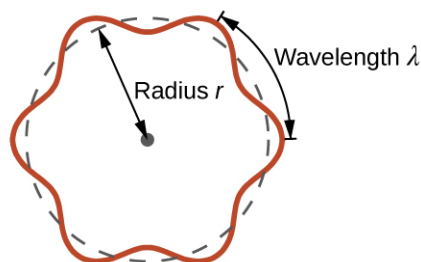


Figure 3.17 If an electron is viewed as a wave circling around the nucleus, an integer number of wavelengths must fit into the orbit for this standing wave behavior to be possible.

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 travelling 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 it 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.

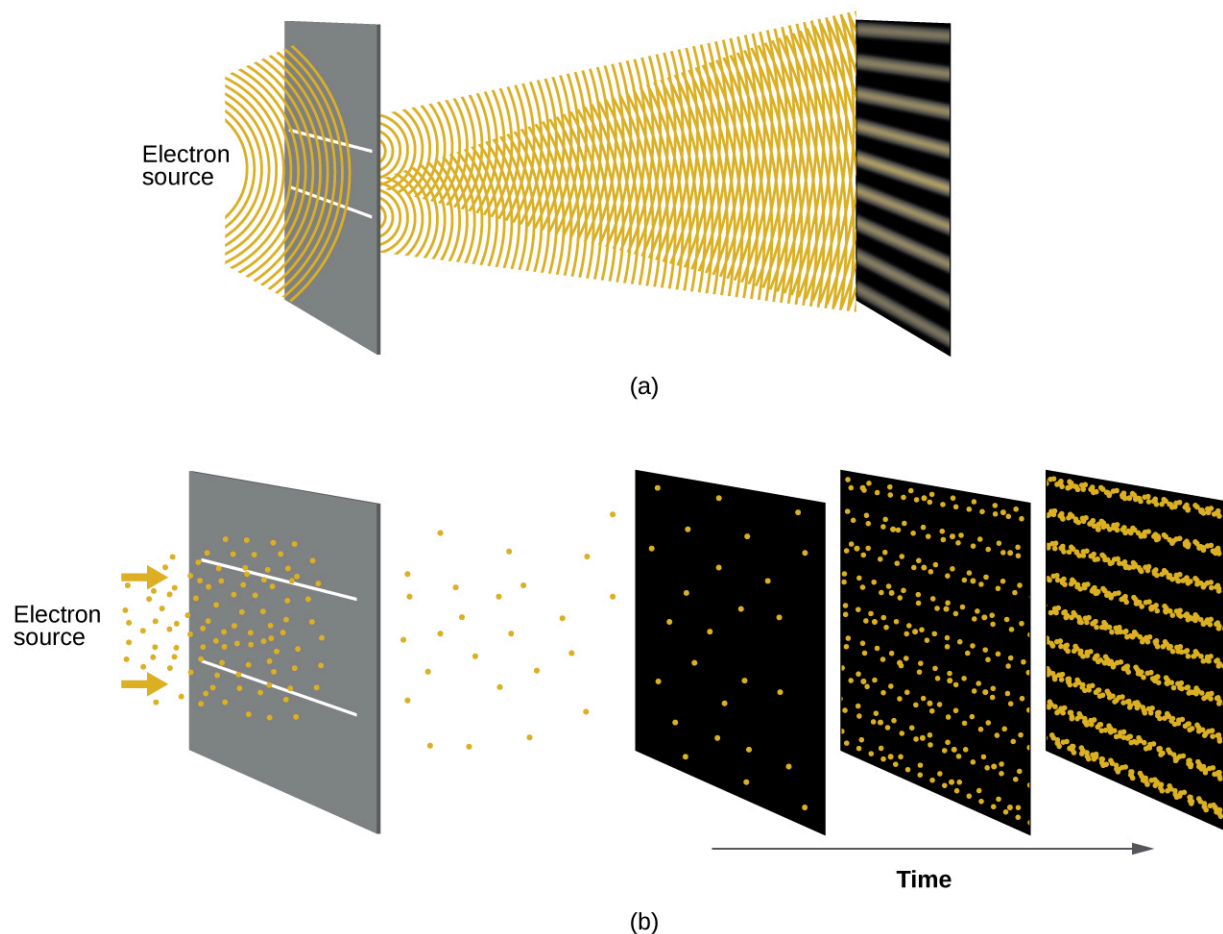


Figure 3.18 (a) The interference pattern for electrons passing through very closely spaced slits demonstrates that quantum particles such as electrons can exhibit wavelike behavior. (b) The experimental results illustrated here demonstrate the wave–particle duality in electrons.

Link to Learning

View the Dr. Quantum – Double Slit Experiment [cartoon \(http://openstaxcollege.org//16duality\)](http://openstaxcollege.org//16duality) 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 g traveling at a velocity of 35 m s⁻¹, assuming that it can be modeled as a single particle.

Answer: 1.9×10^{-34} m. We never think of a thrown softball having a wavelength, since this wavelength is so small it is impossible for our senses or any known instrument to detect (strictly speaking, the wavelength of a real baseball would correspond to the wavelengths of its constituent atoms and molecules, which, while much larger than this value, would still be microscopically tiny). The de Broglie wavelength is only appreciable for matter that has a very small mass and/or a very high velocity.

Werner Heisenberg considered the limits of how accurately we can measure properties of an electron or other microscopic particles. He determined that there is a fundamental limit to how accurately one can measure both a particle's position and its momentum simultaneously. The more accurately we measure the momentum of a particle, the less accurately we can determine its position at that time, and vice versa. This is summed up in what we now call the **Heisenberg uncertainty principle**: *It is fundamentally impossible to determine simultaneously and exactly both the momentum and the position of a particle.* 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, Δx , and the uncertainty in the momentum, Δp_x , must be greater than or equal to $\frac{\hbar}{2}$ (where $\hbar = \frac{h}{2\pi}$, the value of Planck's constant divided by 2π).

$$\Delta x \times \Delta p_x = (\Delta x)(m\Delta v) \geq \frac{\hbar}{2}$$

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 (Δx) 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

$$\left[\Delta p = m\Delta v = \frac{h}{(2\Delta x)} \right] = \frac{(1.055 \times 10^{-34} \text{ kg m}^2/\text{s})}{(2 \times 1 \times 10^{-12} \text{ m})} = 5 \times 10^{-23} \text{ kg m/s}.$$

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 $\Delta E \Delta t \geq \frac{\hbar}{2}$.

Heisenberg's principle imposes ultimate limits on what is knowable in science. The uncertainty principle can be shown to be a consequence of wave-particle duality, which lies at the heart of what distinguishes modern quantum theory from classical mechanics.

Link to Learning

Read this [article \(http://openstaxcollege.org//16uncertainty\)](http://openstaxcollege.org//16uncertainty) 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, ψ . A few years later, Max Born proposed an interpretation of the wavefunction ψ that is still accepted today: Electrons are still particles, and so the waves represented by ψ are not physical waves but, instead, are complex probability amplitudes. The square of the magnitude of a wavefunction $|\psi|^2$ describes the probability of the quantum particle being present near a certain location in space. This means that wavefunctions can be used to determine the distribution of the electron's density with respect to the nucleus in an atom. In the most general form, the Schrödinger equation can be written as:

$$\hat{H}\psi = E\psi$$

\hat{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), ψ 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 \(http://openstaxcollege.org//16superpos\)](http://openstaxcollege.org//16superpos) 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 to 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 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.

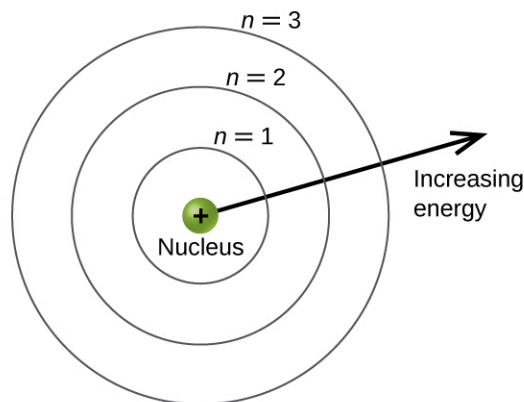


Figure 3.19 Different shells are numbered by principal quantum numbers.

This quantum mechanical model for where electrons reside in an atom can be used to look at electronic transitions, the events when an electron moves from one energy level to another. If the transition is to a higher energy level, energy is absorbed, and the energy change has a positive value. To obtain the amount of energy necessary for the transition to a higher energy level, a photon is absorbed by the atom. A transition to a lower energy level involves a release of energy, and the energy change is negative. This process is accompanied by emission of a photon by the atom. 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 a 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 ψ is zero at this distance for this orbital. Such a value of radius r is called a radial node. The number of radial nodes in an orbital is $n - l - 1$.

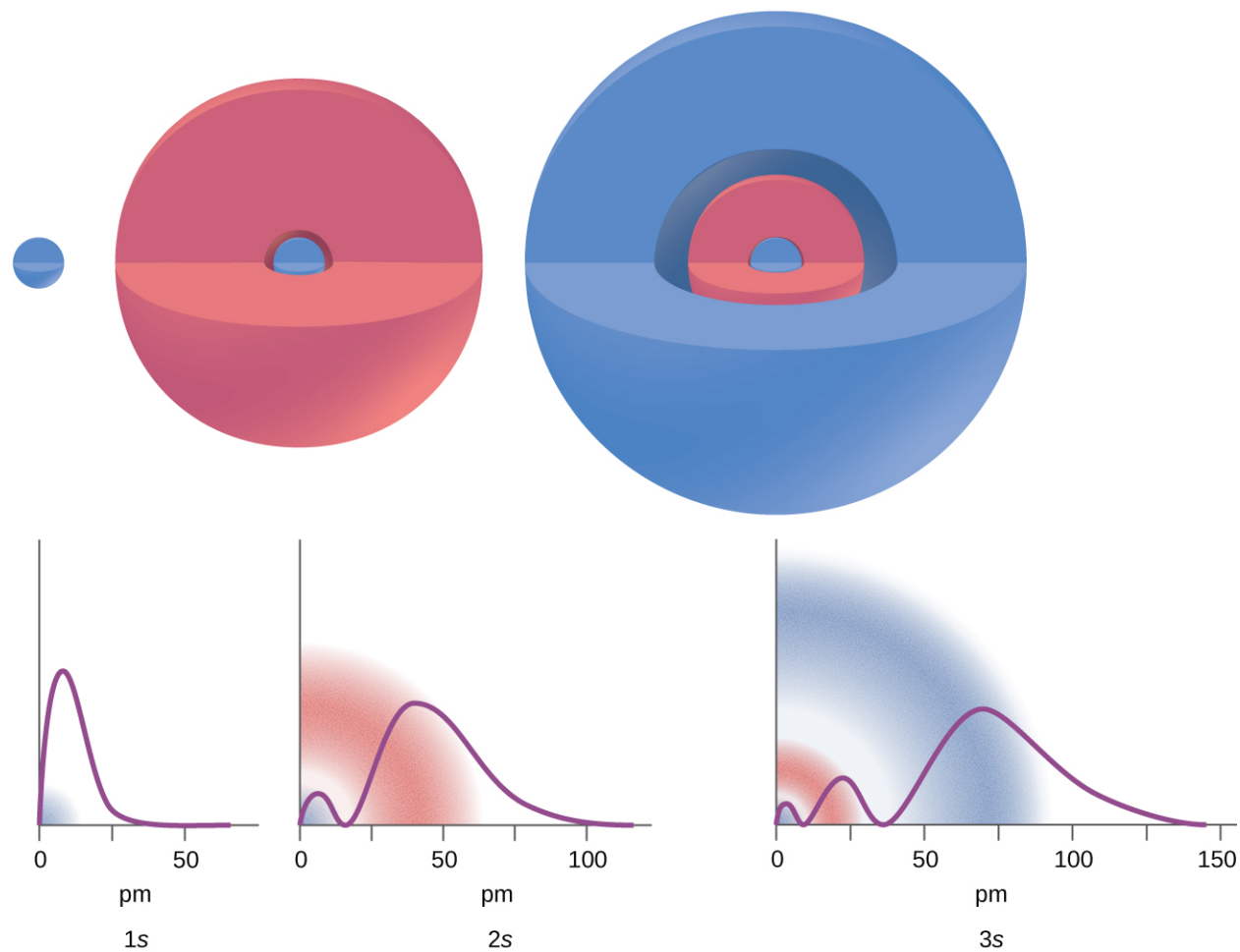


Figure 3.20 The graphs show the probability (y axis) of finding an electron for the 1s, 2s, 3s orbitals as a function of distance from the nucleus.

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.

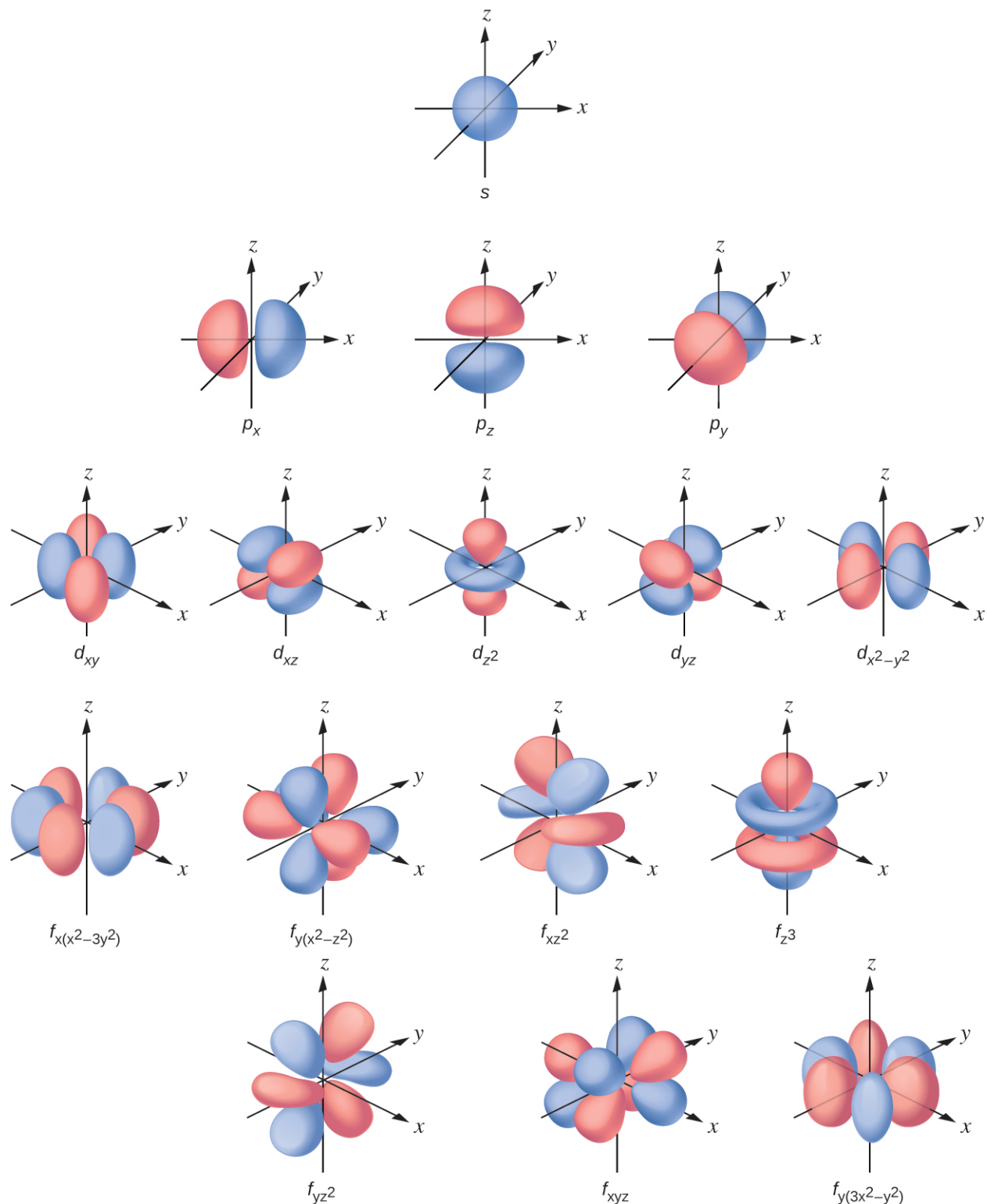


Figure 3.21 Shapes of s, p, d, and f orbitals.

The **magnetic quantum number**, m_l , specifies the relative spatial orientation of a particular orbital. Generally speaking, m_l can be equal to $-l$, $-(l-1)$, \dots , 0 , \dots , $(l-1)$, 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 orientation of the orbital in space, as can be seen in **Figure 3.21**.

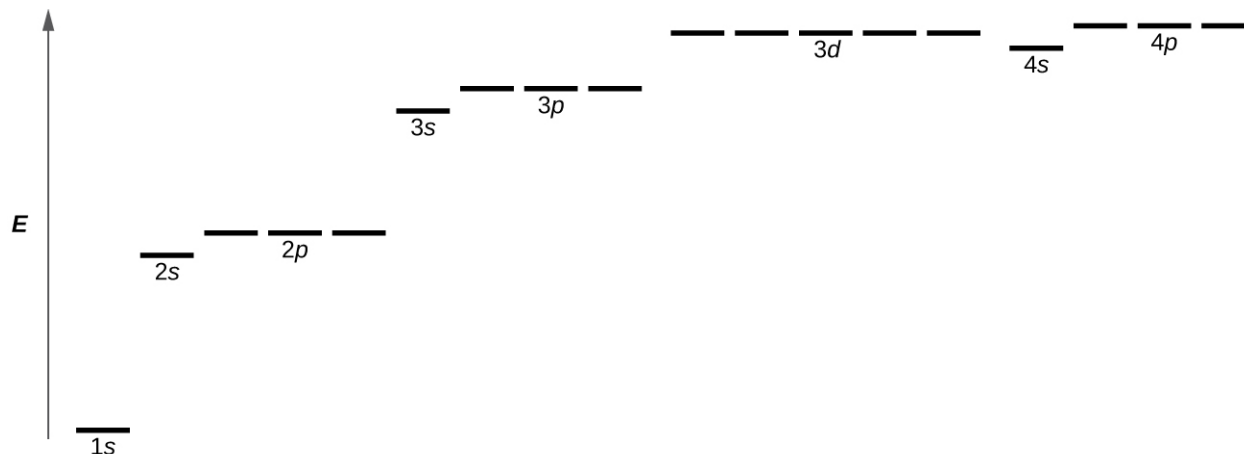


Figure 3.22 The chart shows the energies of electron orbitals in a multi-electron atom.

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 are more than one possible orbitals for $l \geq 1$, each corresponding to a specific value of m_l . In the case of a hydrogen atom or a one-electron ion (such as He^+ , Li^{2+} , and so on), energies of all the orbitals with the same n are the same. This is called a degeneracy, and the energy levels for the same principal quantum number, n , are called **degenerate 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 on **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 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 analogues in the classical realm. In addition, it cannot be derived from solving the Schrödinger equation and is not related to the normal spatial coordinates (such as the Cartesian x , y , and z). Electron spin describes an intrinsic electron "rotation" or "spinning." Each electron acts as a tiny magnet or a tiny rotating object with an angular momentum, 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 α state, with the z component of the spin being in the positive direction of the z axis. This corresponds to the spin quantum number $m_s = \frac{1}{2}$. The other is called the β 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.

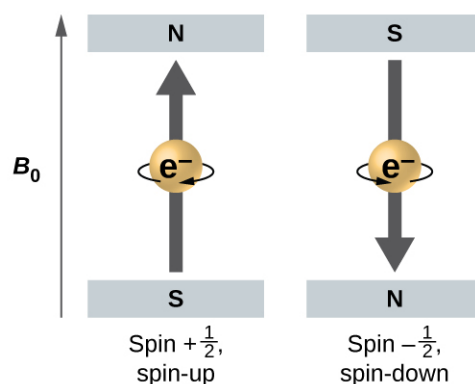


Figure 3.23 Electrons with spin values $\pm\frac{1}{2}$ in an external magnetic field.

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 on **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 the 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 ($\pm\frac{1}{2}$), 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**.

Quantum Numbers, Their Properties, and Significance

Name	Symbol	Allowed values	Physical meaning
principal quantum number	n	1, 2, 3, 4, ...	shell, the general region for the value of energy for an electron on the orbital
angular momentum or azimuthal quantum number	l	$0 \leq l \leq n - 1$	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

Table 3.1

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:

$$\begin{array}{r}
 1 \text{ orbital labeled } 5s \\
 3 \text{ orbitals labeled } 5p \\
 5 \text{ orbitals labeled } 5d \\
 7 \text{ orbitals labeled } 5f \\
 \\
 +9 \text{ orbitals labeled } 5g \\
 \hline
 25 \text{ orbitals total}
 \end{array}$$

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:

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 $n - l - 1$.

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

3.4 Electronic Structure of Atoms (Electron Configurations)

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 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 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.

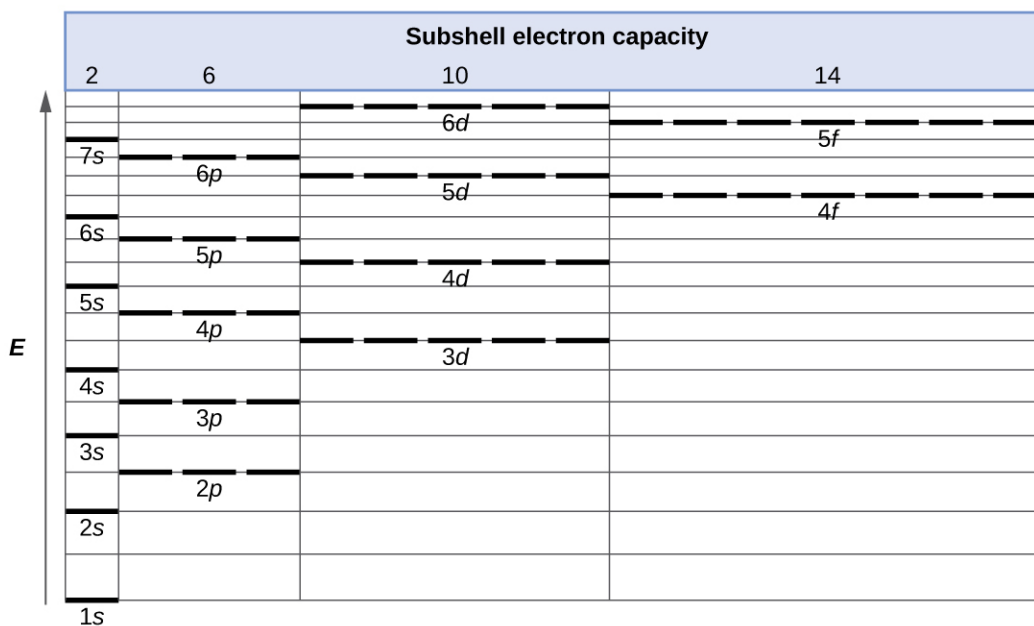


Figure 3.24 Generalized energy-level diagram for atomic orbitals in an atom with two or more electrons (not to scale).

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 $n = 3$.

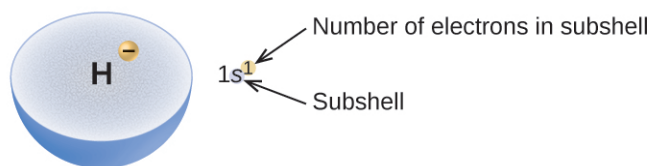


Figure 3.25 The diagram of an electron configuration specifies the subshell (n and l value, with letter symbol) and superscript number of electrons.

The Aufbau Principle

To determine the electron configuration for any particular atom, we can “build” the structures in the order of atomic numbers. Beginning with hydrogen, and continuing across the periods of the periodic table, we add one proton at a time to the nucleus and one electron to the proper subshell until we have described the electron configurations of all the elements. This procedure is called the **Aufbau principle**, from the German word *Aufbau* (“to build up”). Each added electron occupies the subshell of lowest energy available (in the order shown in **Figure 3.24**), 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.

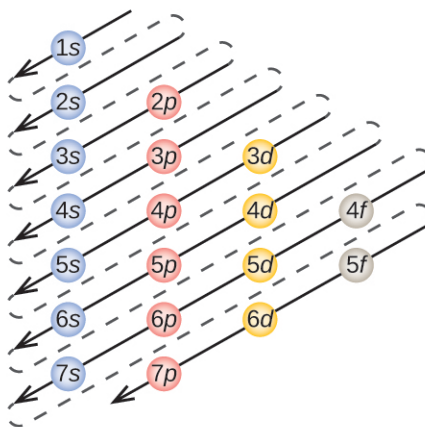


Figure 3.26 This diagram depicts the energy order for atomic orbitals and is useful for deriving ground-state electron configurations.

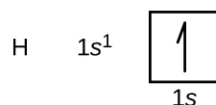
Electron Configuration Table

Period	Group																	18	
1	1																	18	
		H 1																	He 1
2	1 2	Li 1	Be 2											B 1	C 2	N 3	O 4	F 5	Ne 6
		1s												2p					
3	1 2	Na 1	Mg 2											Al 1	Si 2	P 3	S 4	Cl 5	Ar 6
		3s												3p					
4	1 2	K 1	Ca 2	Sc 1	Ti 2	V 3	Cr 4	Mn 5	Fe 6	Co 7	Ni 8	Cu 9	Zn 10	Ga 1	Ge 2	As 3	Se 4	Br 5	Kr 6
		4s		3d										4p					
5	1 2	Rb 1	Sr 2	Y 1	Zr 2	Nb 3	Mo 4	Tc 5	Ru 6	Rh 7	Pd 8	Ag 9	Cd 10	In 1	Sn 2	Sb 3	Te 4	I 5	Xe 6
		5s		4d										5p					
6	1 2	Cs 1	Ba 2	La *1	Hf 2	Ta 3	W 4	Re 5	Os 6	Ir 7	Pt 8	Au 9	Hg 10	Tl 1	Pb 2	Bi 3	Po 4	At 5	Rn 6
		6s		5d										6p					
7	1 2	Fr 1	Ra 2	Ac **1	Rf 2	Db 3	Sg 4	Bh 5	Hs 6	Mt 7	Ds 8	Rg 9	Cn 10	Nh	Fl	Mc	Lv	Ts	Og
		7s		6d															
		* Ce 1 Pr 2 Nd 3 Pm 4 Sm 5 Eu 6 Gd 7 Tb 8 Dy 9 Ho 10 Er 11 Tm 12 Yb 13 Lu 14																	
		4f																	
		** Th 1 Pa 2 U 3 Np 4 Pu 5 Am 6 Cm 7 Bk 8 Cf 9 Es 10 Fm 11 Md 12 No 13 Lr 14																	
		5f																	

Name →	H	1 ←	Electrons
	1s	←	Subshell

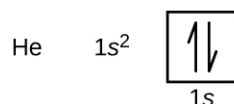
Figure 3.27 This periodic table shows the electron configuration for each subshell. By “building up” from hydrogen, this table can be used to determine the electron configuration for any atom on the periodic table.

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:



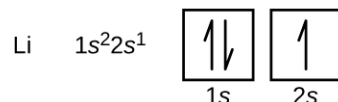
Following hydrogen is the noble gas helium, which has an atomic number of 2. The helium atom contains two protons and two electrons. The first electron has the same four quantum numbers as the hydrogen atom electron ($n = 1, l = 0, m_l = 0, m_s = +\frac{1}{2}$). The second electron also goes into the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

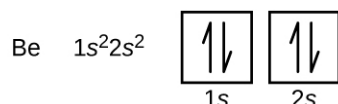


The $n = 1$ shell is completely filled in a helium atom.

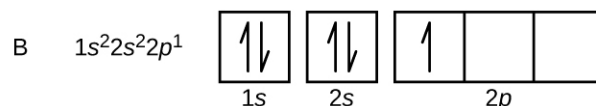
The next atom is the alkali metal lithium with an atomic number of 3. The first two electrons in lithium fill the 1s orbital and have the same sets of four quantum numbers as the two electrons in helium. The remaining electron must occupy the orbital of next lowest energy, the 2s orbital (Figure 3.26 or Figure 3.27). Thus, the electron configuration and orbital diagram of lithium are:



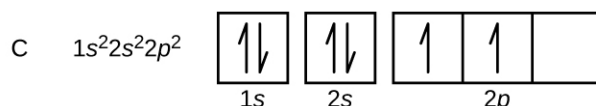
An atom of the alkaline earth metal beryllium, with an atomic number of 4, contains four protons in the nucleus and four electrons surrounding the nucleus. The fourth electron fills the remaining space in the 2s orbital.



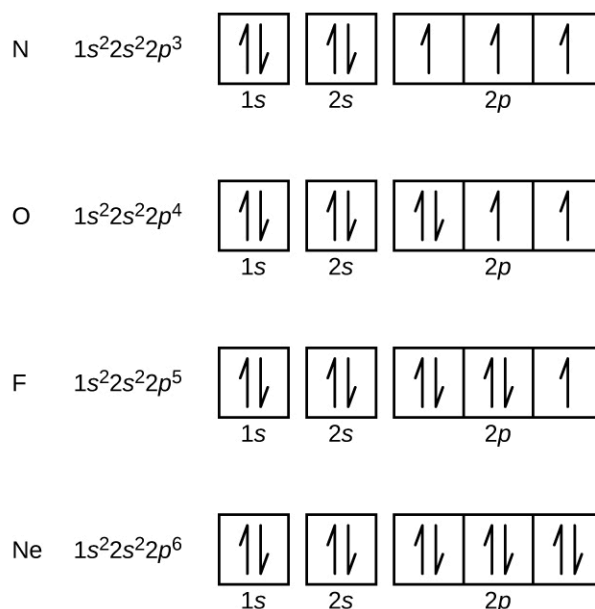
An atom of boron (atomic number 5) contains five electrons. The $n = 1$ shell is filled with two electrons and three electrons will occupy the $n = 2$ shell. Because any s subshell can contain only two electrons, the fifth electron must occupy the next energy level, which will be a $2p$ orbital. There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



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 of leaving the electrons unpaired in two different, but degenerate, p orbitals. The orbitals are filled as described by **Hund's rule**: the lowest-energy configuration for an atom with electrons within a set of degenerate orbitals is that having the maximum number of unpaired electrons. Thus, the two electrons in the carbon $2p$ 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:



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:

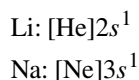


The alkali metal sodium (atomic number 11) has one more electron than the neon atom. This electron must go into the lowest-energy subshell available, the 3s orbital, giving a $1s^2 2s^2 2p^6 3s^1$ configuration. The electrons occupying the outermost shell orbital(s) (highest value of n) are called **valence electrons**, and those occupying the inner shell orbitals are called **core electrons** (Figure 3.28). Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, ($1s^2 2s^2 2p^6$) and our abbreviated or condensed configuration is [Ne] $3s^1$.



Figure 3.28 A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

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



The alkaline earth metal magnesium (atomic number 12), with its 12 electrons in a [Ne] $3s^2$ configuration, is analogous to its family member beryllium, [He] $2s^2$. Both atoms have a filled s subshell outside their filled inner shells. Aluminum (atomic number 13), with 13 electrons and the electron configuration [Ne] $3s^2 3p^1$, is analogous to its family member boron, [He] $2s^2 2p^1$.

The electron configurations of silicon (14 electrons), phosphorus (15 electrons), sulfur (16 electrons), chlorine (17 electrons), and argon (18 electrons) are analogous in the electron configurations of their outer shells to their corresponding family members carbon, nitrogen, oxygen, fluorine, and neon, respectively, except that the principal quantum number of the outer shell of the heavier elements has increased by one to $n = 3$. Figure 3.29 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

1	Group 1	2											13	14	15	16	17	18																																																																																																												
1	1	2											5	6	7	8	9	10																																																																																																												
1	H											2							He																																																																																																											
	$1s^1$																	$1s^2$																																																																																																												
2	3	4											5	6	7	8	9	10																																																																																																												
2	Li	Be											B	C	N	O	F	Ne																																																																																																												
	$2s^1$	$2s^2$											$2s^22p^1$	$2s^22p^2$	$2s^22p^3$	$2s^22p^4$	$2s^22p^5$	$2s^22p^6$																																																																																																												
3	11	12	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18																																																																																																												
3	Na	Mg											Al	Si	P	S	Cl	Ar																																																																																																												
	$3s^1$	$3s^2$											$3s^23p^1$	$3s^23p^2$	$3s^23p^3$	$3s^23p^4$	$3s^23p^5$	$3s^23p^6$																																																																																																												
4	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36																																																																																																												
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																																																																																																												
	$4s^1$	$4s^2$	$4s^23d^1$	$4s^23d^2$	$4s^23d^3$	$4s^13d^5$	$4s^23d^5$	$4s^23d^6$	$4s^23d^7$	$4s^23d^8$	$4s^13d^{10}$	$4s^23d^{10}$	$4s^23d^{10}4p^1$	$4s^23d^{10}4p^2$	$4s^23d^{10}4p^3$	$4s^23d^{10}4p^4$	$4s^23d^{10}4p^5$	$4s^23d^{10}4p^6$																																																																																																												
5	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54																																																																																																												
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																																																																																																												
	$5s^1$	$5s^2$	$5s^24d^1$	$5s^24d^2$	$5s^14d^4$	$5s^24d^5$	$5s^14d^7$	$5s^24d^7$	$5s^14d^8$	$4d^{10}$	$5s^14d^{10}$	$5s^24d^{10}$	$5s^24d^{10}5p^1$	$5s^24d^{10}5p^2$	$5s^24d^{10}5p^3$	$5s^24d^{10}5p^4$	$5s^24d^{10}5p^5$	$5s^24d^{10}5p^6$																																																																																																												
6	55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86																																																																																																												
6	Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn																																																																																																												
	$6s^1$	$6s^2$	$6s^25d^1$	$6s^24f^14d^2$	$6s^24f^14d^3$	$6s^24f^14d^4$	$6s^24f^14d^5$	$6s^24f^14d^6$	$6s^24f^14d^7$	$6s^24f^14d^8$	$6s^14f^14d^9$	$6s^24f^14d^{10}$	$6s^24f^14d^{10}5d^1$	$6s^24f^14d^{10}5d^2$	$6s^24f^14d^{10}5d^3$	$6s^24f^14d^{10}5d^4$	$6s^24f^14d^{10}5d^5$	$6s^24f^14d^{10}5d^6$																																																																																																												
7	87	88	89	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118																																																																																																												
7	Fr	Ra	Ac**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og																																																																																																												
	$7s^1$	$7s^2$	$7s^26d^1$	$7s^25f^14d^2$	$7s^25f^14d^3$	$7s^25f^14d^4$	$7s^25f^14d^5$	$7s^25f^14d^6$	$7s^25f^14d^7$	$7s^25f^14d^8$	$7s^25f^14d^9$	$7s^25f^14d^{10}$																																																																																																																		
	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="text-align: center;">*</td> <td style="text-align: center;">58</td> <td style="text-align: center;">59</td> <td style="text-align: center;">60</td> <td style="text-align: center;">61</td> <td style="text-align: center;">62</td> <td style="text-align: center;">63</td> <td style="text-align: center;">64</td> <td style="text-align: center;">65</td> <td style="text-align: center;">66</td> <td style="text-align: center;">67</td> <td style="text-align: center;">68</td> <td style="text-align: center;">69</td> <td style="text-align: center;">70</td> <td style="text-align: center;">71</td> <td colspan="3"></td> </tr> <tr> <td></td> <td style="text-align: center;">Ce</td> <td style="text-align: center;">Pr</td> <td style="text-align: center;">Nd</td> <td style="text-align: center;">Pm</td> <td style="text-align: center;">Sm</td> <td style="text-align: center;">Eu</td> <td style="text-align: center;">Gd</td> <td style="text-align: center;">Tb</td> <td style="text-align: center;">Dy</td> <td style="text-align: center;">Ho</td> <td style="text-align: center;">Er</td> <td style="text-align: center;">Tm</td> <td style="text-align: center;">Yb</td> <td style="text-align: center;">Lu</td> <td colspan="3"></td> </tr> <tr> <td></td> <td style="text-align: center;">$6s^24f^2$</td> <td style="text-align: center;">$6s^24f^3$</td> <td style="text-align: center;">$6s^24f^4$</td> <td style="text-align: center;">$6s^24f^5$</td> <td style="text-align: center;">$6s^24f^6$</td> <td style="text-align: center;">$6s^24f^7$</td> <td style="text-align: center;">$6s^24f^75d^1$</td> <td style="text-align: center;">$6s^24f^9$</td> <td style="text-align: center;">$6s^24f^{10}$</td> <td style="text-align: center;">$6s^24f^{11}$</td> <td style="text-align: center;">$6s^24f^{12}$</td> <td style="text-align: center;">$6s^24f^{13}$</td> <td style="text-align: center;">$6s^24f^{14}$</td> <td style="text-align: center;">$6s^24f^{14}5d^1$</td> <td colspan="3"></td> </tr> <tr> <td style="text-align: center;">**</td> <td style="text-align: center;">90</td> <td style="text-align: center;">91</td> <td style="text-align: center;">92</td> <td style="text-align: center;">93</td> <td style="text-align: center;">94</td> <td style="text-align: center;">95</td> <td style="text-align: center;">96</td> <td style="text-align: center;">97</td> <td style="text-align: center;">98</td> <td style="text-align: center;">99</td> <td style="text-align: center;">100</td> <td style="text-align: center;">101</td> <td style="text-align: center;">102</td> <td style="text-align: center;">103</td> <td colspan="3"></td> </tr> <tr> <td></td> <td style="text-align: center;">Th</td> <td style="text-align: center;">Pa</td> <td style="text-align: center;">U</td> <td style="text-align: center;">Np</td> <td style="text-align: center;">Pu</td> <td style="text-align: center;">Am</td> <td style="text-align: center;">Cm</td> <td style="text-align: center;">Bk</td> <td style="text-align: center;">Cf</td> <td style="text-align: center;">Es</td> <td style="text-align: center;">Fm</td> <td style="text-align: center;">Md</td> <td style="text-align: center;">No</td> <td style="text-align: center;">Lr</td> <td colspan="3"></td> </tr> <tr> <td></td> <td style="text-align: center;">$7s^26d^2$</td> <td style="text-align: center;">$7s^25f^26d^1$</td> <td style="text-align: center;">$7s^25f^26d^1$</td> <td style="text-align: center;">$7s^25f^46d^1$</td> <td style="text-align: center;">$7s^25f^6$</td> <td style="text-align: center;">$7s^25f^7$</td> <td style="text-align: center;">$7s^25f^76d^1$</td> <td style="text-align: center;">$7s^25f^86d^1$</td> <td style="text-align: center;">$7s^25f^{10}$</td> <td style="text-align: center;">$7s^25f^{11}$</td> <td style="text-align: center;">$7s^25f^{12}$</td> <td style="text-align: center;">$7s^25f^{13}$</td> <td style="text-align: center;">$7s^25f^{14}$</td> <td style="text-align: center;">$7s^25f^{14}6d^1$</td> <td colspan="3"></td> </tr> </table>																		*	58	59	60	61	62	63	64	65	66	67	68	69	70	71					Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu					$6s^24f^2$	$6s^24f^3$	$6s^24f^4$	$6s^24f^5$	$6s^24f^6$	$6s^24f^7$	$6s^24f^75d^1$	$6s^24f^9$	$6s^24f^{10}$	$6s^24f^{11}$	$6s^24f^{12}$	$6s^24f^{13}$	$6s^24f^{14}$	$6s^24f^{14}5d^1$				**	90	91	92	93	94	95	96	97	98	99	100	101	102	103					Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr					$7s^26d^2$	$7s^25f^26d^1$	$7s^25f^26d^1$	$7s^25f^46d^1$	$7s^25f^6$	$7s^25f^7$	$7s^25f^76d^1$	$7s^25f^86d^1$	$7s^25f^{10}$	$7s^25f^{11}$	$7s^25f^{12}$	$7s^25f^{13}$	$7s^25f^{14}$	$7s^25f^{14}6d^1$			
*	58	59	60	61	62	63	64	65	66	67	68	69	70	71																																																																																																																
	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu																																																																																																																
	$6s^24f^2$	$6s^24f^3$	$6s^24f^4$	$6s^24f^5$	$6s^24f^6$	$6s^24f^7$	$6s^24f^75d^1$	$6s^24f^9$	$6s^24f^{10}$	$6s^24f^{11}$	$6s^24f^{12}$	$6s^24f^{13}$	$6s^24f^{14}$	$6s^24f^{14}5d^1$																																																																																																																
**	90	91	92	93	94	95	96	97	98	99	100	101	102	103																																																																																																																
	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr																																																																																																																
	$7s^26d^2$	$7s^25f^26d^1$	$7s^25f^26d^1$	$7s^25f^46d^1$	$7s^25f^6$	$7s^25f^7$	$7s^25f^76d^1$	$7s^25f^86d^1$	$7s^25f^{10}$	$7s^25f^{11}$	$7s^25f^{12}$	$7s^25f^{13}$	$7s^25f^{14}$	$7s^25f^{14}6d^1$																																																																																																																

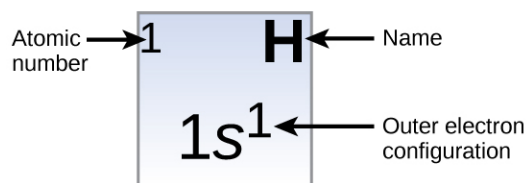


Figure 3.29 This version of the periodic table shows the outer-shell electron configuration of each element. Note that down each group, the configuration is often similar.

When we come to the next element in the periodic table, the alkali metal potassium (atomic number 19), we might expect that we would begin to add electrons to the $3d$ 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 3.29**). 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.

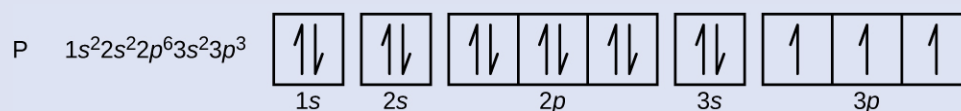
Example 3.10

Quantum Numbers and Electron Configurations

What is the electron configuration and orbital diagram for a phosphorus atom? What are the four quantum numbers for the last electron added?

Solution

The atomic number of phosphorus is 15. Thus, a phosphorus atom contains 15 electrons. The order of filling of the energy levels is $1s$, $2s$, $2p$, $3s$, $3p$, $4s$, . . . The 15 electrons of the phosphorus atom will fill up to the $3p$ orbital, which will contain three electrons:



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 is 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:

- (a) $[\text{Ar}]4s^2 3d^5$
 (b) $[\text{Kr}]5s^2 4d^{10} 5p^6$

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 3.29**) 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 $[\text{Kr}]5s^2 4d^3$. Experimentally, we observe that its ground-state electron configuration is actually $[\text{Kr}]5s^1 4d^4$. 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 3.29**), 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 3.29**, 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 3.29** 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 3.29**. 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 $[\text{Ar}]4s^23d^{10}4p^1$, 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 3.29**) are not technically transition elements. However, the term is frequently used to refer to the entire d block (colored yellow in **Figure 3.29**), 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 3.29**. 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:

- (a) Na^+
- (b) P^{3-}
- (c) Al^{2+}
- (d) Fe^{2+}
- (e) Sm^{3+}

Solution

First, write out the electron configuration for each parent atom. We have chosen to show the full, unabbreviated configurations to provide more practice for students who want it, but listing the core-abbreviated electron configurations is also acceptable.

Next, determine whether an electron is gained or lost. Remember electrons are negatively charged, so ions with a positive charge have *lost* an electron. For main group elements, the last orbital gains or loses the electron. For transition metals, the last s orbital loses an electron before the d orbitals.

(a) Na: $1s^2 2s^2 2p^6 3s^1$. Sodium cation loses one electron, so Na^+ : $1s^2 2s^2 2p^6 3s^1 = \text{Na}^+$: $1s^2 2s^2 2p^6$.

(b) P: $1s^2 2s^2 2p^6 3s^2 3p^3$. Phosphorus trianion gains three electrons, so P^{3-} : $1s^2 2s^2 2p^6 3s^2 3p^6$.

(c) Al: $1s^2 2s^2 2p^6 3s^2 3p^1$. Aluminum dication loses two electrons Al^{2+} : $1s^2 2s^2 2p^6 3s^2 3p^1 = \text{Al}^{2+}$: $1s^2 2s^2 2p^6 3s^1$.

(d) Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$. Iron(II) loses two electrons and, since it is a transition metal, they are removed from the $4s$ orbital Fe^{2+} : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6 = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$.

(e) Sm: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6$. Samarium trication loses three electrons. The first two will be lost from the $6s$ orbital, and the final one is removed from the $4f$ orbital. Sm^{3+} : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6 = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 4f^5$.

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+}

3.5 Periodic Variations in Element Properties

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-grey solid that conducts electricity.

As we go across a period from left to right, we add a proton to the nucleus and an electron to the valence shell with each successive element. As we go down the elements in a group, the number of electrons in the valence shell remains constant, but the principal quantum number increases by one each time. An understanding of the electronic structure of the elements allows us to examine some of the properties that govern their chemical behavior. These properties vary periodically as the electronic structure of the elements changes. They are (1) size (radius) of atoms and ions, (2) ionization energies, and (3) electron affinities.

Link to Learning

Explore **visualizations** (<http://openstaxcollege.org//16pertrends>) 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 3.30**), 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 3.2** and **Figure 3.30**. The trends for the entire periodic table can be seen in **Figure 3.30**.

Covalent Radii of the Halogen Group Elements

Atom	Covalent radius (pm)	Nuclear charge
F	64	+9
Cl	99	+17
Br	114	+35
I	133	+53

Table 3.2

Covalent Radii of the Halogen Group Elements

Atom	Covalent radius (pm)	Nuclear charge
At	148	+85

Table 3.2

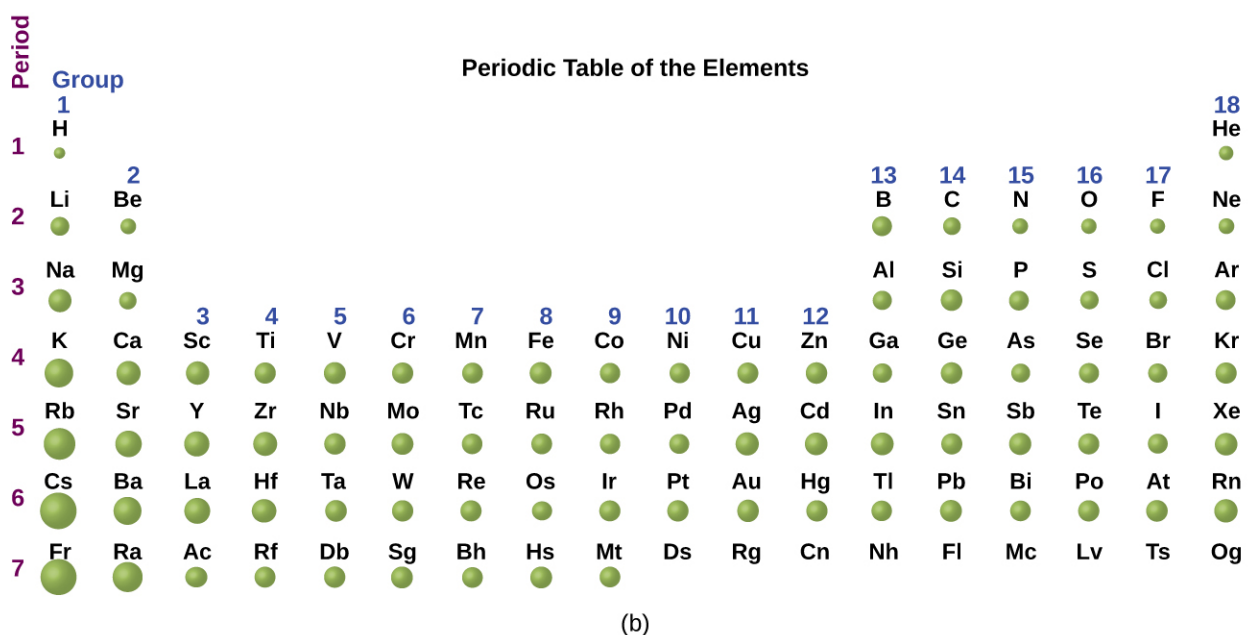
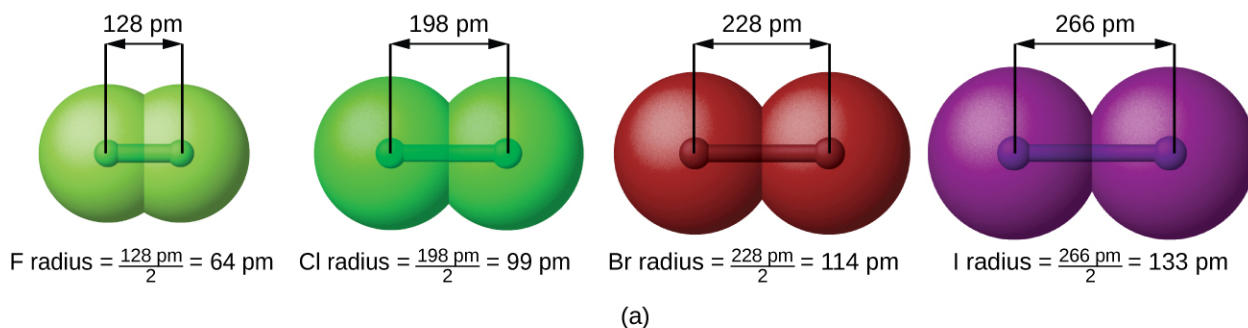


Figure 3.30 (a) The radius of an atom is defined as one-half the distance between the nuclei in a molecule consisting of two identical atoms joined by a covalent bond. The atomic radius for the halogens increases down the group as n increases. (b) Covalent radii of the elements are shown to scale. The general trend is that radii increase down a group and decrease across a period.

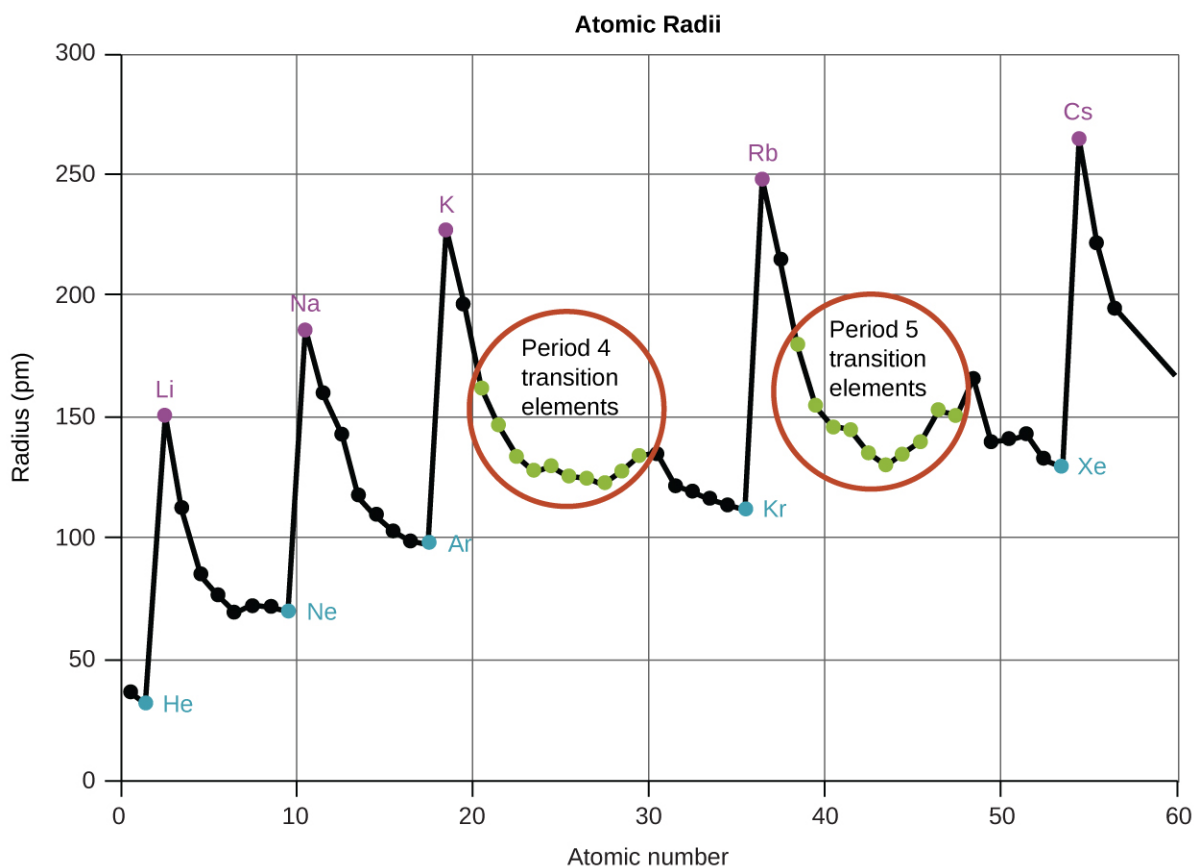


Figure 3.31 Within each period, the trend in atomic radius decreases as Z increases; for example, from K to Kr. Within each group (e.g., the alkali metals shown in purple), the trend is that atomic radius increases as Z increases.

As shown in **Figure 3.31**, as we move across a period from left to right, we generally find that each element has a smaller covalent radius than the element preceding it. This might seem counterintuitive because it implies that atoms with more electrons have a smaller atomic radius. This can be explained with the concept of **effective nuclear charge, Z_{eff}** . This is the pull exerted on a specific electron by the nucleus, taking into account any electron–electron repulsions. For hydrogen, there is only one electron and so the nuclear charge (Z) and the effective nuclear charge (Z_{eff}) are equal. For all other atoms, the inner electrons partially *shield* the outer electrons from the pull of the nucleus, and thus:

$$Z_{\text{eff}} = Z - \text{shielding}$$

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_{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 3.32**). For example, the covalent radius of an aluminum atom ($1s^22s^22p^63s^23p^1$) is 118 pm, whereas the ionic radius of an Al^{3+} ($1s^22s^22p^6$) is 68 pm. As electrons are removed from the outer valence shell, the remaining core electrons occupying smaller shells experience a greater effective nuclear charge Z_{eff} (as discussed) and are drawn even closer to the nucleus.

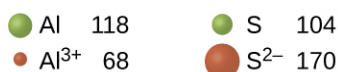


Figure 3.32 The radius for a cation is smaller than the parent atom (Al), due to the lost electrons; the radius for an anion is larger than the parent (S), due to the gained electrons.

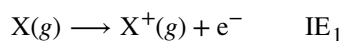
Cations with larger charges are smaller than cations with smaller charges (e.g., V^{2+} has an ionic radius of 79 pm, while that of V^{3+} is 64 pm). Proceeding down the groups of the periodic table, we find that cations of successive elements with the same charge generally have larger radii, corresponding to an increase in the principal quantum number, n .

An anion (negative ion) is formed by the addition of one or more electrons to the valence shell of an atom. This results in a greater repulsion among the electrons and a decrease in Z_{eff} per electron. Both effects (the increased number of electrons and the decreased Z_{eff}) cause the radius of an anion to be larger than that of the parent atom (**Figure 3.32**). 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.

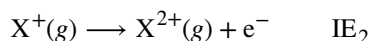
Atoms and ions that have the same electron configuration are said to be **isoelectronic**. Examples of isoelectronic species are N^{3-} , O^{2-} , F^- , Ne, Na^+ , Mg^{2+} , and Al^{3+} ($1s^22s^22p^6$). Another isoelectronic series is P^{3-} , S^{2-} , Cl^- , Ar, K^+ , Ca^{2+} , and Sc^{3+} ($[\text{Ne}]3s^23p^6$). 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** (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 (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 3.33 graphs the relationship between the first ionization energy and the atomic number of several elements. The values of first ionization energy for the elements are given in **Figure 3.34**. 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.

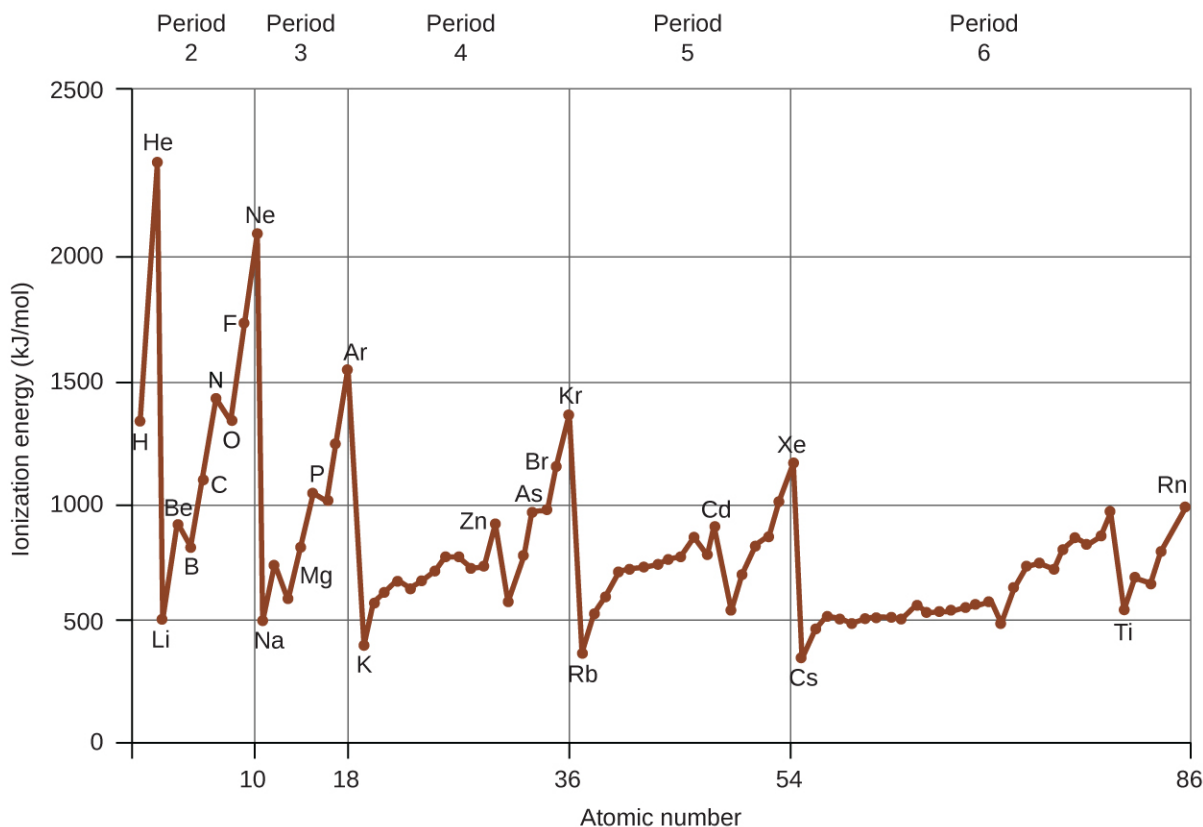


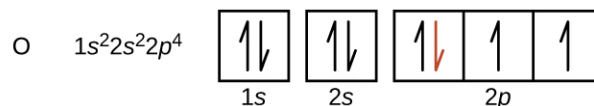
Figure 3.33 The first ionization energy of the elements in the first five periods are plotted against their atomic number.

First Ionization Energies of Some Elements (kJ/mol)

Period	Group 1	Group 2	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18										
1	H 1310							He 2370										
2	Li 520	Be 900	B 800	C 1090	N 1400	O 1310	F 1680	Ne 2080										
3	Na 490	Mg 730	Al 580	Si 780	P 1060	S 1000	Cl 1250	Ar 1520										
4	K 420	Ca 590	Sc 630	Ti 660	V 650	Cr 660	Mn 710	Fe 760	Co 760	Ni 730	Cu 740	Zn 910	Ga 580	Ge 780	As 960	Se 950	Br 1140	Kr 1350
5	Rb 400	Sr 550	Y 620	Zr 660	Nb 670	Mo 680	Tc 700	Ru 710	Rh 720	Pd 800	Ag 730	Cd 870	In 560	Sn 700	Sb 830	Te 870	I 1010	Xe 1170
6	Cs 380	Ba 500	La 540	Hf 700	Ta 760	W 770	Re 760	Os 840	Ir 890	Pt 870	Au 890	Hg 1000	Tl 590	Pb 710	Bi 800	Po 810	At ...	Rn 1030
7	Fr ...	Ra 510																

Figure 3.34 This version of the periodic table shows the first ionization energy (IE_1), in kJ/mol, of selected elements.

Another deviation occurs as orbitals become more than one-half filled. The first ionization energy for oxygen is slightly less than that for nitrogen, despite the trend in increasing IE_1 values across a period. Looking at the orbital diagram of oxygen, we can see that removing one electron will eliminate the electron–electron repulsion caused by pairing the electrons in the $2p$ orbital and will result in a half-filled orbital (which is energetically favorable). Analogous changes occur in succeeding periods (note the dip for sulfur after phosphorus in **Figure 3.34**).



Removing an electron from a cation is more difficult than removing an electron from a neutral atom because of the greater electrostatic attraction to the cation. Likewise, removing an electron from a cation with a higher positive charge is more difficult than removing an electron from an ion with a lower charge. Thus, successive ionization energies for one element always increase. As seen in **Table 3.3**, there is a large increase in the ionization energies for each element. This jump corresponds to removal of the core electrons, which are harder to remove than the valence electrons. For example, Sc and Ga both have three valence electrons, so the rapid increase in ionization energy occurs after the third ionization.

Successive Ionization Energies for Selected Elements (kJ/mol)

Element	IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7
K	418.8	3051.8	4419.6	5876.9	7975.5	9590.6	11343
Ca	589.8	1145.4	4912.4	6490.6	8153.0	10495.7	12272.9
Sc	633.1	1235.0	2388.7	7090.6	8842.9	10679.0	13315.0
Ga	578.8	1979.4	2964.6	6180	8298.7	10873.9	13594.8
Ge	762.2	1537.5	3302.1	4410.6	9021.4	Not available	Not available

Table 3.3

Successive Ionization Energies for Selected Elements (kJ/mol)

Element	IE ₁	IE ₂	IE ₃	IE ₄	IE ₅	IE ₆	IE ₇
As	944.5	1793.6	2735.5	4836.8	6042.9	12311.5	Not available

Table 3.3

Example 3.13

Ranking Ionization Energies

Predict the order of increasing energy for the following processes: IE₁ for Al, IE₁ for Tl, IE₂ for Na, IE₃ for Al.

Solution

Removing the 6p¹ electron from Tl is easier than removing the 3p¹ electron from Al because the higher *n* orbital is farther from the nucleus, so IE₁(Tl) < IE₁(Al). Ionizing the third electron from Al (Al²⁺ → Al³⁺ + e⁻) requires more energy because the cation Al²⁺ exerts a stronger pull on the electron than the neutral Al atom, so IE₁(Al) < IE₃(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: IE₁(Tl) < IE₁(Al) < IE₃(Al) < IE₂(Na).

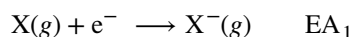
Check Your Learning

Which has the lowest value for IE₁: 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).



This process can be either endothermic or exothermic, depending on the element. The EA of some of the elements is given in **Figure 3.35**. 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 (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												13	14	15	16	17	18			
1	H																		He		
			Group 2																		
2	Li	Be											B	C	N	O	F	Ne			
3	Na	Mg																			
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr			
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe			
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn			
7	Fr	Ra																			

* Calculated value

Figure 3.35 This version of the periodic table displays the electron affinity values (in kJ/mol) for selected elements.

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.

3.6 The Periodic Table

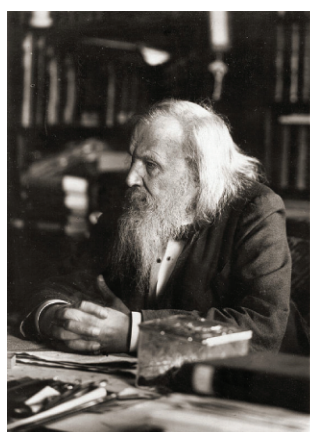
By the end of this section, you will be able to:

- 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 are Ca, Sr, and Ba; Li, Na, and K form compounds with oxygen in a ratio of two of their atoms to one oxygen atom, whereas Ca, Sr, and Ba form compounds with one of their atoms to one oxygen atom. Fluorine (F), chlorine (Cl), bromine (Br), and iodine (I) also exhibit similar properties to each other, but these properties are drastically different from those of any of the elements above.

Dimitri Mendeleev in Russia (1869) and Lothar Meyer in Germany (1870) independently recognized that there was a periodic relationship among the properties of the elements known at that time. Both published tables with the elements arranged according to increasing atomic mass. But Mendeleev went one step further than Meyer: He used his table to predict the existence of elements that would have the properties similar to aluminum and silicon, but were yet unknown. The discoveries of gallium (1875) and germanium (1886) provided great support for Mendeleev's work. Although Mendeleev and Meyer had a long dispute over priority, Mendeleev's contributions to the development of the periodic table are now more widely recognized (**Figure 3.36**).



(a)

Reihen	Gruppo I. — R'O	Gruppo II. — R'O	Gruppo III. — R'O ^s	Gruppo IV. RH ⁴ R'O ^s	Gruppo V. RH ⁵ R'O ^s	Gruppo VI. RH ⁶ R'O ^s	Gruppo VII. RH R'O ^r	Gruppo VIII. — R'O ^t
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,8	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=86	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?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 3.36 (a) Dimitri Mendeleev is widely credited with creating (b) the first periodic table of the elements. (credit a: modification of work by Serge Lachinov; credit b: modification of work by “Den fjättrade ankan”/Wikimedia Commons)

By the twentieth century, it became apparent that the periodic relationship involved atomic numbers rather than atomic masses. The modern statement of this relationship, the **periodic law**, is as follows: *the properties of the elements are periodic functions of their atomic numbers*. A modern **periodic table** arranges the elements in increasing order of their atomic numbers and groups atoms with similar properties in the same vertical column (**Figure 3.37**). 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.

Periodic Table of the Elements

Color Code

Yellow	Metal	Solid
Purple	Metalloid	Liquid
Green	Nonmetal	Gas

Figure 3.37 Elements in the periodic table are organized according to their properties.

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

The elements can also be classified into the **main-group elements** (or **representative elements**) in the columns labeled 1, 2, and 13–18; the **transition metals** in the columns labeled 3–12;^[1] 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 3.38**). 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

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.

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

Group 1	Main group elements										13	14	15	16	17	18	
Alkali metals	2	3	4	5	6	7	8	9	10	11	12			Pnic- to- gens	Chal- co- gens	Halo- gens	Noble gases
		Transition metals															
		Lanthanides															
		Actinides															

Figure 3.38 The periodic table organizes elements with similar properties into groups.

Link to Learning

Click on this [link \(http://openstax.org//16Periodic\)](http://openstax.org//16Periodic) 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 \(http://openstax.org//16Periodic2\)](http://openstax.org//16Periodic2) 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:

- chlorine
- calcium
- 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.

3.7 Molecular and Ionic Compounds

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 3.39**).

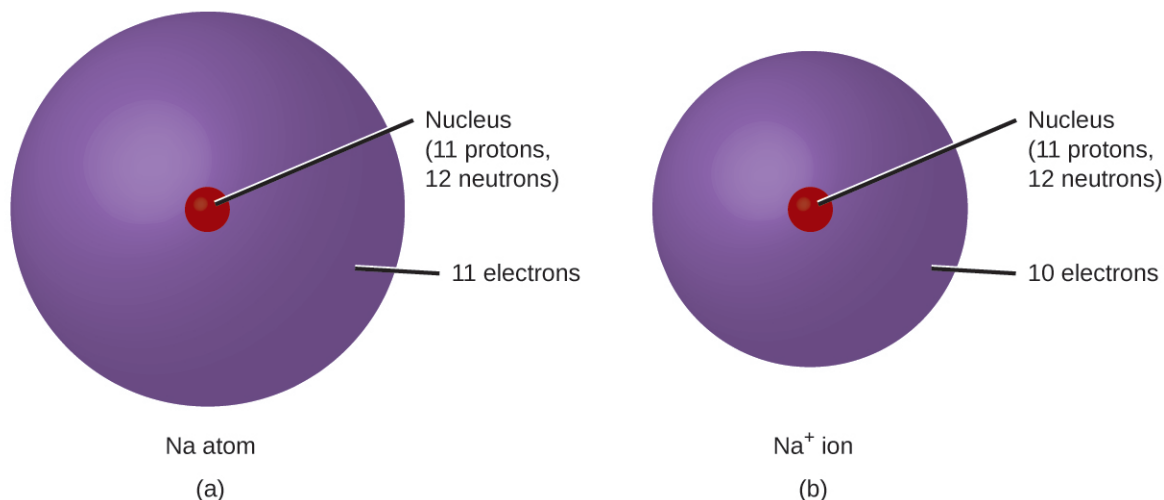


Figure 3.39 (a) A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. (b) A sodium cation (Na^+) has lost an electron, so it has one more proton (11) than electrons (10), giving it an overall positive charge, signified by a superscripted plus sign.

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

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

Note the usefulness of the periodic table in predicting likely ion formation and charge (**Figure 3.40**). 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	Group 2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1																		He
2	Li ⁺	Be ²⁺												C ⁴⁻	N ³⁻	O ²⁻	F ⁻	Ne
3	Na ⁺	Mg ²⁺											Al ³⁺		P ³⁻	S ²⁻	Cl ⁻	Ar
4	K ⁺	Ca ²⁺				Cr ³⁺ Cr ⁶⁺	Mn ²⁺	Fe ²⁺ Fe ³⁺	Co ²⁺	Ni ²⁺	Cu ⁺ Cu ²⁺	Zn ²⁺			As ³⁻	Se ²⁻	Br ⁻	Kr
5	Rb ⁺	Sr ²⁺									Ag ⁺	Cd ²⁺				Te ²⁻	I ⁻	Xe
6	Cs ⁺	Ba ²⁺								Pt ²⁺	Au ⁺ Au ³⁺	Hg ₂ ²⁺ Hg ²⁺					At ⁻	Rn
7	Fr ⁺	Ra ²⁺																

*
**

Figure 3.40 Some elements exhibit a regular pattern of ionic charge when they form ions.

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, Al³⁺.

Check Your Learning

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

Answer: Se²⁻, 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 electrons as an atom of the previous noble gas, neon. Thus, a magnesium atom will form a cation with two fewer electrons than protons and a charge of 2+. The symbol for the ion is Mg^{2+} , and it is called a magnesium ion.

Nitrogen's position in the periodic table (group 15) reveals that it is a nonmetal. Nonmetals form negative ions (anions). A nitrogen atom must gain three electrons to have the same number of electrons as an atom of the following noble gas, neon. Thus, a nitrogen atom will form an anion with three more electrons than protons and a charge of 3-. The symbol for the ion is N^{3-} , and it is called a nitride ion.

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

The ions that we have discussed so far are called **monatomic ions**, that is, they are ions formed from only one atom. We also find many **polyatomic ions**. These ions, which act as discrete units, are electrically charged molecules (a group of bonded atoms with an overall charge). Some of the more important polyatomic ions are listed in **Table 3.4**. **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.

Common Polyatomic Ions

Name	Formula	Related Acid	Formula
ammonium	NH_4^+		
hydronium	H_3O^+		
peroxide	O_2^{2-}		
hydroxide	OH^-		
acetate	CH_3COO^-	acetic acid	CH_3COOH
cyanide	CN^-	hydrocyanic acid	HCN
azide	N_3^-	hydrazoic acid	HN_3
carbonate	CO_3^{2-}	carbonic acid	H_2CO_3
bicarbonate	HCO_3^-		
nitrate	NO_3^-	nitric acid	HNO_3
nitrite	NO_2^-	nitrous acid	HNO_2
sulfate	SO_4^{2-}	sulfuric acid	H_2SO_4
hydrogen sulfate	HSO_4^-		

Table 3.4

Common Polyatomic Ions

Name	Formula	Related Acid	Formula
sulfite	SO_3^{2-}	sulfurous acid	H_2SO_3
hydrogen sulfite	HSO_3^-		
phosphate	PO_4^{3-}	phosphoric acid	H_3PO_4
hydrogen phosphate	HPO_4^{2-}		
dihydrogen phosphate	H_2PO_4^-		
perchlorate	ClO_4^-	perchloric acid	HClO_4
chlorate	ClO_3^-	chloric acid	HClO_3
chlorite	ClO_2^-	chlorous acid	HClO_2
hypochlorite	ClO^-	hypochlorous acid	HClO
chromate	CrO_4^{2-}	chromic acid	$\text{H}_2\text{Cr}_2\text{O}_4$
dichromate	$\text{Cr}_2\text{O}_7^{2-}$	dichromic acid	$\text{H}_2\text{Cr}_2\text{O}_7$
permanganate	MnO_4^-	permanganic acid	HMnO_4

Table 3.4

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

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

Ionic Compounds

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

to each of two chlorine atoms to form CaCl_2 , which is composed of Ca^{2+} and Cl^- ions in the ratio of one Ca^{2+} ion to two Cl^- ions.

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

You can often recognize ionic compounds because of their properties. Ionic compounds are solids that typically melt at high temperatures and boil at even higher temperatures. For example, sodium chloride melts at 801°C and boils at 1413°C . (As a comparison, the molecular compound water melts at 0°C and boils at 100°C .) In solid form, an ionic compound is not electrically conductive because its ions are unable to flow (“electricity” is the flow of charged particles). When molten, however, it can conduct electricity because its ions are able to move freely through the liquid (**Figure 3.41**).

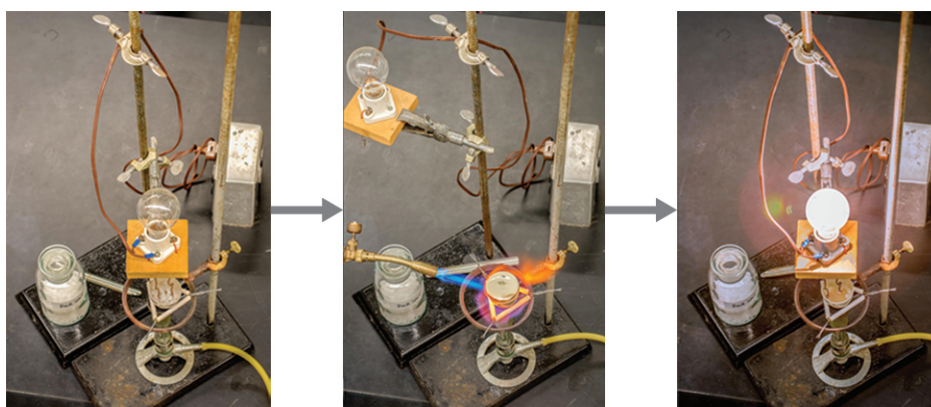


Figure 3.41 Sodium chloride melts at 801°C and conducts electricity when molten. (credit: modification of work by Mark Blaser and Matt Evans)

Link to Learning

Watch this [video \(http://openstax.org//16moltensalt\)](http://openstax.org//16moltensalt) 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 3.42**) is mostly a compound of aluminum and oxygen that contains aluminum cations, Al^{3+} , and oxygen anions, O^{2-} . What is the formula of this compound?



Figure 3.42 Although pure aluminum oxide is colorless, trace amounts of iron and titanium give blue sapphire its characteristic color. (credit: modification of work by Stanislav Doronenko)

Solution

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

Check Your Learning

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

Answer: Na_2S

Many ionic compounds contain polyatomic ions (**Table 3.4**) as the cation, the anion, or both. As with simple ionic compounds, these compounds must also be electrically neutral, so their formulas can be predicted by treating the polyatomic ions as discrete units. We use parentheses in a formula to indicate a group of atoms that behave as a unit. For example, the formula for calcium phosphate, one of the minerals in our bones, is $Ca_3(PO_4)_2$. This formula indicates that there are three calcium ions (Ca^{2+}) for every two phosphate (PO_4^{3-}) groups. The PO_4^{3-} groups are discrete units, each consisting of one phosphorus atom and four oxygen atoms, and having an overall charge of $3-$. The compound is electrically neutral, and its formula shows a total count of three Ca, two P, and eight O atoms.

Example 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 Ca^{2+} and $H_2PO_4^-$. What is the formula of this compound?

Solution

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

Check Your Learning

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

Answer: Li_2O_2

Because an ionic compound is not made up of single, discrete molecules, it may not be properly symbolized using a *molecular* formula. Instead, ionic compounds must be symbolized by a formula indicating the *relative numbers* of its

constituent ions. For compounds containing only monatomic ions (such as NaCl) and for many compounds containing polyatomic ions (such as CaSO₄), 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⁺ and C₂O₄²⁻ ions combined in a 2:1 ratio, and its formula is written as Na₂C₂O₄. The subscripts in this formula are not the smallest-possible whole numbers, as each can be divided by 2 to yield the empirical formula, NaCO₂. This is not the accepted formula for sodium oxalate, however, as it does not accurately represent the compound's polyatomic anion, C₂O₄²⁻.

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) H₂O₂, the bleach and disinfectant hydrogen peroxide
- (c) CHCl₃, the anesthetic chloroform
- (d) Li₂CO₃, 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; H₂O₂ 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; CHCl₃ is predicted to be molecular.
- (d) Lithium (group 1) is a metal, and carbonate is a polyatomic ion; Li₂CO₃ is predicted to be ionic.

Check Your Learning

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

- (a) SO₂
- (b) CaF₂
- (c) N₂H₄

(d) $\text{Al}_2(\text{SO}_4)_3$

Answer: (a) molecular; (b) ionic; (c) molecular; (d) ionic

Key Terms

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

alkali metal element in group 1

alkaline earth metal element in group 2

amplitude extent of the displacement caused by a wave

atomic orbital mathematical function that describes the behavior of an electron in an atom (also called the wavefunction)

Aufbau principle procedure in which the electron configuration of the elements is determined by “building” them in order of atomic numbers, adding one proton to the nucleus and one electron to the proper subshell at a time

blackbody idealized perfect absorber of all incident electromagnetic radiation; such bodies emit electromagnetic radiation in characteristic continuous spectra called blackbody radiation

Bohr’s model of the hydrogen atom structural model in which an electron moves around the nucleus only in circular orbits, each with a specific allowed radius

chalcogen element in group 16

continuous spectrum electromagnetic radiation given off in an unbroken series of wavelengths (e.g., white light from the sun)

core electron electron in an atom that occupies the orbitals of the inner shells

covalent bond attractive force between the nuclei of a molecule’s atoms and pairs of electrons between the atoms

covalent compound (also, molecular compound) composed of molecules formed by atoms of two or more different elements

covalent radius one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond

d orbital region of space with high electron density that is either four lobed or contains a dumbbell and torus shape; describes orbitals with $l = 2$.

degenerate orbitals orbitals that have the same energy

effective nuclear charge charge that leads to the Coulomb force exerted by the nucleus on an electron, calculated as the nuclear charge minus shielding

electromagnetic radiation energy transmitted by waves that have an electric-field component and a magnetic-field component

electromagnetic spectrum range of energies that electromagnetic radiation can comprise, including radio, microwaves, infrared, visible, ultraviolet, X-rays, and gamma rays

electron affinity energy change associated with addition of an electron to a gaseous atom or ion

electron configuration listing that identifies the electron occupancy of an atom’s shells and subshells

electron density a measure of the probability of locating an electron in a particular region of space, it is equal to the squared absolute value of the wave function ψ

endothermic processes that increase the energy of an atom and involve the absorption of light

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

exothermic processes that decrease the energy of an atom and involve the emission of light

f orbital multilobed region of space with high electron density, describes orbitals with $l = 3$

frequency (ν) number of wave cycles (peaks or troughs) that pass a specified point in space per unit time

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

group vertical column of the periodic table

halogen element in group 17

Heisenberg uncertainty principle rule stating that it is impossible to exactly determine both certain conjugate dynamical properties such as the momentum and the position of a particle at the same time. The uncertainty principle is a consequence of quantum particles exhibiting wave-particle duality

hertz (Hz) the unit of frequency, which is the number of cycles per second, s^{-1}

Hund's rule every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin

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

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

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

interference pattern pattern typically consisting of alternating bright and dark fringes; it results from constructive and destructive interference of waves

ionic bond electrostatic forces of attraction between the oppositely charged ions of an ionic compound

ionic compound compound composed of cations and anions combined in ratios, yielding an electrically neutral substance

ionization energy energy required to remove an electron from a gaseous atom or ion

isoelectronic group of ions or atoms that have identical electron configurations

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

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

magnetic quantum number (m_l) quantum number signifying the orientation of an atomic orbital around the nucleus

main-group element (also, representative element) element in groups 1, 2, and 13–18

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

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

some properties of nonmetals

molecular compound (also, covalent compound) composed of molecules formed by atoms of two or more different elements

monatomic ion ion composed of a single atom

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

node any point of a standing wave with zero amplitude

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

orbital diagram pictorial representation of the electron configuration showing each orbital as a box and each electron as an arrow

oxyanion polyatomic anion composed of a central atom bonded to oxygen atoms

p orbital dumbbell-shaped region of space with high electron density, describes orbitals with $l = 1$

Pauli exclusion principle specifies that no two electrons in an atom can have the same value for all four quantum numbers

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

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

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

photon smallest possible packet of electromagnetic radiation, a particle of light

pnictogen element in group 15

polyatomic ion ion composed of more than one atom

principal quantum number (n) quantum number specifying the shell an electron occupies in an atom

quantization limitation of some property to specific discrete values, not continuous

quantum mechanics field of study that includes quantization of energy, wave-particle duality, and the Heisenberg uncertainty principle to describe matter

quantum number number having only specific allowed values and used to characterize the arrangement of electrons in an atom

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

s orbital spherical region of space with high electron density, describes orbitals with $l = 0$

secondary (angular momentum) quantum number (l) quantum number distinguishing the different shapes of orbitals; it is also a measure of the orbital angular momentum

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

shell atomic orbitals with the same principal quantum number, n

spin quantum number (m_s) number specifying the electron spin direction, either $+\frac{1}{2}$ or $-\frac{1}{2}$

standing wave (also, stationary wave) localized wave phenomenon characterized by discrete wavelengths determined by the boundary conditions used to generate the waves; standing waves are inherently quantized

subshell atomic orbitals with the same values of n and l

transition metal element in groups 3–12 (more strictly defined, 3–11; see chapter on transition metals and coordination chemistry)

valence electrons electrons in the outermost or valence shell (highest value of n) of a ground-state atom

valence shell outermost shell of electrons in a ground-state atom

wave oscillation of a property over time or space; can transport energy from one point to another

wave-particle duality observation that elementary particles can exhibit both wave-like and particle-like properties

wavefunction (ψ) mathematical description of an atomic orbital that describes the shape of the orbital; it can be used to calculate the probability of finding the electron at any given location in the orbital, as well as dynamical variables such as the energy and the angular momentum

wavelength (λ) distance between two consecutive peaks or troughs in a wave

Key Equations

- $c = \lambda\nu$
- $E = h\nu = \frac{hc}{\lambda}$, where $h = 6.626 \times 10^{-34}$ J s
- $\frac{1}{\lambda} = R_{\infty} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$
- $E_n = -\frac{kZ^2}{n^2}$, $n = 1, 2, 3, \dots$
- $\Delta E = kZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$
- $r = \frac{n^2}{Z} a_0$

Summary

3.1 Electromagnetic Energy

Light and other forms of electromagnetic radiation move through a vacuum with a constant speed, c , of 2.998×10^8 m s⁻¹. This radiation shows wavelike behavior, which can be characterized by a frequency, ν , and a wavelength, λ , such that $c = \lambda\nu$. Light is an example of a travelling wave. Other important wave phenomena include standing waves, periodic oscillations, and vibrations. Standing waves exhibit quantization, since their wavelengths are limited to discrete integer multiples of some characteristic lengths. Electromagnetic radiation that passes through two closely spaced narrow slits having dimensions roughly similar to the wavelength will show an interference pattern that is a result of constructive and destructive interference of the waves. Electromagnetic radiation also demonstrates properties of particles called photons. The energy of a photon is related to the frequency (or alternatively, the wavelength) of the radiation as $E = h\nu$ (or $E = \frac{hc}{\lambda}$), where h is Planck's constant. That light demonstrates both wavelike and particle-like behavior is known as wave-particle duality. All forms of electromagnetic radiation share these properties, although various forms including X-rays, visible light, microwaves, and radio waves interact differently with matter and have very different practical applications. Electromagnetic radiation can be generated by

exciting matter to higher energies, such as by heating it. The emitted light can be either continuous (incandescent sources like the sun) or discrete (from specific types of excited atoms). Continuous spectra often have distributions that can be approximated as blackbody radiation at some appropriate temperature. The line spectrum of hydrogen can be obtained by passing the light from an electrified tube of hydrogen gas through a prism. This line spectrum was simple enough that an empirical formula called the Rydberg formula could be derived from the spectrum. Three historically important paradoxes from the late 19th and early 20th centuries that could not be explained within the existing framework of classical mechanics and classical electromagnetism were the blackbody problem, the photoelectric effect, and the discrete spectra of atoms. The resolution of these paradoxes ultimately led to quantum theories that superseded the classical theories.

3.2 The Bohr Model

Bohr incorporated Planck's and Einstein's quantization ideas into a model of the hydrogen atom that resolved the paradox of atom stability and discrete spectra. The Bohr model of the hydrogen atom explains the connection between the quantization of photons and the quantized emission from atoms. Bohr described the hydrogen atom in terms of an electron moving in a circular orbit about a nucleus. He postulated that the electron was restricted to certain orbits characterized by discrete energies. Transitions between these allowed orbits result in the absorption or emission of photons. When an electron moves from a higher-energy orbit to a more stable one, energy is emitted in the form of a photon. To move an electron from a stable orbit to a more excited one, a photon of energy must be absorbed. Using the Bohr model, we can calculate the energy of an electron and the radius of its orbit in any one-electron system.

3.3 Development of Quantum Theory

Macroscopic objects act as particles. Microscopic objects (such as electrons) have properties of both a particle and a wave. Their exact trajectories cannot be determined. The quantum mechanical model of atoms describes the three-dimensional position of the electron in a *probabilistic* manner according to a mathematical function called a wavefunction, often denoted as ψ . Atomic wavefunctions are also called orbitals. The squared magnitude of the wavefunction describes the distribution of the probability of finding the electron in a particular region in space. Therefore, atomic orbitals describe the areas in an atom where electrons are most likely to be found.

An atomic orbital is characterized by three quantum numbers. The principal quantum number, n , can be any positive integer. The general region for value of energy of the orbital and the average distance of an electron from the nucleus are related to n . Orbitals having the same value of n are said to be in the same shell. The secondary (angular momentum) quantum number, l , can have any integer value from 0 to $n - 1$. This quantum number describes the shape or type of the orbital. Orbitals with the same principal quantum number and the same l value belong to the same subshell. The magnetic quantum number, m_l , with $2l + 1$ values ranging from $-l$ to $+l$, describes the orientation of the orbital in space. In addition, each electron has a spin quantum number, m_s , that can be equal to $\pm \frac{1}{2}$. No two electrons in the same atom can have the same set of values for all the four quantum numbers.

3.4 Electronic Structure of Atoms (Electron Configurations)

The relative energy of the subshells determine the order in which atomic orbitals are filled ($1s$, $2s$, $2p$, $3s$, $3p$, $4s$, $3d$, $4p$, and so on). Electron configurations and orbital diagrams can be determined by applying the Pauli exclusion principle (no two electrons can have the same set of four quantum numbers) and Hund's rule (whenever possible, electrons retain unpaired spins in degenerate orbitals).

Electrons in the outermost orbitals, called valence electrons, are responsible for most of the chemical behavior of elements. In the periodic table, elements with analogous valence electron configurations usually occur within the same group. There are some exceptions to the predicted filling order, particularly when half-filled or completely filled orbitals can be formed. The periodic table can be divided into three categories based on the orbital in which the last electron to be added is placed: main group elements (s and p orbitals), transition elements (d orbitals), and inner transition elements (f orbitals).

3.5 Periodic Variations in Element Properties

Electron configurations allow us to understand many periodic trends. Covalent radius increases as we move down a group because the n level (orbital size) increases. Covalent radius mostly decreases as we move left to right across a period because the effective nuclear charge experienced by the electrons increases, and the electrons are pulled in tighter to the nucleus. Anionic radii are larger than the parent atom, while cationic radii are smaller, because the number of valence electrons has changed while the nuclear charge has remained constant. Ionization energy (the energy associated with forming a cation) decreases down a group and mostly increases across a period because it is easier to remove an electron from a larger, higher energy orbital. Electron affinity (the energy associated with forming an anion) is more favorable (exothermic) when electrons are placed into lower energy orbitals, closer to the nucleus. Therefore, electron affinity becomes increasingly negative as we move left to right across the periodic table and decreases as we move down a group. For both IE and electron affinity data, there are exceptions to the trends when dealing with completely filled or half-filled subshells.

3.6 The Periodic Table

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

3.7 Molecular and Ionic Compounds

Metals (particularly those in groups 1 and 2) tend to lose the number of electrons that would leave them with the same number of electrons as in the preceding noble gas in the periodic table. By this means, a positively charged ion is formed. Similarly, nonmetals (especially those in groups 16 and 17, and, to a lesser extent, those in Group 15) can gain the number of electrons needed to provide atoms with the same number of electrons as in the next noble gas in the periodic table. Thus, nonmetals tend to form negative ions. Positively charged ions are called cations, and negatively charged ions are called anions. Ions can be either monatomic (containing only one atom) or polyatomic (containing more than one atom).

Compounds that contain ions are called ionic compounds. Ionic compounds generally form from metals and nonmetals. Compounds that do not contain ions, but instead consist of atoms bonded tightly together in molecules (uncharged groups of atoms that behave as a single unit), are called covalent compounds. Covalent compounds usually form from two nonmetals.

Exercises

3.1 Electromagnetic Energy

1. The light produced by a red neon sign is due to the emission of light by excited neon atoms. Qualitatively describe the spectrum produced by passing light from a neon lamp through a prism.
2. An FM radio station found at 103.1 on the FM dial broadcasts at a frequency of $1.031 \times 10^8 \text{ s}^{-1}$ (103.1 MHz). What is the wavelength of these radio waves in meters?
3. FM-95, an FM radio station, broadcasts at a frequency of $9.51 \times 10^7 \text{ s}^{-1}$ (95.1 MHz). What is the wavelength of these radio waves in meters?
4. A bright violet line occurs at 435.8 nm in the emission spectrum of mercury vapor. What amount of energy, in joules, must be released by an electron in a mercury atom to produce a photon of this light?
5. Light with a wavelength of 614.5 nm looks orange. What is the energy, in joules, per photon of this orange light? What is the energy in eV ($1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$)?

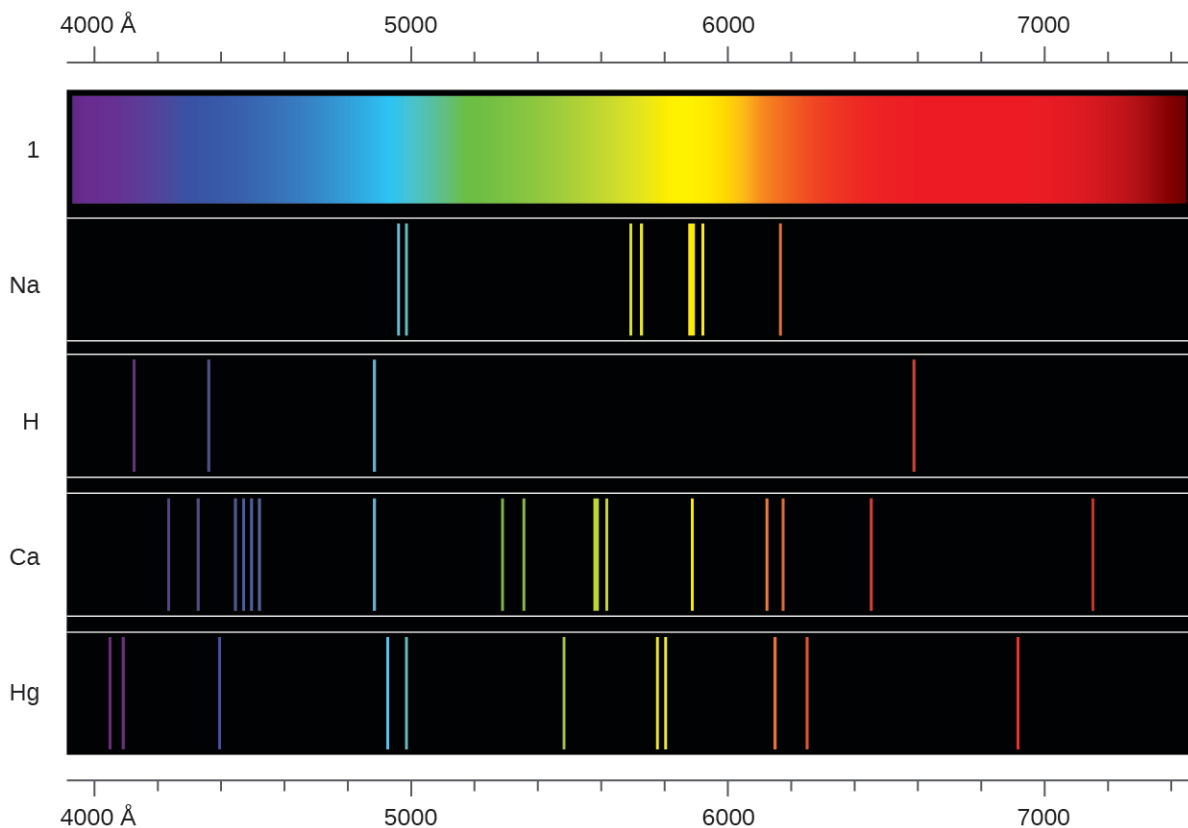
6. Heated lithium atoms emit photons of light with an energy of 2.961×10^{-19} J. Calculate the frequency and wavelength of one of these photons. What is the total energy in 1 mole of these photons? What is the color of the emitted light?
7. A photon of light produced by a surgical laser has an energy of 3.027×10^{-19} J. Calculate the frequency and wavelength of the photon. What is the total energy in 1 mole of photons? What is the color of the emitted light?
8. When rubidium ions are heated to a high temperature, two lines are observed in its line spectrum at wavelengths (a) 7.9×10^{-7} m and (b) 4.2×10^{-7} m. What are the frequencies of the two lines? What color do we see when we heat a rubidium compound?
9. The emission spectrum of cesium contains two lines whose frequencies are (a) 3.45×10^{14} Hz and (b) 6.53×10^{14} Hz. What are the wavelengths and energies per photon of the two lines? What color are the lines?
10. Photons of infrared radiation are responsible for much of the warmth we feel when holding our hands before a fire. These photons will also warm other objects. How many infrared photons with a wavelength of 1.5×10^{-6} m must be absorbed by the water to warm a cup of water (175 g) from 25.0 °C to 40 °C?
11. One of the radiographic devices used in a dentist's office emits an X-ray of wavelength 2.090×10^{-11} m. What is the energy, in joules, and frequency of this X-ray?
12. The eyes of certain reptiles pass a single visual signal to the brain when the visual receptors are struck by photons of a wavelength of 850 nm. If a total energy of 3.15×10^{-14} J is required to trip the signal, what is the minimum number of photons that must strike the receptor?
13. RGB color television and computer displays use cathode ray tubes that produce colors by mixing red, green, and blue light. If we look at the screen with a magnifying glass, we can see individual dots turn on and off as the colors change. Using a spectrum of visible light, determine the approximate wavelength of each of these colors. What is the frequency and energy of a photon of each of these colors?
14. Answer the following questions about a Blu-ray laser:
- (a) The laser on a Blu-ray player has a wavelength of 405 nm. In what region of the electromagnetic spectrum is this radiation? What is its frequency?
- (b) A Blu-ray laser has a power of 5 milliwatts ($1 \text{ watt} = 1 \text{ J s}^{-1}$). How many photons of light are produced by the laser in 1 hour?
- (c) The ideal resolution of a player using a laser (such as a Blu-ray player), which determines how close together data can be stored on a compact disk, is determined using the following formula: $\text{Resolution} = 0.60(\lambda/\text{NA})$, where λ is the wavelength of the laser and NA is the numerical aperture. Numerical aperture is a measure of the size of the spot of light on the disk; the larger the NA, the smaller the spot. In a typical Blu-ray system, $\text{NA} = 0.95$. If the 405-nm laser is used in a Blu-ray player, what is the closest that information can be stored on a Blu-ray disk?
- (d) The data density of a Blu-ray disk using a 405-nm laser is 1.5×10^7 bits mm^{-2} . Disks have an outside diameter of 120 mm and a hole of 15-mm diameter. How many data bits can be contained on the disk? If a Blu-ray disk can hold 9,400,000 pages of text, how many data bits are needed for a typed page? (Hint: Determine the area of the disk that is available to hold data. The area inside a circle is given by $A = \pi r^2$, where the radius r is one-half of the diameter.)
15. What is the threshold frequency for sodium metal if a photon with frequency $6.66 \times 10^{14} \text{ s}^{-1}$ ejects an electron with 7.74×10^{-20} J kinetic energy? Will the photoelectric effect be observed if sodium is exposed to orange light?

3.2 The Bohr Model

16. Why is the electron in a Bohr hydrogen atom bound less tightly when it has a quantum number of 3 than when it has a quantum number of 1?
17. What does it mean to say that the energy of the electrons in an atom is quantized?
18. Using the Bohr model, determine the energy, in joules, necessary to ionize a ground-state hydrogen atom. Show your calculations.

- 19.** The electron volt (eV) is a convenient unit of energy for expressing atomic-scale energies. It is the amount of energy that an electron gains when subjected to a potential of 1 volt; $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$. Using the Bohr model, determine the energy, in electron volts, of the photon produced when an electron in a hydrogen atom moves from the orbit with $n = 5$ to the orbit with $n = 2$. Show your calculations.
- 20.** Using the Bohr model, determine the lowest possible energy, in joules, for the electron in the Li^{2+} ion.
- 21.** Using the Bohr model, determine the lowest possible energy for the electron in the He^+ ion.
- 22.** Using the Bohr model, determine the energy of an electron with $n = 6$ in a hydrogen atom.
- 23.** Using the Bohr model, determine the energy of an electron with $n = 8$ in a hydrogen atom.
- 24.** How far from the nucleus in angstroms ($1 \text{ angstrom} = 1 \times 10^{-10} \text{ m}$) is the electron in a hydrogen atom if it has an energy of $-8.72 \times 10^{-20} \text{ J}$?
- 25.** What is the radius, in angstroms, of the orbital of an electron with $n = 8$ in a hydrogen atom?
- 26.** Using the Bohr model, determine the energy in joules of the photon produced when an electron in a He^+ ion moves from the orbit with $n = 5$ to the orbit with $n = 2$.
- 27.** Using the Bohr model, determine the energy in joules of the photon produced when an electron in a Li^{2+} ion moves from the orbit with $n = 2$ to the orbit with $n = 1$.
- 28.** Consider a large number of hydrogen atoms with electrons randomly distributed in the $n = 1, 2, 3,$ and 4 orbits.
- (a) How many different wavelengths of light are emitted by these atoms as the electrons fall into lower-energy orbitals?
- (b) Calculate the lowest and highest energies of light produced by the transitions described in part (a).
- (c) Calculate the frequencies and wavelengths of the light produced by the transitions described in part (b).
- 29.** How are the Bohr model and the Rutherford model of the atom similar? How are they different?

30. The spectra of hydrogen and of calcium are shown here.



What causes the lines in these spectra? Why are the colors of the lines different? Suggest a reason for the observation that the spectrum of calcium is more complicated than the spectrum of hydrogen.

3.3 Development of Quantum Theory

31. How are the Bohr model and the quantum mechanical model of the hydrogen atom similar? How are they different?
32. What are the allowed values for each of the four quantum numbers: n , l , m_l , and m_s ?
33. Describe the properties of an electron associated with each of the following four quantum numbers: n , l , m_l , and m_s .
34. Answer the following questions:
- Without using quantum numbers, describe the differences between the shells, subshells, and orbitals of an atom.
 - How do the quantum numbers of the shells, subshells, and orbitals of an atom differ?
35. Identify the subshell in which electrons with the following quantum numbers are found:
- $n = 2, l = 1$
 - $n = 4, l = 2$
 - $n = 6, l = 0$
36. Which of the subshells described in the previous question contain degenerate orbitals? How many degenerate orbitals are in each?

37. Identify the subshell in which electrons with the following quantum numbers are found:

(a) $n = 3, l = 2$

(b) $n = 1, l = 0$

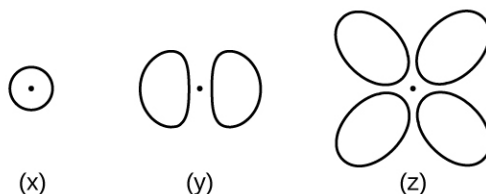
(c) $n = 4, l = 3$

38. Which of the subshells described in the previous question contain degenerate orbitals? How many degenerate orbitals are in each?

39. Sketch the boundary surface of a $d_{x^2-y^2}$ and a p_y orbital. Be sure to show and label the axes.

40. Sketch the p_x and d_{xz} orbitals. Be sure to show and label the coordinates.

41. Consider the orbitals shown here in outline.



(a) What is the maximum number of electrons contained in an orbital of type (x)? Of type (y)? Of type (z)?

(b) How many orbitals of type (x) are found in a shell with $n = 2$? How many of type (y)? How many of type (z)?

(c) Write a set of quantum numbers for an electron in an orbital of type (x) in a shell with $n = 4$. Of an orbital of type (y) in a shell with $n = 2$. Of an orbital of type (z) in a shell with $n = 3$.

(d) What is the smallest possible n value for an orbital of type (x)? Of type (y)? Of type (z)?

(e) What are the possible l and m_l values for an orbital of type (x)? Of type (y)? Of type (z)?

42. State the Heisenberg uncertainty principle. Describe briefly what the principle implies.

43. How many electrons could be held in the second shell of an atom if the spin quantum number m_s could have three values instead of just two? (Hint: Consider the Pauli exclusion principle.)

44. Which of the following equations describe particle-like behavior? Which describe wavelike behavior? Do any involve both types of behavior? Describe the reasons for your choices.

(a) $c = \lambda\nu$

(b) $E = \frac{mv^2}{2}$

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

(d) $E = h\nu$

(e) $\lambda = \frac{h}{mv}$

45. Write a set of quantum numbers for each of the electrons with an n of 4 in a Se atom.

3.4 Electronic Structure of Atoms (Electron Configurations)

46. Read the labels of several commercial products and identify monatomic ions of at least four transition elements contained in the products. Write the complete electron configurations of these cations.

47. Read the labels of several commercial products and identify monatomic ions of at least six main group elements contained in the products. Write the complete electron configurations of these cations and anions.

48. Using complete subshell notation (not abbreviations, $1s^22s^22p^6$, and so forth), predict the electron configuration of each of the following atoms:

- (a) C
- (b) P
- (c) V
- (d) Sb
- (e) Sm

49. Using complete subshell notation ($1s^22s^22p^6$, and so forth), predict the electron configuration of each of the following atoms:

- (a) N
- (b) Si
- (c) Fe
- (d) Te
- (e) Tb

50. Is $1s^22s^22p^6$ the symbol for a macroscopic property or a microscopic property of an element? Explain your answer.

51. What additional information do we need to answer the question “Which ion has the electron configuration $1s^22s^22p^63s^23p^6$ ”?

52. Draw the orbital diagram for the valence shell of each of the following atoms:

- (a) C
- (b) P
- (c) V
- (d) Sb
- (e) Ru

53. Use an orbital diagram to describe the electron configuration of the valence shell of each of the following atoms:

- (a) N
- (b) Si
- (c) Fe
- (d) Te
- (e) Mo

54. Using complete subshell notation ($1s^22s^22p^6$, and so forth), predict the electron configurations of the following ions.

- (a) N^{3-}
- (b) Ca^{2+}
- (c) S^-
- (d) Cs^{2+}
- (e) Cr^{2+}
- (f) Gd^{3+}

55. Which atom has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^2$?
56. Which atom has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$?
57. Which ion with a +1 charge has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$? Which ion with a -2 charge has this configuration?
58. Which of the following atoms contains only three valence electrons: Li, B, N, F, Ne?
59. Which of the following has two unpaired electrons?
- (a) Mg
- (b) Si
- (c) S
- (d) Both Mg and S
- (e) Both Si and S.
60. Which atom would be expected to have a half-filled $6p$ subshell?
61. Which atom would be expected to have a half-filled $4s$ subshell?
62. In one area of Australia, the cattle did not thrive despite the presence of suitable forage. An investigation showed the cause to be the absence of sufficient cobalt in the soil. Cobalt forms cations in two oxidation states, Co^{2+} and Co^{3+} . Write the electron structure of the two cations.
63. Thallium was used as a poison in the Agatha Christie mystery story "The Pale Horse." Thallium has two possible cationic forms, +1 and +3. The +1 compounds are the more stable. Write the electron structure of the +1 cation of thallium.
64. Write the electron configurations for the following atoms or ions:
- (a) B^{3+}
- (b) O^-
- (c) Cl^{3+}
- (d) Ca^{2+}
- (e) Ti
65. Cobalt-60 and iodine-131 are radioactive isotopes commonly used in nuclear medicine. How many protons, neutrons, and electrons are in atoms of these isotopes? Write the complete electron configuration for each isotope.
66. Write a set of quantum numbers for each of the electrons with an n of 3 in a Sc atom.

3.5 Periodic Variations in Element Properties

67. Based on their positions in the periodic table, predict which has the smallest atomic radius: Mg, Sr, Si, Cl, I.
68. Based on their positions in the periodic table, predict which has the largest atomic radius: Li, Rb, N, F, I.
69. Based on their positions in the periodic table, predict which has the largest first ionization energy: Mg, Ba, B, O, Te.
70. Based on their positions in the periodic table, predict which has the smallest first ionization energy: Li, Cs, N, F, I.
71. Based on their positions in the periodic table, rank the following atoms in order of increasing first ionization energy: F, Li, N, Rb
72. Based on their positions in the periodic table, rank the following atoms in order of increasing first ionization energy: Mg, O, S, Si
73. Atoms of which group in the periodic table have a valence shell electron configuration of $ns^2 np^3$?
74. Atoms of which group in the periodic table have a valence shell electron configuration of ns^2 ?
75. Based on their positions in the periodic table, list the following atoms in order of increasing radius: Mg, Ca, Rb, Cs.

76. Based on their positions in the periodic table, list the following atoms in order of increasing radius: Sr, Ca, Si, Cl.
77. Based on their positions in the periodic table, list the following ions in order of increasing radius: K^+ , Ca^{2+} , Al^{3+} , Si^{4+} .
78. List the following ions in order of increasing radius: Li^+ , Mg^{2+} , Br^- , Te^{2-} .
79. Which atom and/or ion is (are) isoelectronic with Br^+ : Se^{2+} , Se, As^- , Kr, Ga^{3+} , Cl^- ?
80. Which of the following atoms and ions is (are) isoelectronic with S^{2+} : Si^{4+} , Cl^{3+} , Ar, As^{3+} , Si, Al^{3+} ?
81. Compare both the numbers of protons and electrons present in each to rank the following ions in order of increasing radius: As^{3-} , Br^- , K^+ , Mg^{2+} .
82. Of the five elements Al, Cl, I, Na, Rb, which has the most exothermic reaction? (E represents an atom.) What name is given to the energy for the reaction? Hint: Note the process depicted does *not* correspond to electron affinity.)
$$E^+(g) + e^- \longrightarrow E(g)$$
83. Of the five elements Sn, Si, Sb, O, Te, which has the most endothermic reaction? (E represents an atom.) What name is given to the energy for the reaction?
$$E(g) \longrightarrow E^+(g) + e^-$$
84. The ionic radii of the ions S^{2-} , Cl^- , and K^+ are 184, 181, 138 pm respectively. Explain why these ions have different sizes even though they contain the same number of electrons.
85. Which main group atom would be expected to have the lowest second ionization energy?
86. Explain why Al is a member of group 13 rather than group 3?

3.6 The Periodic Table

87. Using the periodic table, classify each of the following elements as a metal or a nonmetal, and then further classify each as a main-group (representative) element, transition metal, or inner transition metal:
- (a) uranium
 - (b) bromine
 - (c) strontium
 - (d) neon
 - (e) gold
 - (f) americium
 - (g) rhodium
 - (h) sulfur
 - (i) carbon
 - (j) potassium

88. Using the periodic table, classify each of the following elements as a metal or a nonmetal, and then further classify each as a main-group (representative) element, transition metal, or inner transition metal:

- (a) cobalt
- (b) europium
- (c) iodine
- (d) indium
- (e) lithium
- (f) oxygen
- (g) cadmium
- (h) terbium
- (i) rhenium

89. Using the periodic table, identify the lightest member of each of the following groups:

- (a) noble gases
- (b) alkaline earth metals
- (c) alkali metals
- (d) chalcogens

90. Using the periodic table, identify the heaviest member of each of the following groups:

- (a) alkali metals
- (b) chalcogens
- (c) noble gases
- (d) alkaline earth metals

91. Use the periodic table to give the name and symbol for each of the following elements:

- (a) the noble gas in the same period as germanium
- (b) the alkaline earth metal in the same period as selenium
- (c) the halogen in the same period as lithium
- (d) the chalcogen in the same period as cadmium

92. Use the periodic table to give the name and symbol for each of the following elements:

- (a) the halogen in the same period as the alkali metal with 11 protons
- (b) the alkaline earth metal in the same period with the neutral noble gas with 18 electrons
- (c) the noble gas in the same row as an isotope with 30 neutrons and 25 protons
- (d) the noble gas in the same period as gold

93. Write a symbol for each of the following neutral isotopes. Include the atomic number and mass number for each.

- (a) the alkali metal with 11 protons and a mass number of 23
- (b) the noble gas element with 75 neutrons in its nucleus and 54 electrons in the neutral atom
- (c) the isotope with 33 protons and 40 neutrons in its nucleus
- (d) the alkaline earth metal with 88 electrons and 138 neutrons

94. Write a symbol for each of the following neutral isotopes. Include the atomic number and mass number for each.

- (a) the chalcogen with a mass number of 125
- (b) the halogen whose longest-lived isotope is radioactive
- (c) the noble gas, used in lighting, with 10 electrons and 10 neutrons
- (d) the lightest alkali metal with three neutrons

3.7 Molecular and Ionic Compounds

95. Using the periodic table, predict whether the following chlorides are ionic or covalent: KCl, NCl₃, ICl, MgCl₂, PCl₅, and CCl₄.

96. Using the periodic table, predict whether the following chlorides are ionic or covalent: SiCl₄, PCl₃, CaCl₂, CsCl, CuCl₂, and CrCl₃.

97. For each of the following compounds, state whether it is ionic or covalent. If it is ionic, write the symbols for the ions involved:

- (a) NF₃
- (b) BaO,
- (c) (NH₄)₂CO₃
- (d) Sr(H₂PO₄)₂
- (e) IBr
- (f) Na₂O

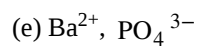
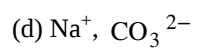
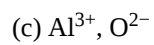
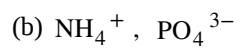
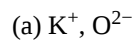
98. For each of the following compounds, state whether it is ionic or covalent, and if it is ionic, write the symbols for the ions involved:

- (a) KClO₄
- (b) MgC₂H₃O₂
- (c) H₂S
- (d) Ag₂S
- (e) N₂Cl₄
- (f) Co(NO₃)₂

99. For each of the following pairs of ions, write the symbol for the formula of the compound they will form.

- (a) Ca²⁺, S²⁻
- (b) NH₄⁺, SO₄²⁻
- (c) Al³⁺, Br⁻
- (d) Na⁺, HPO₄²⁻
- (e) Mg²⁺, PO₄³⁻

100. For each of the following pairs of ions, write the symbol for the formula of the compound they will form.



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). (credit middle: modification of work by “Petey21”/Wikimedia Commons; credit right: modification of work by Bill Morrow)

Chapter Outline

- 4.1 Ionic Bonding
- 4.2 Covalent Bonding
- 4.3 Chemical Nomenclature
- 4.4 Lewis Symbols and Structures
- 4.5 Formal Charges and Resonance
- 4.6 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.

4.1 Ionic Bonding

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, 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). (credit a: modification of work by “Jurii”/Wikimedia Commons)

The Formation of Ionic Compounds

Binary ionic compounds are composed of just two elements: a metal (which forms the cations) and a nonmetal (which forms the anions). For example, NaCl is a binary ionic compound. We can think about the formation of such compounds in terms of the periodic properties of the elements. Many metallic elements have relatively low ionization potentials and lose electrons easily. These elements lie to the left in a period or near the bottom of a group on the periodic table. Nonmetal atoms have relatively high electron affinities and thus readily gain electrons lost by metal atoms, thereby filling their valence shells. Nonmetallic elements are found in the upper-right corner of the periodic table.

As all substances must be electrically neutral, the total number of positive charges on the cations of an ionic compound must equal the total number of negative charges on its anions. The formula of an ionic compound represents the simplest ratio of the numbers of ions necessary to give identical numbers of positive and negative charges. For example, the formula for aluminum oxide, Al_2O_3 , indicates that this ionic compound contains two aluminum cations, Al^{3+} , for every three oxide anions, O^{2-} [thus, $(2 \times +3) + (3 \times -2) = 0$].

It is important to note, however, that the formula for an ionic compound does *not* represent the physical arrangement of its ions. It is incorrect to refer to a sodium chloride (NaCl) “molecule” because there is not a single ionic bond, per se, between any specific pair of sodium and chloride ions. The attractive forces between ions are isotropic—the same in all directions—meaning that any particular ion is equally attracted to all of the nearby ions of opposite charge. This results in the ions arranging themselves into a tightly bound, three-dimensional lattice structure. Sodium chloride, for example, consists of a regular arrangement of equal numbers of Na^+ cations and Cl^- anions (**Figure 4.3**).

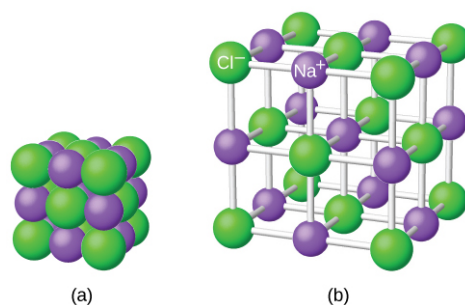
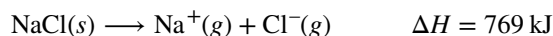


Figure 4.3 The atoms in sodium chloride (common table salt) are arranged to (a) maximize opposite charges interacting. The smaller spheres represent sodium ions, the larger ones represent chloride ions. In the expanded view (b), the geometry can be seen more clearly. Note that each ion is “bonded” to all of the surrounding ions—six in this case.

The strong electrostatic attraction between Na^+ and Cl^- ions holds them tightly together in solid NaCl . It requires 769 kJ of energy to dissociate one mole of solid NaCl into separate gaseous Na^+ and Cl^- ions:



Electronic Structures of Cations

When forming a cation, an atom of a main group element tends to lose all of its valence electrons, thus assuming the electronic structure of the noble gas that precedes it in the periodic table. For groups 1 (the alkali metals) and 2 (the alkaline earth metals), the group numbers are equal to the numbers of valence shell electrons and, consequently, to the charges of the cations formed from atoms of these elements when all valence shell electrons are removed. For example, calcium is a group 2 element whose neutral atoms have 20 electrons and a ground state electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$. When a Ca atom loses both of its valence electrons, the result is a cation with 18 electrons, a 2+ charge, and an electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6$. The Ca^{2+} ion is therefore isoelectronic with the noble gas Ar.

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 (Al^{3+}).

Exceptions to the expected behavior involve elements toward the bottom of the groups. In addition to the expected ions Tl^{3+} , Sn^{4+} , Pb^{4+} , and Bi^{5+} , a partial loss of these atoms’ valence shell electrons can also lead to the formation of Tl^+ , Sn^{2+} , Pb^{2+} , and Bi^{3+} ions. The formation of these 1+, 2+, and 3+ cations is ascribed to the **inert pair effect**, which reflects the relatively low energy of the valence *s*-electron pair for atoms of the heavy elements of groups 13, 14, and 15. Mercury (group 12) also exhibits an unexpected behavior: it forms a diatomic ion, Hg_2^{2+} (an ion formed

from two mercury atoms, with an Hg-Hg bond), in addition to the expected monatomic ion Hg^{2+} (formed from only one mercury atom).

Transition and inner transition metal elements behave differently than main group elements. Most transition metal cations have $2+$ or $3+$ charges that result from the loss of their outermost s electron(s) first, sometimes followed by the loss of one or two d electrons from the next-to-outermost shell. For example, iron ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$) forms the ion Fe^{2+} ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$) by the loss of the $4s$ electron and the ion 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.

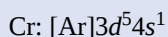
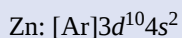
Example 4.1

Determining the Electronic Structures of Cations

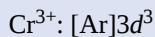
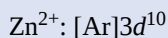
There are at least 14 elements categorized as “essential trace elements” for the human body. They are called “essential” because they are required for healthy bodily functions, “trace” because they are required only in small amounts, and “elements” in spite of the fact that they are really ions. Two of these essential trace elements, chromium and zinc, are required as Cr^{3+} and 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

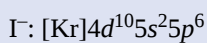
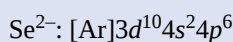
Most monatomic anions form when a neutral nonmetal atom gains enough electrons to completely fill its outer s and p orbitals, thereby reaching the electron configuration of the next noble gas. Thus, it is simple to determine the charge on such a negative ion: The charge is equal to the number of electrons 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 $2-$ (O^{2-}).

Example 4.2

Determining the Electronic Structure of Anions

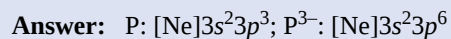
Selenium and iodine are two essential trace elements that form anions. Write the electron configurations of the anions.

Solution



Check Your Learning

Write the electron configurations of a phosphorus atom and its negative ion. Give the charge on the anion.



4.2 Covalent Bonding

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 H_2 molecule; each hydrogen atom in the H_2 molecule has two electrons stabilizing it, giving each atom the same number of valence electrons as the noble gas He.

Compounds that contain covalent bonds exhibit different physical properties than ionic compounds. Because the attraction between molecules, which are electrically neutral, is weaker than that between electrically charged ions, covalent compounds generally have much lower melting and boiling points than ionic compounds. In fact, many covalent compounds are liquids or gases at room temperature, and, in their solid states, they are typically much softer than ionic solids. Furthermore, whereas ionic compounds are good conductors of electricity when dissolved in water, most covalent compounds 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, 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.

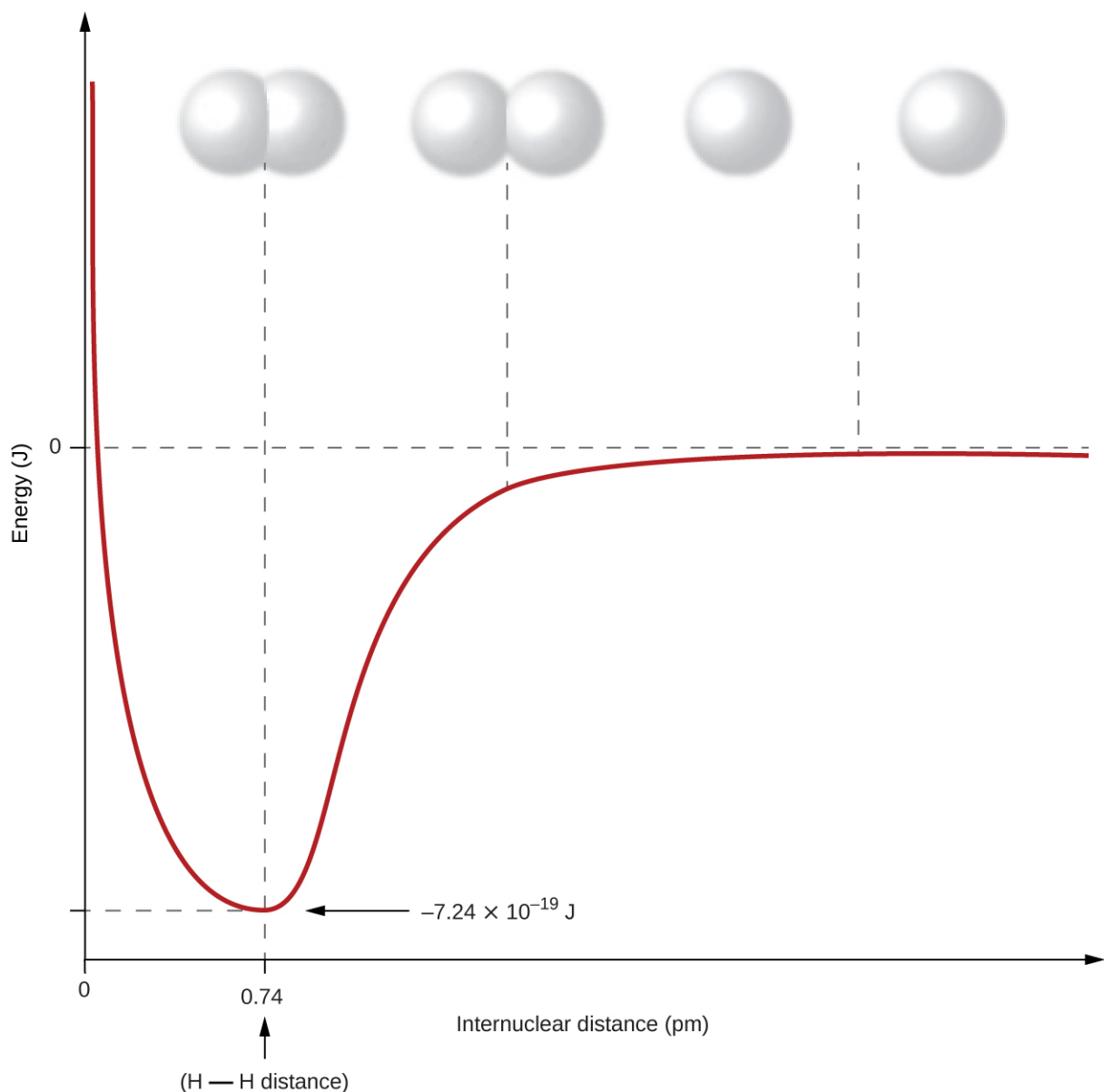


Figure 4.4 The potential energy of two separate hydrogen atoms (right) decreases as they approach each other, and the single electrons on each atom are shared to form a covalent bond. The bond length is the internuclear distance at which the lowest potential energy is achieved.

It is essential to remember that energy must be added to break chemical bonds (an endothermic process), whereas forming chemical bonds releases energy (an exothermic process). In the case of H_2 , the covalent bond is very strong; a large amount of energy, 436 kJ, must be added to break the bonds in one mole of hydrogen molecules and cause the atoms to separate:



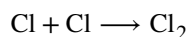
Conversely, the same amount of energy is released when one mole of H_2 molecules forms from two moles of H atoms:



Pure vs. Polar Covalent Bonds

If the atoms that form a covalent bond are identical, as in H_2 , Cl_2 , and other diatomic molecules, then the electrons in the bond must be shared equally. We refer to this as a **pure covalent bond**. Electrons shared in pure covalent bonds have an equal probability of being near each nucleus.

In the case of Cl_2 , each atom starts off with seven valence electrons, and each Cl shares one electron with the other, forming one covalent bond:



The total number of electrons around each individual atom consists of six nonbonding electrons and two shared (i.e., bonding) electrons for eight total electrons, matching the number of valence electrons in the noble gas argon. Since the bonding atoms are identical, Cl_2 also features a pure covalent bond.

When the atoms linked by a covalent bond are different, the bonding electrons are shared, but no longer equally. Instead, the bonding electrons are more attracted to one atom than the other, giving rise to a shift of electron density toward that atom. This unequal distribution of electrons is known as a **polar covalent bond**, characterized by a partial positive charge on one atom and a partial negative charge on the other. The atom that attracts the electrons more strongly acquires the partial negative charge and vice versa. For example, the electrons in the H–Cl bond of a hydrogen chloride molecule spend more time near the chlorine atom than near the hydrogen atom. Thus, in an HCl molecule, the chlorine atom carries a partial negative charge and the hydrogen atom has a partial positive charge. **Figure 4.5** 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 H_2 nonpolar bond.

We sometimes designate the positive and negative atoms in a polar covalent bond using a lowercase Greek letter “delta,” δ , with a plus sign or minus sign to indicate whether the atom has a partial positive charge ($\delta+$) or a partial negative charge ($\delta-$). This symbolism is shown for the H–Cl molecule in **Figure 4.5**.

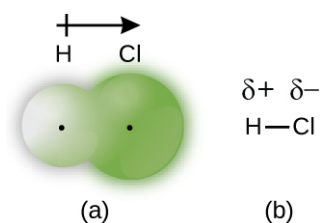


Figure 4.5 (a) The distribution of electron density in the HCl molecule is uneven. The electron density is greater around the chlorine nucleus. The small, black dots indicate the location of the hydrogen and chlorine nuclei in the molecule. (b) Symbols $\delta+$ and $\delta-$ indicate the polarity of the H–Cl bond.

Electronegativity

Whether a bond is nonpolar or polar covalent is determined by a property of the bonding atoms called **electronegativity**. Electronegativity is a measure of the tendency of an atom to attract electrons (or electron density) towards itself. It determines how the shared electrons are distributed between the two atoms in a bond. The more strongly an atom attracts the electrons in its bonds, the larger its electronegativity. Electrons in a polar covalent bond are shifted toward the more electronegative atom; thus, the more electronegative atom is the one with the partial negative charge. The greater the difference in electronegativity, the more polarized the electron distribution and the

larger the partial charges of the atoms.

Figure 4.6 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_2 do exist, they can only be formed under extreme conditions, and thus they do not fit neatly into the general model of electronegativity.)

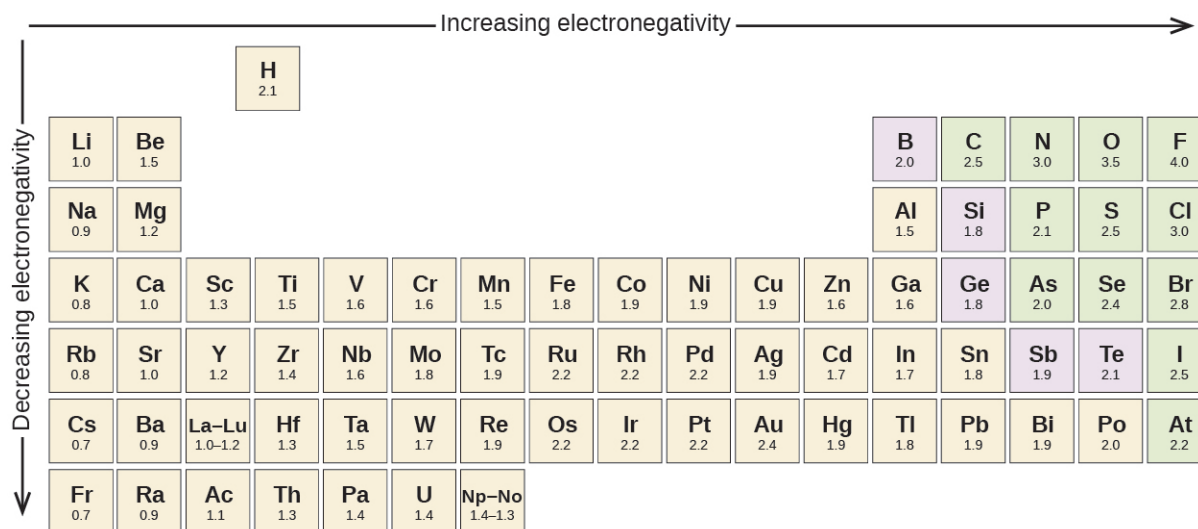


Figure 4.6 The electronegativity values derived by Pauling follow predictable periodic trends, with the higher electronegativities toward the upper right of the periodic table.

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.

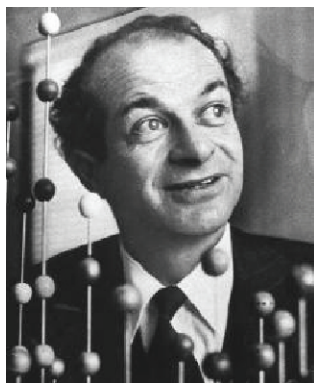


Figure 4.7 Linus Pauling (1901–1994) made many important contributions to the field of chemistry. He was also a prominent activist, publicizing issues related to health and nuclear weapons.

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.

Electronegativity and Bond Type

The absolute value of the difference in electronegativity (ΔEN) of two bonded atoms provides a rough measure of the polarity to be expected in the bond and, thus, the bond type. When the difference is very small or zero, the bond is covalent and nonpolar. When it is large, the bond is polar covalent or ionic. The absolute values of the electronegativity differences between the atoms in the bonds H–H, H–Cl, and Na–Cl are 0 (nonpolar), 0.9 (polar covalent), and 2.1 (ionic), respectively. The degree to which electrons are shared between atoms varies from completely equal (pure covalent bonding) to not at all (ionic bonding). **Figure 4.8** shows the relationship between electronegativity difference and bond type.

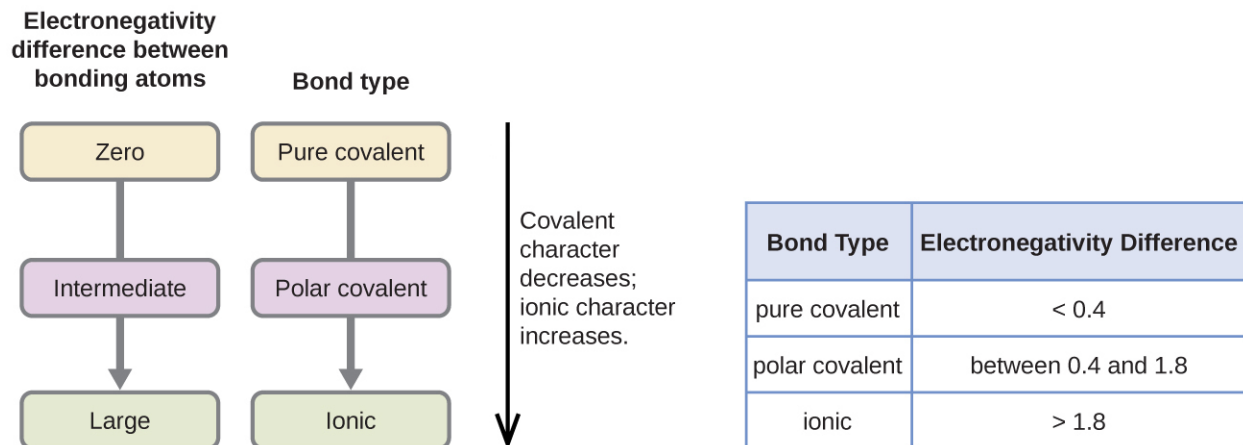


Figure 4.8 As the electronegativity difference increases between two atoms, the bond becomes more ionic.

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 NH₃ 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 MnI₂ have a difference of 1.0, yet both of these substances form ionic compounds.

The best guide to the covalent or ionic character of a bond is to consider the types of atoms involved and their relative positions in the periodic table. Bonds between two nonmetals are generally covalent; bonding between a metal and a nonmetal is often ionic.

Some compounds contain both covalent and ionic bonds. The atoms in polyatomic ions, such as OH⁻, NO₃⁻, and NH₄⁺, 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, KNO₃, contains the K⁺ cation and the polyatomic NO₃⁻ anion. Thus, bonding in potassium nitrate is ionic, resulting from the electrostatic attraction between the ions K⁺ and NO₃⁻, as well as covalent between the nitrogen and oxygen atoms in NO₃⁻.

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 δ^+ and δ^- :

C–H, C–N, C–O, N–H, O–H, S–H

Solution

The polarity of these bonds increases as the absolute value of the electronegativity difference increases. The atom with the δ^- designation is the more electronegative of the two. **Table 4.1** shows these bonds in order of increasing polarity.

Bond Polarity and Electronegativity Difference

Bond	ΔEN	Polarity
C–H	0.4	$\delta^- \delta^+$ C–H
S–H	0.4	$\delta^- \delta^+$ S–H
C–N	0.5	$\delta^+ \delta^-$ C–N
N–H	0.9	$\delta^- \delta^+$ N–H
C–O	1.0	$\delta^+ \delta^-$ C–O
O–H	1.4	$\delta^- \delta^+$ O–H

Table 4.1

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 δ^+ and δ^- .

Answer:

Bond	Electronegativity Difference	Polarity
C–C	0.0	nonpolar
C–H	0.4	$\delta^- \delta^+$ C–H
Si–C	0.7	$\delta^+ \delta^-$ Si–C
Si–O	1.7	$\delta^+ \delta^-$ Si–O

4.3 Chemical Nomenclature

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 NaCl, CaCO₃, and N₂O₄. 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 4.2**.

Names of Some Ionic Compounds

NaCl, sodium chloride	Na ₂ O, sodium oxide
KBr, potassium bromide	CdS, cadmium sulfide
CaI ₂ , calcium iodide	Mg ₃ N ₂ , magnesium nitride
CsF, cesium fluoride	Ca ₃ P ₂ , calcium phosphide
LiCl, lithium chloride	Al ₄ C ₃ , aluminum carbide

Table 4.2

Compounds Containing Polyatomic Ions

Compounds containing polyatomic ions are named similarly to those containing only monatomic ions, i.e., by naming first the cation and then the anion. Examples are shown in **Table 4.3**.

Names of Some Polyatomic Ionic Compounds

KC ₂ H ₃ O ₂ , potassium acetate	NH ₄ Cl, ammonium chloride
NaHCO ₃ , sodium bicarbonate	CaSO ₄ , calcium sulfate
Al ₂ (CO ₃) ₃ , aluminum carbonate	Mg ₃ (PO ₄) ₂ , magnesium phosphate

Table 4.3

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 4.4**. 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.

Everyday Ionic Compounds

Ionic Compound	Use
NaCl, sodium chloride	ordinary table salt
KI, potassium iodide	added to "iodized" salt for thyroid health
NaF, sodium fluoride	ingredient in toothpaste
NaHCO ₃ , sodium bicarbonate	baking soda; used in cooking (and as antacid)
Na ₂ CO ₃ , sodium carbonate	washing soda; used in cleaning agents
NaOCl, sodium hypochlorite	active ingredient in household bleach
CaCO ₃ , calcium carbonate	ingredient in antacids
Mg(OH) ₂ , magnesium hydroxide	ingredient in antacids

Everyday Ionic Compounds

Ionic Compound	Use
$\text{Al}(\text{OH})_3$, aluminum hydroxide	ingredient in antacids
NaOH , sodium hydroxide	lye; used as drain cleaner
K_3PO_4 , potassium phosphate	food additive (many purposes)
MgSO_4 , magnesium sulfate	added to purified water
Na_2HPO_4 , sodium hydrogen phosphate	anti-caking agent; used in powdered products
Na_2SO_3 , sodium sulfite	preservative

Table 4.4

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 FeCl_2 and FeCl_3 . The simplest name, “iron chloride,” will, in this case, be ambiguous, as it does not distinguish between these two compounds. In cases like this, the charge of the metal ion is included as a Roman numeral in parentheses immediately following the metal name. These two compounds are then unambiguously named iron(II) chloride and iron(III) chloride, respectively. Other examples are provided in [Table 4.5](#).

Some Ionic Compounds with Variably Charged Metal Ions

Compound	Name
FeCl_2	iron(II) chloride
FeCl_3	iron(III) chloride
Hg_2O	mercury(I) oxide
HgO	mercury(II) oxide
SnF_2	tin(II) fluoride
SnF_4	tin(IV) fluoride

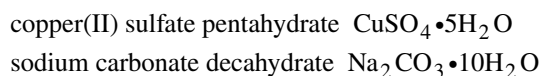
Table 4.5

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

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 4.6**) and ends with “hydrate.” For example, the anhydrous compound copper(II) sulfate also exists as a hydrate containing five water molecules and 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



Nomenclature Prefixes

Number	Prefix		Number	Prefix
1 (sometimes omitted)	mono-		6	hexa-
2	di-		7	hepta-
3	tri-		8	octa-
4	tetra-		9	nona-
5	penta-		10	deca-

Table 4.6

Example 4.4

Naming Ionic Compounds

Name the following ionic compounds:

- (a) Fe_2S_3
- (b) CuSe
- (c) 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 (S^{2-} , Se^{2-} , N^{3-} , Cl^- , and SO_4^{2-}), and the compounds must be neutral. Because the total number of positive charges in each compound must equal the total number of negative charges, the positive ions must be Fe^{3+} , Cu^{2+} , Ga^{3+} , Cr^{3+} , and Ti^{3+} . These charges are used in the names of the metal ions:

- (a) iron(III) sulfide
- (b) copper(II) selenide
- (c) gallium(III) nitride

(d) 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) CrP; (b) HgS; (c) Mn₃(PO₄)₂; (d) Cu₂O; (e) FeCl₃·2H₂O

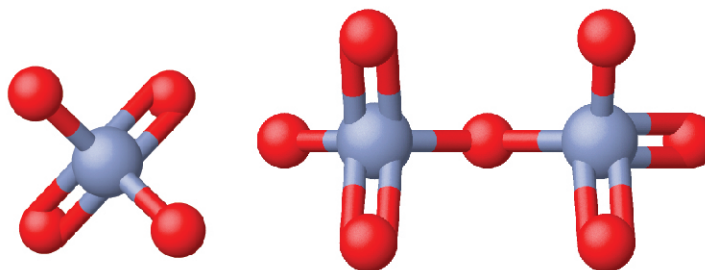
Chemistry in Everyday Life

Erin Brokovich 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 Brokovich* (for which Julia Roberts won an Oscar), Erin and lawyer Edward Masry sued PG&E for contaminating the water near Hinckley in 1993. The settlement they won in 1996—\$333 million—was the largest amount ever awarded for a direct-action lawsuit in the US at that time.



(a)



(b)

Figure 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, CrO₄²⁻ (left), and dichromate, Cr₂O₇²⁻ (right).

Chromium compounds are widely used in industry, such as for chrome plating, in dye-making, as preservatives, and to prevent corrosion in cooling tower water, as occurred near Hinckley. In the environment, chromium exists primarily in either the Cr(III) or Cr(VI) forms. Cr(III), an ingredient of many vitamin and nutritional supplements, forms compounds that are not very soluble in water, and it has low toxicity. 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 CO₂. Since these are different substances with different properties, they cannot both have the same name (they cannot both be called carbon oxide). To deal with this situation, we use a naming method that is somewhat similar to that used for ionic compounds, but with added prefixes to specify the numbers of atoms of each element. The name of the more metallic element (the one farther to the left and/or bottom of the periodic table) is first, followed by the name of the more nonmetallic element (the one farther to the right and/or top) with its ending changed to the suffix *-ide*. The numbers of atoms of each element are designated by the Greek prefixes shown in [Table 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 CO₂ 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 4.7](#).

Names of Some Molecular Compounds Composed of Two Elements

Compound	Name	Compound	Name
SO ₂	sulfur dioxide	BCl ₃	boron trichloride
SO ₃	sulfur trioxide	SF ₆	sulfur hexafluoride
NO ₂	nitrogen dioxide	PF ₅	phosphorus pentafluoride
N ₂ O ₄	dinitrogen tetroxide	P ₄ O ₁₀	tetraphosphorus decaoxide
N ₂ O ₅	dinitrogen pentoxide	IF ₇	iodine heptafluoride

Table 4.7

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, N₂O is known as nitrous oxide even though our rules would specify the name dinitrogen monoxide. (And H₂O 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) SF₆
- (b) N₂O₃
- (c) Cl₂O₇
- (d) P₄O₆

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) PCl₅; (b) N₂O; (c) IF₇; (d) CCl₄

Link to Learning

The following [website \(http://openstax.org//16chemcompname\)](http://openstax.org//16chemcompname) 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, H⁺, when dissolved in water. To denote this distinct chemical property, a mixture of water with an acid is given a name derived from the compound's name. If the compound is a **binary acid** (comprised of hydrogen and one other nonmetallic element):

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

For example, when the gas HCl (hydrogen chloride) is dissolved in water, the solution is called *hydrochloric acid*. Several other examples of this nomenclature are shown in **Table 4.8**.

Names of Some Simple Acids

Name of Gas	Name of Acid
HF(<i>g</i>), hydrogen fluoride	HF(<i>aq</i>), hydrofluoric acid
HCl(<i>g</i>), hydrogen chloride	HCl(<i>aq</i>), hydrochloric acid
HBr(<i>g</i>), hydrogen bromide	HBr(<i>aq</i>), hydrobromic acid
HI(<i>g</i>), hydrogen iodide	HI(<i>aq</i>), hydroiodic acid
H ₂ S(<i>g</i>), hydrogen sulfide	H ₂ S(<i>aq</i>), hydrosulfuric acid

Table 4.8

Oxyacids

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

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

For example, consider H₂CO₃ (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 4.9**. There are some exceptions to the general naming method (e.g., H₂SO₄ is called sulfuric acid, not sulfic acid, and H₂SO₃ is sulfurous, not sulfous, acid).

Names of Common Oxyacids

Formula	Anion Name	Acid Name
HC ₂ H ₃ O ₂	acetate	acetic acid
HNO ₃	nitrate	nitric acid
HNO ₂	nitrite	nitrous acid
HClO ₄	perchlorate	perchloric acid
H ₂ CO ₃	carbonate	carbonic acid
H ₂ SO ₄	sulfate	sulfuric acid

Table 4.9

Names of Common Oxyacids

Formula	Anion Name	Acid Name
H ₂ SO ₃	sulfite	sulfurous acid
H ₃ PO ₄	phosphate	phosphoric acid

Table 4.9

4.4 Lewis Symbols and Structures

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 4.10 shows the Lewis symbols for the elements of the third period of the periodic table.

Atoms	Electronic Configuration	Lewis Symbol
sodium	[Ne]3s ¹	Na ·
magnesium	[Ne]3s ²	·Mg·
aluminum	[Ne]3s ² 3p ¹	· $\overset{\cdot}{\text{Al}}$ ·
silicon	[Ne]3s ² 3p ²	· $\overset{\cdot}{\underset{\cdot}{\text{Si}}}$ ·
phosphorus	[Ne]3s ² 3p ³	· $\overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{P}}}}$ ·
sulfur	[Ne]3s ² 3p ⁴	· $\overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{S}}}}$ ·
chlorine	[Ne]3s ² 3p ⁵	· $\overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{Cl}}}}$ ·
argon	[Ne]3s ² 3p ⁶	· $\overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{Ar}}}}$ ·

Figure 4.10 Lewis symbols illustrating 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:



Likewise, they can be used to show the formation of anions from atoms, as shown here for chlorine and sulfur:



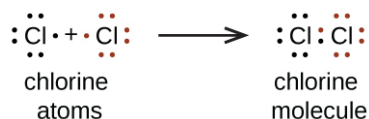
Figure 4.11 demonstrates the use of Lewis symbols to show the transfer of electrons during the formation of ionic compounds.

Metal		Nonmetal		Ionic Compound
Na·	+	· $\ddot{\text{Cl}}$ ·	→	Na ⁺ [· $\ddot{\text{Cl}}$ ·] ⁻ sodium chloride (sodium ion and chloride ion)
·Mg·	+	· $\ddot{\text{O}}$ ·	→	Mg ²⁺ [· $\ddot{\text{O}}$ ·] ²⁻ magnesium oxide (magnesium ion and oxide ion)
·Ca·	+	2 · $\ddot{\text{F}}$ ·	→	Ca ²⁺ [· $\ddot{\text{F}}$ ·] ₂ ⁻ calcium fluoride (calcium ion and two fluoride ions)

Figure 4.11 Cations are formed when atoms lose electrons, represented by fewer Lewis dots, whereas anions are formed by atoms gaining electrons. The total number of electrons does not change.

Lewis Structures

We also use Lewis symbols to indicate the formation of covalent bonds, which are shown in **Lewis structures**, drawings that describe the bonding in molecules and polyatomic ions. For example, when two chlorine atoms form a chlorine molecule, they share one pair of electrons:



The Lewis structure indicates that each Cl atom has three pairs of electrons that are not used in bonding (called **lone pairs**) and one shared pair of electrons (written between the atoms). A dash (or line) is sometimes used to indicate a shared pair of electrons:

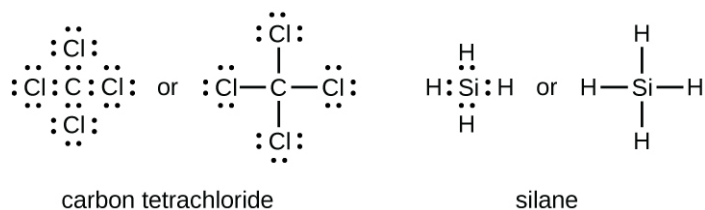


A single shared pair of electrons is called a **single bond**. Each Cl atom interacts with eight valence electrons: the six in the lone pairs and the two in the single bond.

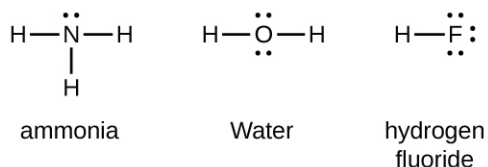
The Octet Rule

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:

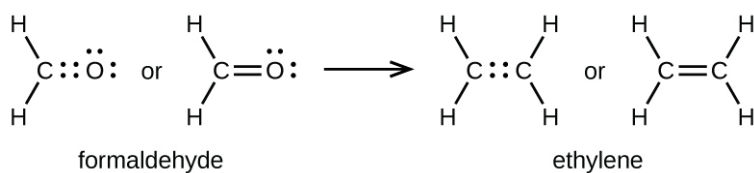


Group 15 elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form three covalent bonds, as in NH_3 (ammonia). Oxygen and other atoms in group 16 obtain an octet by forming two covalent bonds:

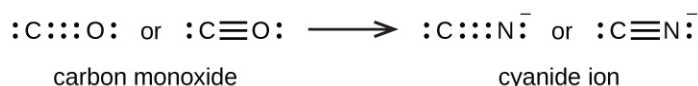


Double and Triple Bonds

As previously mentioned, when a pair of atoms shares one pair of electrons, we call this a single bond. However, a pair of atoms may need to share more than one pair of electrons in order to achieve the requisite octet. A **double bond** forms when two pairs of electrons are shared between a pair of atoms, as between the carbon and oxygen atoms in CH_2O (formaldehyde) and between the two carbon atoms in C_2H_4 (ethylene):

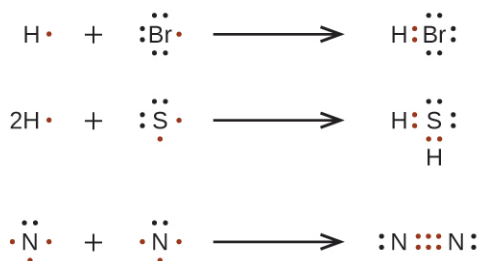


A **triple bond** forms when three electron pairs are shared by a pair of atoms, as in carbon monoxide (CO) and the cyanide ion (CN^-):



Writing Lewis Structures with the Octet Rule

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



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

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

Let us determine the Lewis structures of SiH_4 , CHO_2^- , NO^+ , and OF_2 as examples in following this procedure:

1. Determine the total number of valence (outer shell) electrons in the molecule or ion.
 - For a molecule, we add the number of valence electrons on each atom in the molecule:

$$\begin{array}{r} \text{SiH}_4 \\ \text{Si: } 4 \text{ valence electrons/atom} \times 1 \text{ atom} = 4 \\ + \text{H: } 1 \text{ valence electron/atom} \times 4 \text{ atoms} = 4 \\ \hline = 8 \text{ valence electrons} \end{array}$$

- For a *negative ion*, such as CHO_2^- , we add the number of valence electrons on the atoms to the number of negative charges on the ion (one electron is gained for each single negative charge):

$$\begin{array}{r} \text{CHO}_2^- \\ \text{C: } 4 \text{ valence electrons/atom} \times 1 \text{ atom} = 4 \\ \text{H: } 1 \text{ valence electron/atom} \times 1 \text{ atom} = 1 \\ \text{O: } 6 \text{ valence electrons/atom} \times 2 \text{ atoms} = 12 \\ + \qquad \qquad \qquad 1 \text{ additional electron} = 1 \\ \hline = 18 \text{ valence electrons} \end{array}$$

- For a *positive ion*, such as NO^+ , we add the number of valence electrons on the atoms in the ion and then subtract the number of positive charges on the ion (one electron is lost for each single positive charge) from the total number of valence electrons:

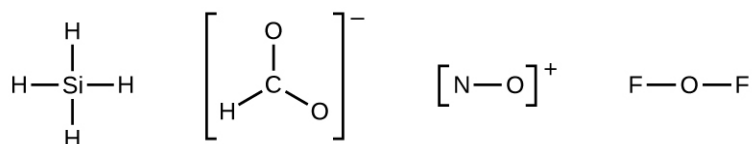


$$\begin{array}{r} \text{N: } 5 \text{ valence electrons/atom} \times 1 \text{ atom} = 5 \\ \text{O: } 6 \text{ valence electron/atom} \times 1 \text{ atom} = 6 \\ + \text{ } -1 \text{ electron (positive charge)} = -1 \\ \hline = 10 \text{ valence electrons} \end{array}$$

- Since OF_2 is a neutral molecule, we simply add the number of valence electrons:

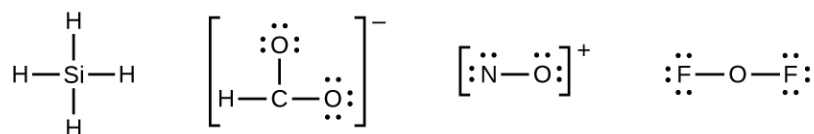
$$\begin{array}{r} \text{OF}_2 \\ \text{O: } 6 \text{ valence electrons/atom} \times 1 \text{ atom} = 6 \\ + \text{ F: } 7 \text{ valence electrons/atom} \times 2 \text{ atoms} = 14 \\ \hline = 20 \text{ valence electrons} \end{array}$$

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:)

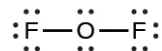


When several arrangements of atoms are possible, as for CHO_2^- , we must use experimental evidence to choose the correct one. In general, the less electronegative elements are more likely to be central atoms. In CHO_2^- , the less electronegative carbon atom occupies the central position with the oxygen and hydrogen atoms surrounding it. Other examples include P in POCl_3 , S in SO_2 , and Cl in ClO_4^- . An exception is that hydrogen is almost never a central atom. As the most electronegative element, fluorine also cannot be a central atom.

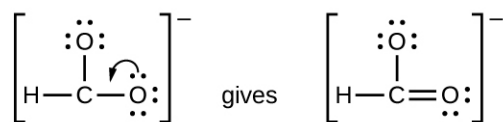
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.
 - There are no remaining electrons on SiH_4 , so it is unchanged:



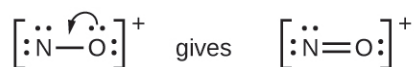
4. Place all remaining electrons on the central atom.
 - For SiH_4 , CHO_2^- , and NO^+ , there are no remaining electrons; we already placed all of the electrons determined in Step 1.
 - For OF_2 , we had 16 electrons remaining in Step 3, and we placed 12, leaving 4 to be placed on the central atom:



5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.
 - SiH_4 : Si already has an octet, so nothing needs to be done.
 - CHO_2^- : We have distributed the valence electrons as lone pairs on the oxygen atoms, but the carbon atom lacks an octet:



- NO^+ : For this ion, we added eight 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:



This still does not produce an octet, so we must move another pair, forming a triple bond:



- In OF_2 , each atom has an octet as drawn, so nothing changes.

Example 4.6

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 (H_3CCH_3), acetylene (HCCH), and ammonia (NH_3). What are the Lewis structures of these molecules?

Solution

Step 1. Calculate the number of valence electrons.

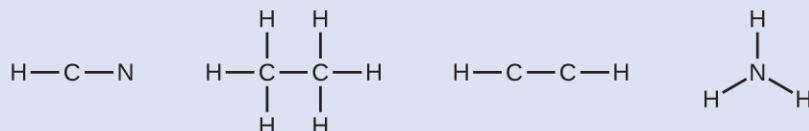
$$\text{HCN: } (1 \times 1) + (4 \times 1) + (5 \times 1) = 10$$

$$\text{H}_3\text{CCH}_3: (1 \times 3) + (2 \times 4) + (1 \times 3) = 14$$

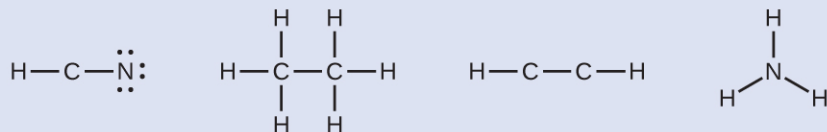
$$\text{HCCH: } (1 \times 1) + (2 \times 4) + (1 \times 1) = 10$$

$$\text{NH}_3: (5 \times 1) + (3 \times 1) = 8$$

Step 2. Draw a skeleton and connect the atoms with single bonds. Remember that H is never a central atom:



Step 3. Where needed, distribute electrons to the terminal atoms:



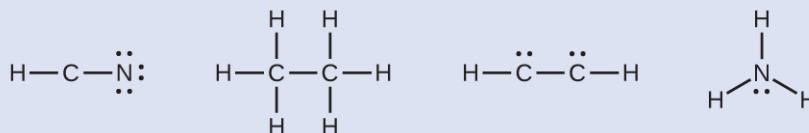
HCN: six electrons placed on N

H_3CCH_3 : no electrons remain

HCCH: no terminal atoms capable of accepting electrons

NH_3 : no terminal atoms capable of accepting electrons

Step 4. Where needed, place remaining electrons on the central atom:



HCN: no electrons remain

H₃CCH₃: no electrons remain

HCCH: four electrons placed on carbon

NH₃: two electrons placed on nitrogen

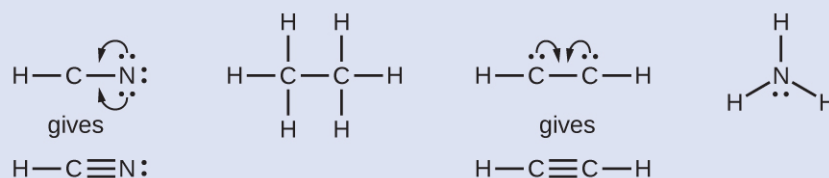
Step 5. Where needed, rearrange electrons to form multiple bonds in order to obtain an octet on each atom:

HCN: form two more C–N bonds

H₃CCH₃: all atoms have the correct number of electrons

HCCH: form a triple bond between the two carbon atoms

NH₃: all atoms have the correct number of electrons



Check Your Learning

Both carbon monoxide, CO, and carbon dioxide, CO₂, are products of the combustion of fossil fuels. Both of these gases also cause problems: CO is toxic and CO₂ has been implicated in global climate change. What are the Lewis structures of these two molecules?

Answer:



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 4.12**), Robert Curl, and Harold Kroto for their work in discovering a new form of carbon, the C₆₀ buckminsterfullerene molecule (**Figure 4.1**). An entire class of compounds, including spheres and tubes of various shapes, were discovered based on C₆₀. 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.

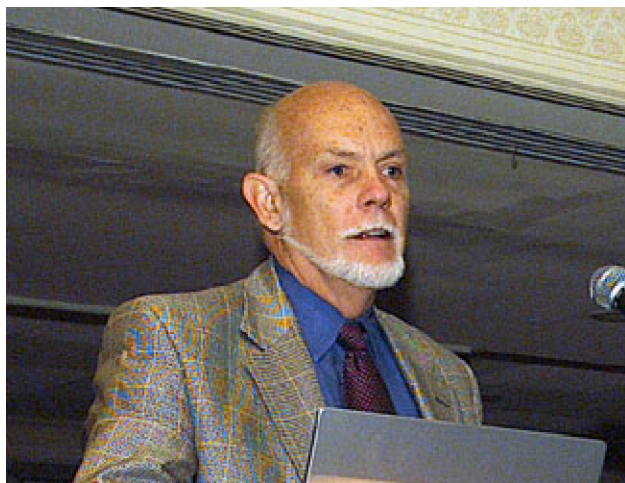


Figure 4.12 Richard Smalley (1943–2005), a professor of physics, chemistry, and astronomy at Rice University, was one of the leading advocates for fullerene chemistry. Upon his death in 2005, the US Senate honored him as the “Father of Nanotechnology.” (credit: United States Department of Energy)

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:

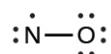
- Odd-electron molecules have an odd number of valence electrons, and therefore have an unpaired electron.
- Electron-deficient molecules have a central atom that has fewer electrons than needed for a noble gas configuration.
- Hypervalent molecules have a central atom that has more electrons than needed 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.

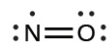
To draw the Lewis structure for an odd-electron molecule like NO, we follow the same five steps we would for other molecules, but with a few minor changes:

1. *Determine the total number of valence (outer shell) electrons.* The sum of the valence electrons is 5 (from N) + 6 (from O) = 11. The odd number immediately tells us that we have a free radical, so we know that not every atom can have eight electrons in its valence shell.
2. *Draw a skeleton structure of the molecule.* We can easily draw a skeleton with an N–O single bond:
N–O
3. *Distribute the remaining electrons as lone pairs on the terminal atoms.* In this case, there is no central atom, so we distribute the electrons around both atoms. We give eight electrons to the more electronegative atom in these situations; thus oxygen has the filled valence shell:



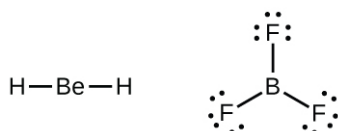
4. *Place all remaining electrons on the central atom.* Since there are no remaining electrons, this step does not apply.
5. *Rearrange the electrons to make multiple bonds with the central atom in order to obtain octets wherever*

possible. We know that an odd-electron molecule cannot have an octet for every atom, but we want to get each atom as close to an octet as possible. In this case, nitrogen has only five electrons around it. To move closer to an octet for nitrogen, we take one of the lone pairs from oxygen and use it to form a NO double bond. (We cannot take another lone pair of electrons on oxygen and form a triple bond because nitrogen would then have nine electrons:)

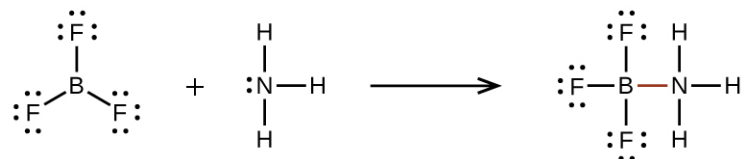


Electron-deficient Molecules

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, BeH_2 , and boron trifluoride, BF_3 , the beryllium and boron atoms each have only four and six electrons, respectively. It is possible to draw a structure with a double bond between a boron atom and a fluorine atom in BF_3 , satisfying the octet rule, but experimental evidence indicates the bond lengths are closer to that expected for B–F single bonds. This suggests the best Lewis structure has three B–F single bonds and an electron deficient boron. The reactivity of the compound is also consistent with an electron deficient boron. However, the B–F bonds are slightly shorter than what is actually expected for B–F single bonds, indicating that some double bond character is found in the actual molecule.



An atom like the boron atom in BF_3 , which does not have eight electrons, is very reactive. It readily combines with a molecule containing an atom with a lone pair of electrons. For example, NH_3 reacts with BF_3 because the lone pair on nitrogen can be shared with the boron atom:



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 4.13** shows the Lewis structures for two hypervalent molecules, PCl_5 and SF_6 .

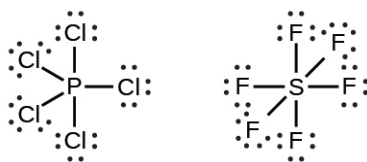
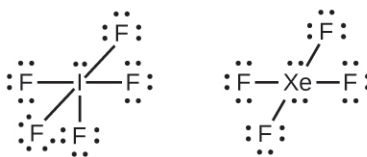


Figure 4.13 In PCl_5 , the central atom phosphorus shares five pairs of electrons. In SF_6 , sulfur shares six pairs of electrons.

In some hypervalent molecules, such as IF_5 and XeF_4 , some of the electrons in the outer shell of the central atom are lone pairs:



When we write the Lewis structures for these molecules, we find that we have electrons left over after filling the valence shells of the outer atoms with eight electrons. These additional electrons must be assigned to the central atom.

Example 4.7

Writing Lewis Structures: Octet Rule Violations

Xenon is a noble gas, but it forms a number of stable compounds. We examined XeF_4 earlier. What are the Lewis structures of XeF_2 and XeF_6 ?

Solution

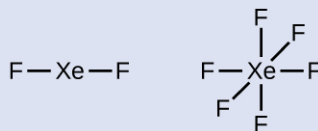
We can draw the Lewis structure of any covalent molecule by following the six steps discussed earlier. In this case, we can condense the last few steps, since not all of them apply.

Step 1. Calculate the number of valence electrons:

$$\text{XeF}_2: 8 + (2 \times 7) = 22$$

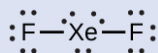
$$\text{XeF}_6: 8 + (6 \times 7) = 50$$

Step 2. Draw a skeleton joining the atoms by single bonds. Xenon will be the central atom because fluorine cannot be a central atom:

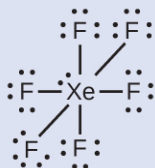


Step 3. Distribute the remaining electrons.

XeF_2 : We place three lone pairs of electrons around each F atom, accounting for 12 electrons and giving each F atom 8 electrons. Thus, six electrons (three lone pairs) remain. These lone pairs must be placed on the Xe atom. This is acceptable because Xe atoms have empty valence shell d orbitals and can accommodate more than eight electrons. The Lewis structure of XeF_2 shows two bonding pairs and three lone pairs of electrons around the Xe atom:

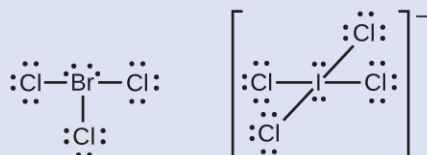


XeF_6 : We place three lone pairs of electrons around each F atom, accounting for 36 electrons. Two electrons remain, and this lone pair is placed on the Xe atom:



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 BrCl_3 and ICl_4^- .

Answer:

4.5 Formal Charges and Resonance

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 formal charge as follows:

$$\text{formal charge} = \# \text{ valence shell electrons (free atom)} - \# \text{ lone pair electrons} - \frac{1}{2} \# \text{ bonding electrons}$$

We can double-check formal charge calculations by determining the sum of the formal charges for the whole structure. The sum of the formal charges of all atoms in a molecule must be zero; the sum of the formal charges in an ion should equal the charge of the ion.

We must remember that the formal charge calculated for an atom is not the *actual* charge of the atom in the molecule. Formal charge is only a useful bookkeeping procedure; it does not indicate the presence of actual charges.

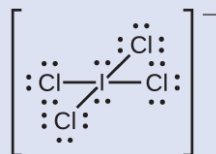
Example 4.8

Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen ion ICl_4^- .

Solution

Step 1. We divide the bonding electron pairs equally for all I–Cl bonds:



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:

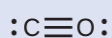
$$\text{I: } 7 - 8 = -1$$

$$\text{Cl: } 7 - 7 = 0$$

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:



Answer: C -1 , O $+1$

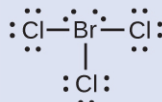
Example 4.9

Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen molecule BrCl_3 .

Solution

Step 1. Assign one of the electrons in each $\text{Br}-\text{Cl}$ bond to the Br atom and one to the Cl atom in that bond:



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:

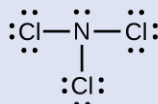
$$\text{Br: } 7 - 7 = 0$$

$$\text{Cl: } 7 - 7 = 0$$

All atoms in 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 NCl_3 .



Answer: N: 0; all three Cl atoms: 0

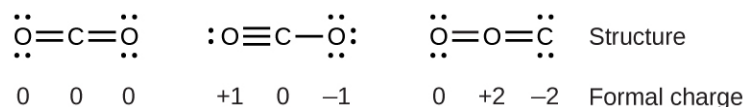
Using Formal Charge to Predict Molecular Structure

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:

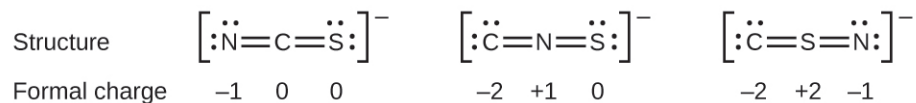
1. A molecular structure in which all formal charges are zero is preferable to one in which some formal charges are not zero.
2. If the Lewis structure must have nonzero formal charges, the arrangement with the smallest nonzero formal charges is preferable.
3. Lewis structures are preferable when adjacent 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, CO_2 . We know from our previous discussion that the less electronegative atom typically occupies the central position, but formal charges allow us to understand *why* this occurs. We can draw three possibilities for the structure: carbon in the center and double bonds, carbon in the center with a single and triple bond, and oxygen in the center with double bonds:



Comparing the three formal charges, we can definitively identify the structure on the left as preferable because it has only formal charges of zero (Guideline 1).

As another example, the thiocyanate ion, an ion formed from a carbon atom, a nitrogen atom, and a sulfur atom, could have three different molecular structures: CNS^- , NCS^- , or CSN^- . The formal charges present in each of these molecular structures can help us pick the most likely arrangement of atoms. Possible Lewis structures and the formal charges for each of the three possible structures for the thiocyanate ion are shown here:

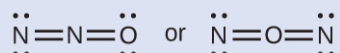


Note that the sum of the formal charges in each case is equal to the charge of the ion (-1). However, the first arrangement of atoms is preferred because it has the lowest number of atoms with nonzero formal charges (Guideline 2). Also, it places the least electronegative atom in the center, and the negative charge on the more electronegative element (Guideline 4).

Example 4.10

Using Formal Charge to Determine Molecular Structure

Nitrous oxide, N_2O , commonly known as laughing gas, is used as an anesthetic in minor surgeries, such as the routine extraction of wisdom teeth. Which is the likely structure for nitrous oxide?

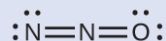


Solution

Determining formal charge yields the following:



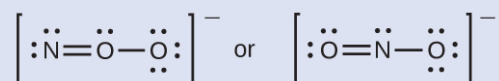
The structure with a terminal oxygen atom best satisfies the criteria for the most stable distribution of formal charge:



The number of atoms with formal charges are minimized (Guideline 2), and there is no formal charge larger than one (Guideline 2). This is again consistent with the preference for having the less electronegative atom in the central position.

Check Your Learning

Which is the most likely molecular structure for the nitrite (NO_2^-) ion?



Answer: ONO^-

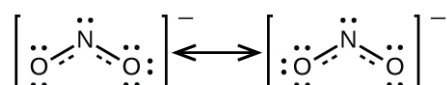
Resonance

You may have noticed that the nitrite anion in **Example 4.10** can have two possible structures with the atoms in the same positions. The electrons involved in the N–O double bond, however, are in different positions:



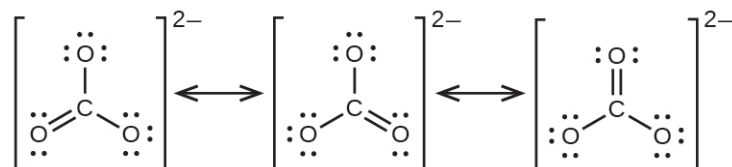
If nitrite ions do indeed contain a single and a double bond, we would expect for the two bond lengths to be different. A double bond between two atoms is shorter (and stronger) than a single bond between the same two atoms. Experiments show, however, that both N–O bonds in NO_2^- have the same strength and length, and are identical in all other properties.

It is not possible to write a single Lewis structure for NO_2^- in which nitrogen has an octet and both bonds are equivalent. Instead, we use the concept of **resonance**: if two or more Lewis structures with the same arrangement of atoms can be written for a molecule or ion, the actual distribution of electrons is an *average* of that shown by the various Lewis structures. The actual distribution of electrons in each of the nitrogen-oxygen bonds in NO_2^- is the average of a double bond and a single bond. We call the individual Lewis structures **resonance forms**. The actual electronic structure of the molecule (the average of the resonance forms) is called a **resonance hybrid** of the individual resonance forms. A double-headed arrow between Lewis structures indicates that they are resonance forms. Thus, the electronic structure of the NO_2^- ion is shown as:



We should remember that a molecule described as a resonance hybrid *never* possesses an electronic structure described by either resonance form. It does not fluctuate between resonance forms; rather, the actual electronic structure is *always* the average of that shown by all resonance forms. George Wheland, one of the pioneers of resonance theory, used a historical analogy to describe the relationship between resonance forms and resonance hybrids. A medieval traveler, having never before seen a rhinoceros, described it as a hybrid of a dragon and a unicorn because it had many properties in common with both. Just as a rhinoceros is neither a dragon sometimes nor a unicorn at other times, a resonance hybrid is neither of its resonance forms at any given time. Like a rhinoceros, it is a real entity that experimental evidence has shown to exist. It has some characteristics in common with its resonance forms, but the resonance forms themselves are convenient, imaginary images (like the unicorn and the dragon).

The carbonate anion, CO_3^{2-} , provides a second example of resonance:



One oxygen atom must have a double bond to carbon to complete the octet on the central atom. All oxygen atoms, however, are equivalent, and the double bond could form from any one of the three atoms. This gives rise to three resonance forms of the carbonate ion. Because we can write three identical resonance structures, we know that the actual arrangement of electrons in the carbonate ion is the average of the three structures. Again, experiments show that all three C–O bonds are exactly the same.

Link to Learning

The online **Lewis Structure Make** (<http://openstaxcollege.org//16LewisMake>) includes many examples to practice drawing resonance structures.

4.6 Molecular Structure and Polarity

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, 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 4.14**). 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 ($1 \text{ \AA} = 10^{-10} \text{ m}$) or picometers ($1 \text{ pm} = 10^{-12} \text{ m}$, $100 \text{ pm} = 1 \text{ \AA}$).

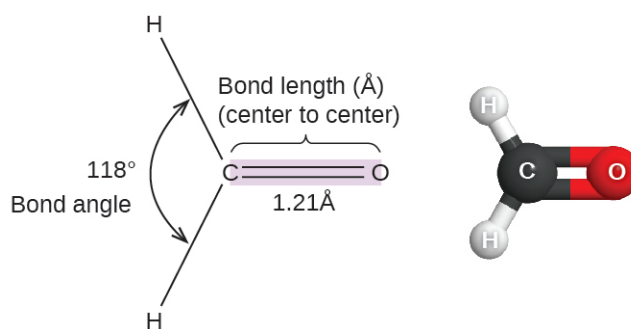


Figure 4.14 Bond distances (lengths) and angles are shown for the formaldehyde molecule, H₂CO.

VSEPR Theory

Valence shell electron-pair repulsion theory (VSEPR theory) enables us to predict the molecular structure, including approximate bond angles around a central atom, of a molecule from an examination of the number of bonds and lone electron pairs in its Lewis structure. The VSEPR model assumes that electron pairs in the valence shell of a central atom will adopt an arrangement that minimizes repulsions between these electron pairs by maximizing the distance between them. The electrons in the valence shell of a central atom form either bonding pairs of electrons, located primarily between bonded atoms, or lone pairs. The electrostatic repulsion of these electrons is reduced when the various regions of high electron density assume positions as far from each other as possible.

VSEPR theory predicts the arrangement of electron pairs around each central atom and, usually, the correct

arrangement of atoms in a molecule. We should understand, however, that the theory only considers electron-pair repulsions. Other interactions, such as nuclear-nuclear repulsions and nuclear-electron attractions, are also involved in the final arrangement that atoms adopt in a particular molecular structure.

As a simple example of VSEPR theory, let us predict the structure of a gaseous BeF_2 molecule. The Lewis structure of BeF_2 (Figure 4.15) shows only two electron pairs around the central beryllium atom. With two bonds and no lone pairs on the central atom, the bonds are as far apart as possible, and the electrostatic repulsion between these regions of high electron density is reduced to a minimum when they are on opposite sides of the central atom. The bond angle is 180° (Figure 4.15).

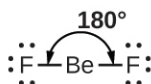


Figure 4.15 The BeF_2 molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the Be atom.

Figure 4.16 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.

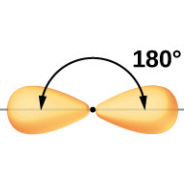
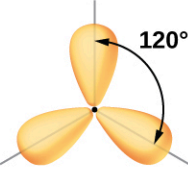
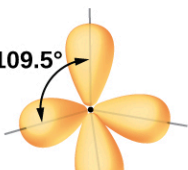
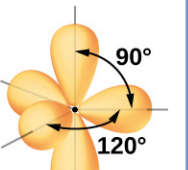
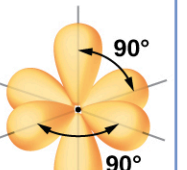
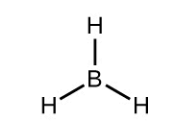
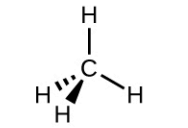

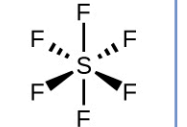
Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions 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° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angles of 90° or 120° An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).	Octahedral; all angles 90° or 180°

Figure 4.16 The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs).

Electron-pair Geometry versus Molecular Structure

It is important to note that electron-pair geometry around a central atom is *not* the same thing as its molecular structure. The electron-pair geometries shown in **Figure 4.16** 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, 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 4.17**). On the other hand, the ammonia molecule, NH_3 , also has four electron pairs associated with the nitrogen atom, and thus has a tetrahedral electron-pair geometry. One of these regions, however, is a lone pair, which is not included in the molecular structure, and this lone pair influences the shape of the molecule (**Figure 4.18**).

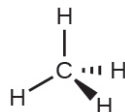


Figure 4.17 The molecular structure of the methane molecule, CH_4 , is shown with a tetrahedral arrangement of the hydrogen atoms. VSEPR structures like this one are often drawn using the wedge and dash notation, in which solid lines represent bonds in the plane of the page, solid wedges represent bonds coming up out of the plane, and dashed lines represent bonds going down into the plane.

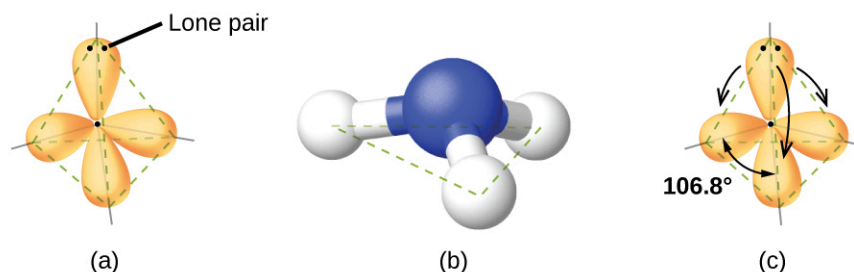
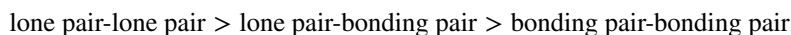
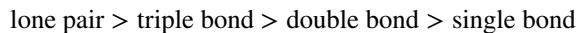


Figure 4.18 (a) The electron-pair geometry for the ammonia molecule is tetrahedral with one lone pair and three single bonds. (b) The trigonal pyramidal molecular structure is determined from the electron-pair geometry. (c) The actual bond angles deviate slightly from the idealized angles because the 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° .

As seen in **Figure 4.18**, small distortions from the ideal angles in **Figure 4.16** 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:



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:



Consider formaldehyde, H_2CO , which is used as a preservative for biological and anatomical specimens (**Figure 4.14**). This molecule has regions of high electron density that consist of two single bonds and one double bond. The basic geometry is trigonal planar with 120° bond angles, but we see that the double bond causes slightly larger angles (121°), and the angle between the single bonds is slightly smaller (118°).

In the ammonia molecule, the three hydrogen atoms attached to the central nitrogen are not arranged in a flat, trigonal planar molecular structure, but rather in a three-dimensional trigonal pyramid (**Figure 4.18**) with the nitrogen atom at the apex and the three hydrogen atoms forming the base. The ideal bond angles in a trigonal pyramid are based on the tetrahedral electron pair geometry. Again, there are slight deviations from the ideal because lone pairs occupy larger regions of space than do bonding electrons. The H–N–H bond angles in NH_3 are slightly smaller than the 109.5° angle in a regular tetrahedron (**Figure 4.16**) because the lone pair-bonding pair repulsion is greater than the bonding pair-bonding pair repulsion (**Figure 4.18**). **Figure 4.19** illustrates the ideal molecular structures, which are predicted based on the electron-pair geometries for various combinations of lone pairs and bonding pairs.

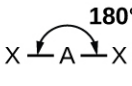
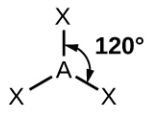
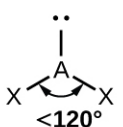
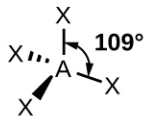


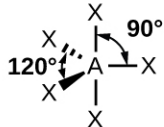
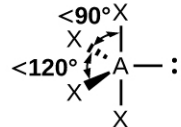
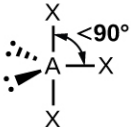
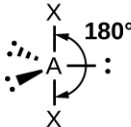
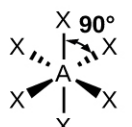
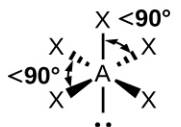

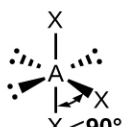
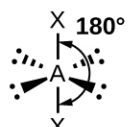
Number of electron pairs	Electron pair geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal planar	 Bent or angular			
4	 Tetrahedral	 Trigonal pyramid	 Bent or angular		
5	 Trigonal bipyramid	 Sawhorse or seesaw	 T-shape	 Linear	
6	 Octahedral	 Square pyramid	 Square planar	 T-shape	 Linear

Figure 4.19 The molecular structures are identical to the electron-pair geometries when there are no lone pairs present (first column). For a particular number of electron pairs (row), the molecular structures for one or more lone pairs are determined based on modifications of the corresponding electron-pair geometry.

According to VSEPR theory, the terminal atom locations (Xs in **Figure 4.19**) 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 4.20**: 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 4.19**, the axial position is surrounded by bond angles of 90° , whereas the equatorial position has more space available because of the 120° bond angles. In a trigonal bipyramidal electron-pair geometry, lone pairs always occupy equatorial positions because these more spacious positions can more easily accommodate the larger lone pairs.

Theoretically, we can come up with three possible arrangements for the three bonds and two lone pairs for the ClF_3 molecule (**Figure 4.20**). The stable structure is the one that puts the lone pairs in equatorial locations, giving a T-shaped molecular structure.

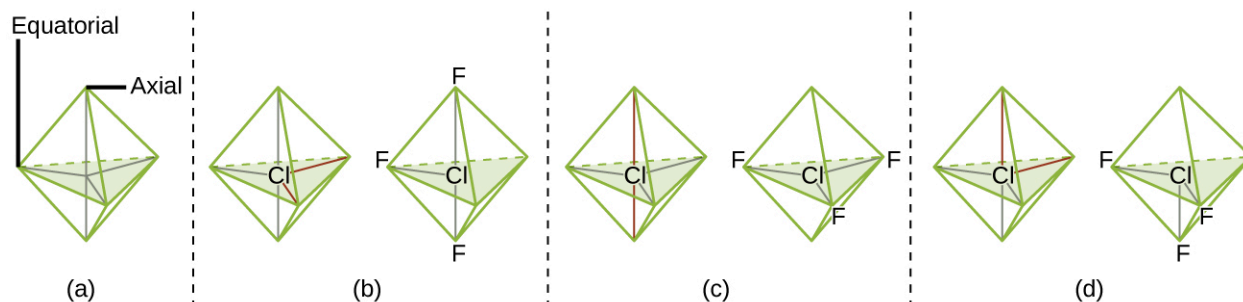


Figure 4.20 (a) In a trigonal bipyramid, the two axial positions are located directly across from one another, whereas the three equatorial positions are located in a triangular arrangement. (b–d) The two lone pairs (red lines) in ClF_3 have several possible arrangements, but the T-shaped molecular structure (b) is the one actually observed, consistent with the larger lone pairs both occupying equatorial positions.

When a central atom has two lone electron pairs and four bonding regions, we have an octahedral electron-pair geometry. The two lone pairs are on opposite sides of the octahedron (180° apart), giving a square planar molecular structure that minimizes lone pair-lone pair repulsions (**Figure 4.19**).

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 4.19**, first column).
4. Use the number of lone pairs to determine the molecular structure (**Figure 4.19**). If more than one arrangement of lone pairs and chemical bonds is possible, choose the one that will minimize repulsions, remembering that lone pairs occupy more space than multiple bonds, which occupy more space than single bonds. In trigonal bipyramidal arrangements, repulsion is minimized when every lone pair is in an equatorial position. In an octahedral arrangement with two lone pairs, repulsion is minimized when the lone pairs are on opposite sides of the central atom.

The following examples illustrate the use of VSEPR theory to predict the molecular structure of molecules or ions that have no lone pairs of electrons. In this case, the molecular structure is identical to the electron pair geometry.

Example 4.11

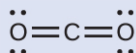
Predicting Electron-pair Geometry and Molecular Structure: CO_2 and BCl_3

Predict the electron-pair geometry and molecular structure for each of the following:

- (a) carbon dioxide, CO_2 , a molecule produced by the combustion of fossil fuels
- (b) boron trichloride, BCl_3 , an important industrial chemical

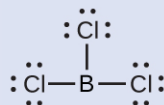
Solution

- (a) We write the Lewis structure of CO_2 as:



This shows us two regions of high electron density around the carbon atom—each double bond counts as one region, and there are no lone pairs on the carbon atom. Using VSEPR theory, we predict that the two regions of electron density arrange themselves on opposite sides of the central atom with a bond angle of 180° . The electron-pair geometry and molecular structure are identical, and CO_2 molecules are linear.

(b) We write the Lewis structure of BCl_3 as:



Thus we see that BCl_3 contains three bonds, and there are no lone pairs of electrons on boron. The arrangement of three regions of high electron density gives a trigonal planar electron-pair geometry. The B–Cl bonds lie in a plane with 120° angles between them. BCl_3 also has a trigonal planar molecular structure (Figure 4.21).

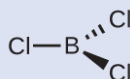


Figure 4.21

The electron-pair geometry and molecular structure of BCl_3 are both trigonal planar. Note that the VSEPR geometry indicates the correct bond angles (120°), unlike the Lewis structure shown above.

Check Your Learning

Carbonate, CO_3^{2-} , is a common polyatomic ion found in various materials from eggshells to antacids. What are the electron-pair geometry and molecular structure of this polyatomic ion?

Answer: The electron-pair geometry is trigonal planar and the molecular structure is trigonal planar. Due to resonance, all three C–O bonds are identical. Whether they are single, double, or an average of the two, each bond counts as one region of electron density.

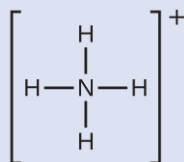
Example 4.12

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 NH_4^+ cation.

Solution

We write the Lewis structure of NH_4^+ as:



We can see that 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 4.19**). Therefore, the electron pair geometry of NH_4^+ is tetrahedral, and the molecular structure is also tetrahedral (**Figure 4.22**).

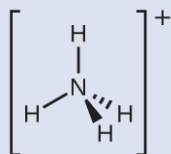


Figure 4.22 The ammonium ion displays a tetrahedral electron-pair geometry as well as a tetrahedral molecular structure.

Check Your Learning

Identify a molecule with trigonal bipyramidal molecular structure.

Answer: Any molecule with five electron pairs around the central atoms including no lone pairs will be trigonal bipyramidal. PF_5 is a common example.

The next several examples illustrate the effect of lone pairs of electrons on molecular structure.

Example 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 H_2O indicates that there are four regions of high electron density around the oxygen atom: two lone pairs and two chemical bonds:



We predict that these four regions are arranged in a tetrahedral fashion (**Figure 4.23**), as indicated in **Figure 4.19**. Thus, the electron-pair geometry is tetrahedral and the molecular structure is bent with an angle slightly less than 109.5° . In fact, the bond angle is 104.5° .

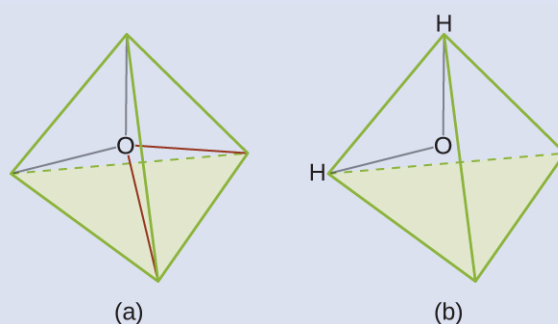


Figure 4.23 (a) H_2O has four regions of electron density around the central atom, so it has a tetrahedral electron-pair geometry. (b) Two of the electron regions are lone pairs, so the molecular structure is bent.

Check Your Learning

The hydronium ion, H_3O^+ , forms when acids are dissolved in water. Predict the electron-pair geometry and molecular structure of this cation.

Answer: electron pair geometry: tetrahedral; molecular structure: trigonal pyramidal

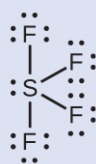
Example 4.14

Predicting Electron-pair Geometry and Molecular Structure: SF_4

Sulfur tetrafluoride, SF_4 , is extremely valuable for the preparation of fluorine-containing compounds used as herbicides (i.e., SF_4 is used as a fluorinating agent). Predict the electron-pair geometry and molecular structure of a SF_4 molecule.

Solution

The Lewis structure of SF_4 indicates five regions of electron density around the sulfur atom: one lone pair and four bonding pairs:



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 4.24**) is that of a seesaw (**Figure 4.19**).

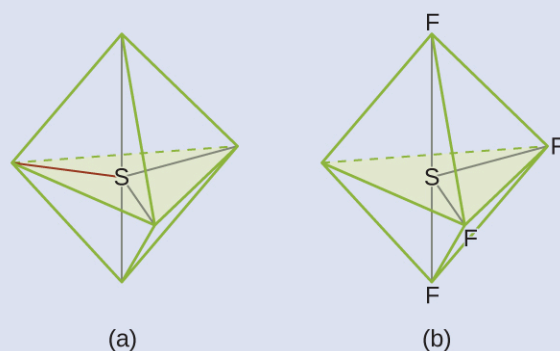


Figure 4.24 (a) SF₄ has a trigonal bipyramidal arrangement of the five regions of electron density. (b) One of the regions is a lone pair, which results in a seesaw-shaped molecular structure.

Check Your Learning

Predict the electron pair geometry and molecular structure for molecules of XeF₂.

Answer: The electron-pair geometry is trigonal bipyramidal. The molecular structure is linear.

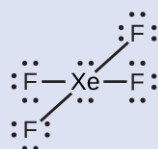
Example 4.15

Predicting Electron-pair Geometry and Molecular Structure: XeF₄

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 XeF₄ molecule.

Solution

The Lewis structure of XeF₄ indicates six regions of high electron density around the xenon atom: two lone pairs and four bonds:



These six regions adopt an octahedral arrangement (**Figure 4.19**), which is the electron-pair geometry. To minimize repulsions, the lone pairs should be on opposite sides of the central atom (**Figure 4.25**). The five atoms are all in the same plane and have a square planar molecular structure.

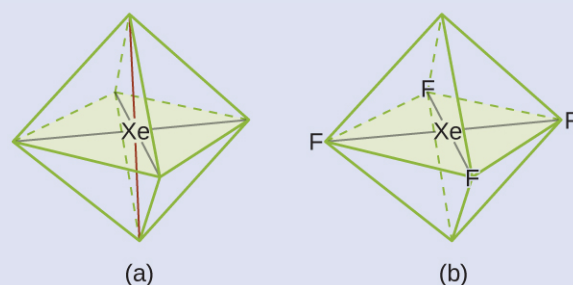


Figure 4.25 (a) XeF_4 adopts an octahedral arrangement with two lone pairs (red lines) and four bonds in the electron-pair geometry. (b) The molecular structure is square planar with the lone pairs directly across from one another.

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

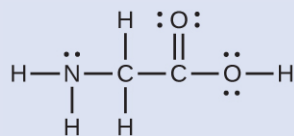
Molecular Structure for Multicenter Molecules

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.

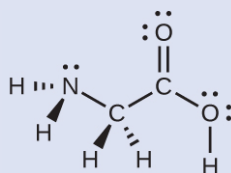
Example 4.16

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:



Solution



Consider each central atom independently. The electron-pair geometries:

- nitrogen—four regions of electron density; tetrahedral
- carbon (CH_2)—four regions of electron density; tetrahedral
- carbon (CO_2)—three regions of electron density; trigonal planar

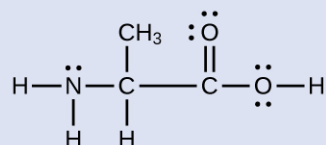
- oxygen (QH)—four regions of electron density; tetrahedral

The local structures:

- nitrogen—three bonds, one lone pair; trigonal pyramidal
- carbon (CH_2)—four bonds, no lone pairs; tetrahedral
- carbon (CO_2)—three bonds (double bond counts as one bond), no lone pairs; trigonal planar
- oxygen (QH)—two bonds, two lone pairs; bent (109°)

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:



Answer: electron-pair geometries: nitrogen—tetrahedral; carbon (CH)—tetrahedral; carbon (CH_3)—tetrahedral; carbon (CO_2)—trigonal planar; oxygen (QH)—tetrahedral; local structures: nitrogen—trigonal pyramidal; carbon (CH)—tetrahedral; carbon (CH_3)—tetrahedral; carbon (CO_2)—trigonal planar; oxygen (QH)—bent (109°)

Link to Learning

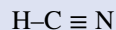
The [molecular shape simulator \(http://openstaxcollege.org//16MolecShape\)](http://openstaxcollege.org//16MolecShape) lets you build various molecules and practice naming their electron-pair geometries and molecular structures.

Example 4.17

Molecular Simulation

Using [molecular shape simulator \(http://openstaxcollege.org//16MolecShape\)](http://openstaxcollege.org//16MolecShape) allows us to control whether bond angles and/or lone pairs are displayed by checking or unchecking the boxes under “Options” on the right. We can also use the “Name” checkboxes at bottom-left to display or hide the electron pair geometry (called “electron geometry” in the simulator) and/or molecular structure (called “molecular shape” in the simulator).

Build the molecule HCN in the simulator based on the following Lewis structure:



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_4 is a molecule that adopts this structure.

Molecular Polarity and Dipole Moment

As discussed previously, polar covalent bonds connect two atoms with differing electronegativities, leaving one atom with a partial positive charge (δ^+) and the other atom with a partial negative charge (δ^-), as the electrons are pulled toward the more electronegative atom. This separation of charge gives rise to a **bond dipole moment**. The magnitude of a bond dipole moment is represented by the Greek letter mu (μ) 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:

$$\mu = Qr$$

This bond moment can be represented as a **vector**, a quantity having both direction and magnitude (Figure 4.26). Dipole vectors are shown as arrows pointing along the bond from the less electronegative atom toward the more electronegative atom. A small plus sign is drawn on the less electronegative end to indicate the partially positive end of the bond. The length of the arrow is proportional to the magnitude of the electronegativity difference between the two atoms.

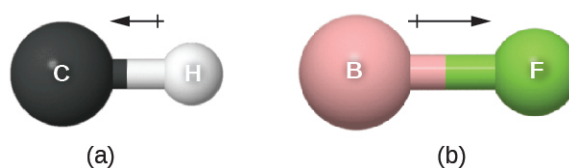


Figure 4.26 (a) There is a small difference in electronegativity between C and H, represented as a short vector. (b) The electronegativity difference between B and F is much larger, so the vector representing the bond moment is much longer.

A whole molecule may also have a separation of charge, depending on its molecular structure and the polarity of each of its bonds. If such a charge separation exists, the molecule is said to be a **polar molecule** (or dipole); otherwise the molecule is said to be nonpolar. The **dipole moment** measures the extent of net charge separation in the molecule as a whole. We determine the dipole moment by adding the bond moments in three-dimensional space, taking into account the molecular structure.

For diatomic molecules, there is only one bond, so its bond dipole moment determines the molecular polarity. Homonuclear diatomic molecules such as Br_2 and N_2 have no difference in electronegativity, so their dipole moment is zero. For heteronuclear molecules such as CO , there is a small dipole moment. For HF , there is a larger dipole moment because there is a larger difference in electronegativity.

When a molecule contains more than one bond, the geometry must be taken into account. If the bonds in a molecule are arranged such that their bond moments cancel (vector sum equals zero), then the molecule is nonpolar. This is the situation in CO_2 (Figure 4.27). Each of the bonds is polar, but the molecule as a whole is nonpolar. From the Lewis structure, and using VSEPR theory, we determine that the CO_2 molecule is linear with polar $\text{C}=\text{O}$ 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 4.27), 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).

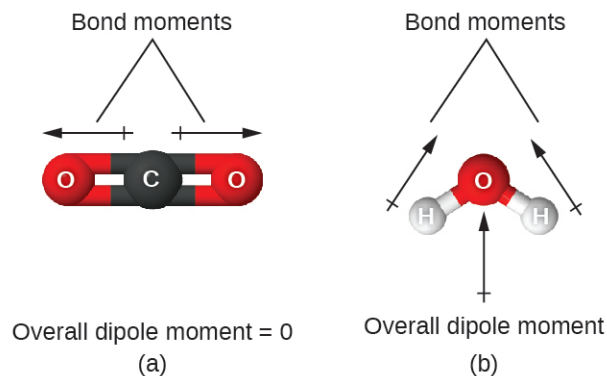
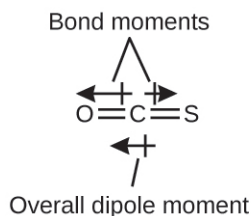


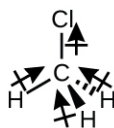
Figure 4.27 The overall dipole moment of a molecule depends on the individual bond dipole moments and how they are arranged. (a) Each CO bond has a bond dipole moment, but they point in opposite directions so that the net CO_2 molecule is nonpolar. (b) In contrast, water is polar because the OH bond moments do not cancel out.

The OCS molecule has a structure similar to CO_2 , but a sulfur atom has replaced one of the oxygen atoms. To determine if this molecule is polar, we draw the molecular structure. VSEPR theory predicts a linear molecule:

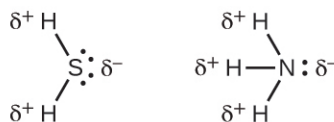


The C-O bond is considerably polar. Although C and S have very similar electronegativity values, S is slightly more electronegative than C, and so the C-S bond is just slightly polar. Because oxygen is more electronegative than sulfur, the oxygen end of the molecule is the negative end.

Chloromethane, CH_3Cl , is a tetrahedral molecule with three slightly polar C-H bonds and a more polar C-Cl bond. The relative electronegativities of the bonded atoms is $\text{H} < \text{C} < \text{Cl}$, 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).



For molecules of high symmetry such as BF_3 (trigonal planar), CH_4 (tetrahedral), PF_5 (trigonal bipyramidal), and 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, H_2S (nonlinear), and ammonia, NH_3 (trigonal pyramidal).



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 4.28**). 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.

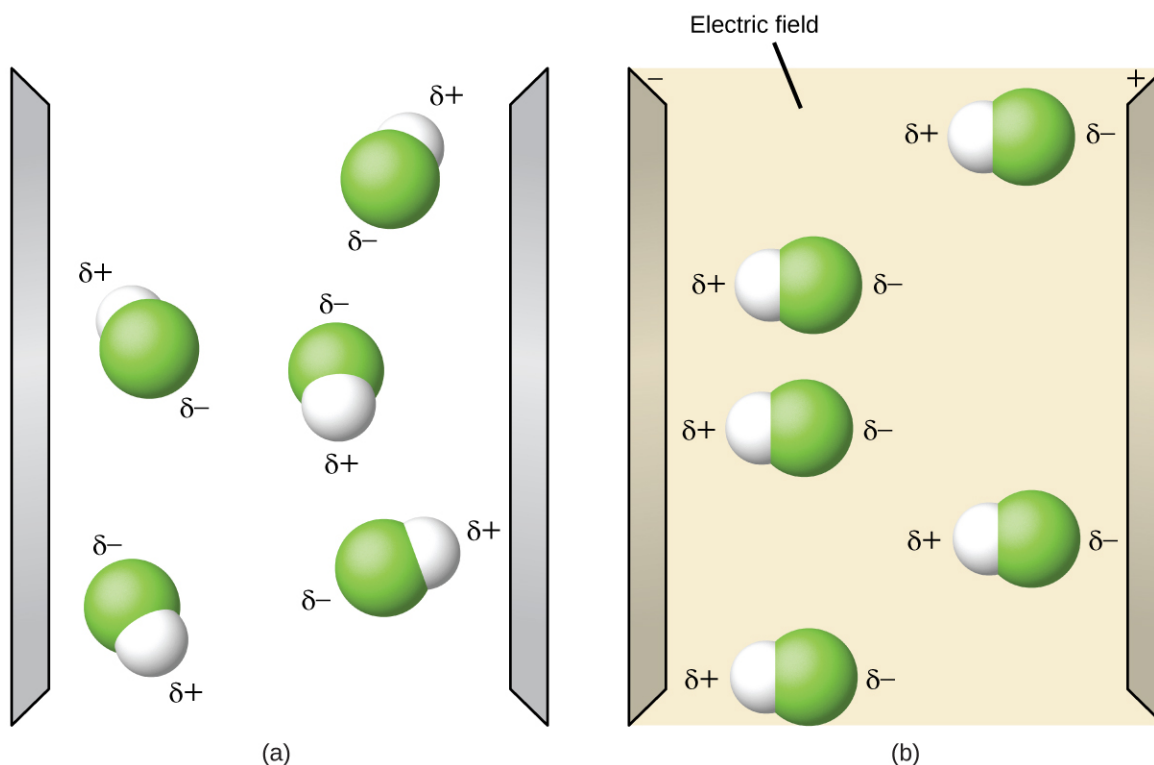


Figure 4.28 (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction.

Link to Learning

The **molecule polarity simulation** (<http://openstaxcollege.org//16MolecPolarity>) provides many ways to explore dipole moments of bonds and molecules.

Example 4.18

Polarity Simulations

Open the **molecule polarity simulation** (<http://openstaxcollege.org//16MolecPolarity>) 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 4.28**.

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.

Key Terms

axial position location in a trigonal bipyramidal geometry in which there is another atom at a 180° angle and the equatorial positions are at a 90° angle

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

binary compound compound containing two different elements.

bond angle angle between any two covalent bonds that share a common atom

bond dipole moment separation of charge in a bond that depends on the difference in electronegativity and the bond distance represented by partial charges or a vector

bond distance (also, bond length) distance between the nuclei of two bonded atoms

bond length distance between the nuclei of two bonded atoms at which the lowest potential energy is achieved

covalent bond bond formed when electrons are shared between atoms

dipole moment property of a molecule that describes the separation of charge determined by the sum of the individual bond moments based on the molecular structure

double bond covalent bond in which two pairs of electrons are shared between two atoms

electron-pair geometry arrangement around a central atom of all regions of electron density (bonds, lone pairs, or unpaired electrons)

electronegativity tendency of an atom to attract electrons in a bond to itself

equatorial position one of the three positions in a trigonal bipyramidal geometry with 120° angles between them; the axial positions are located at a 90° angle

formal charge charge that would result on an atom by taking the number of valence electrons on the neutral atom and subtracting the nonbonding electrons and the number of bonds (one-half of the bonding electrons)

free radical molecule that contains an odd number of electrons

hypervalent molecule molecule containing at least one main group element that has more than eight electrons in its valence shell

inert pair effect tendency of heavy atoms to form ions in which their valence s electrons are not lost

ionic bond strong electrostatic force of attraction between cations and anions in an ionic compound

Lewis structure diagram showing lone pairs and bonding pairs of electrons in a molecule or an ion

Lewis symbol symbol for an element or monatomic ion that uses a dot to represent each valence electron in the element or ion

linear shape in which two outside groups are placed on opposite sides of a central atom

lone pair two (a pair of) valence electrons that are not used to form a covalent bond

molecular structure arrangement of atoms in a molecule or ion

molecular structure structure that includes only the placement of the atoms in the molecule

nomenclature system of rules for naming objects of interest

octahedral shape in which six outside groups are placed around a central atom such that a three-dimensional shape is generated with four groups forming a square and the other two forming the apex of two pyramids, one above and one below the square plane

octet rule guideline that states main group atoms will form structures in which eight valence electrons interact with each nucleus, counting bonding electrons as interacting with both atoms connected by the bond

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

polar covalent bond covalent bond between atoms of different electronegativities; a covalent bond with a positive end and a negative end

polar molecule (also, dipole) molecule with an overall dipole moment

pure covalent bond (also, nonpolar covalent bond) covalent bond between atoms of identical electronegativities

resonance situation in which one Lewis structure is insufficient to describe the bonding in a molecule and the average of multiple structures is observed

resonance forms two or more Lewis structures that have the same arrangement of atoms but different arrangements of electrons

resonance hybrid average of the resonance forms shown by the individual Lewis structures

single bond bond in which a single pair of electrons is shared between two atoms

tetrahedral shape in which four outside groups are placed around a central atom such that a three-dimensional shape is generated with four corners and 109.5° angles between each pair and the central atom

trigonal bipyramidal shape in which five outside groups are placed around a central atom such that three form a flat triangle with 120° angles between each pair and the central atom, and the other two form the apex of two pyramids, one above and one below the triangular plane

trigonal planar shape in which three outside groups are placed in a flat triangle around a central atom with 120° angles between each pair and the central atom

triple bond bond in which three pairs of electrons are shared between two atoms

valence shell electron-pair repulsion theory (VSEPR) theory used to predict the bond angles in a molecule based on positioning regions of high electron density as far apart as possible to minimize electrostatic repulsion

vector quantity having magnitude and direction

Key Equations

- formal charge = # valence shell electrons (free atom) - # one pair electrons - $\frac{1}{2}$ # bonding electrons

Summary

4.1 Ionic Bonding

Atoms gain or lose electrons to form ions with particularly stable electron configurations. The charges of cations formed by the representative metals may be determined readily because, with few exceptions, the electronic structures

of these ions have either a noble gas configuration or a completely filled electron shell. The charges of anions formed by the nonmetals may also be readily determined because these ions form when nonmetal atoms gain enough electrons to fill their valence shells.

4.2 Covalent Bonding

Covalent bonds form when electrons are shared between atoms and are attracted by the nuclei of both atoms. In pure covalent bonds, the electrons are shared equally. In polar covalent bonds, the electrons are shared unequally, as one atom exerts a stronger force of attraction on the electrons than the other. The ability of an atom to attract a pair of electrons in a chemical bond is called its electronegativity. The difference in electronegativity between two atoms determines how polar a bond will be. In a diatomic molecule with two identical atoms, there is no difference in electronegativity, so the bond is nonpolar or pure covalent. When the electronegativity difference is very large, as is the case between metals and nonmetals, the bonding is characterized as ionic.

4.3 Chemical Nomenclature

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

4.4 Lewis Symbols and Structures

Valence electronic structures can be visualized by drawing Lewis symbols (for atoms and monatomic ions) and Lewis structures (for molecules and polyatomic ions). Lone pairs, unpaired electrons, and single, double, or triple bonds are used to indicate where the valence electrons are located around each atom in a Lewis structure. Most structures—especially those containing second row elements—obey the octet rule, in which every atom (except H) is surrounded by eight electrons. Exceptions to the octet rule occur for odd-electron molecules (free radicals), electron-deficient molecules, and hypervalent molecules.

4.5 Formal Charges and Resonance

In a Lewis structure, formal charges can be assigned to each atom by treating each bond as if one-half of the electrons are assigned to each atom. These hypothetical formal charges are a guide to determining the most appropriate Lewis structure. A structure in which the formal charges are as close to zero as possible is preferred. Resonance occurs in cases where two or more Lewis structures with identical arrangements of atoms but different distributions of electrons can be written. The actual distribution of electrons (the resonance hybrid) is an average of the distribution indicated by the individual Lewis structures (the resonance forms).

4.6 Molecular Structure and Polarity

VSEPR theory predicts the three-dimensional arrangement of atoms in a molecule. It states that valence electrons will assume an electron-pair geometry that minimizes repulsions between areas of high electron density (bonds and/or lone pairs). Molecular structure, which refers only to the placement of atoms in a molecule and not the electrons, is equivalent to electron-pair geometry only when there are no lone electron pairs around the central atom. A dipole moment measures a separation of charge. For one bond, the bond dipole moment is determined by the difference in electronegativity between the two atoms. For a molecule, the overall dipole moment is determined by both the individual bond moments and how these dipoles are arranged in the molecular structure. Polar molecules (those with

an appreciable dipole moment) interact with electric fields, whereas nonpolar molecules do not.

Exercises

4.1 Ionic Bonding

1. Does a cation gain protons to form a positive charge or does it lose electrons?
2. Iron(III) sulfate $[\text{Fe}_2(\text{SO}_4)_3]$ is composed of Fe^{3+} and SO_4^{2-} ions. Explain why a sample of iron(III) sulfate is uncharged.
3. Which of the following atoms would be expected to form negative ions in binary ionic compounds and which would be expected to form positive ions: P, I, Mg, Cl, In, Cs, O, Pb, Co?
4. Which of the following atoms would be expected to form negative ions in binary ionic compounds and which would be expected to form positive ions: Br, Ca, Na, N, F, Al, Sn, S, Cd?
5. Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:
 - (a) P
 - (b) Mg
 - (c) Al
 - (d) O
 - (e) Cl
 - (f) Cs
6. Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:
 - (a) I
 - (b) Sr
 - (c) K
 - (d) N
 - (e) S
 - (f) In
7. Write the electron configuration for each of the following ions:
 - (a) As^{3-}
 - (b) I^-
 - (c) Be^{2+}
 - (d) Cd^{2+}
 - (e) O^{2-}
 - (f) Ga^{3+}
 - (g) Li^+
 - (h) N^{3-}
 - (i) Sn^{2+}
 - (j) Co^{2+}
 - (k) Fe^{2+}
 - (l) As^{3+}

8. Write the electron configuration for the monatomic ions formed from the following elements (which form the greatest concentration of monatomic ions in seawater):

- (a) Cl
- (b) Na
- (c) Mg
- (d) Ca
- (e) K
- (f) Br
- (g) Sr
- (h) F

9. Write out the full electron configuration for each of the following atoms and for the monatomic ion found in binary ionic compounds containing the element:

- (a) Al
- (b) Br
- (c) Sr
- (d) Li
- (e) As
- (f) S

10. From the labels of several commercial products, prepare a list of six ionic compounds in the products. For each compound, write the formula. (You may need to look up some formulas in a suitable reference.)

4.2 Covalent Bonding

11. Why is it incorrect to speak of a molecule of solid NaCl?

12. What information can you use to predict whether a bond between two atoms is covalent or ionic?

13. Predict which of the following compounds are ionic and which are covalent, based on the location of their constituent atoms in the periodic table:

- (a) Cl_2CO
- (b) MnO
- (c) NCl_3
- (d) CoBr_2
- (e) K_2S
- (f) CO
- (g) CaF_2
- (h) HI
- (i) CaO
- (j) IBr
- (k) CO_2

14. Explain the difference between a nonpolar covalent bond, a polar covalent bond, and an ionic bond.

15. From its position in the periodic table, determine which atom in each pair is more electronegative:

- (a) Br or Cl
- (b) N or O
- (c) S or O
- (d) P or S
- (e) Si or N
- (f) Ba or P
- (g) N or K

16. From its position in the periodic table, determine which atom in each pair is more electronegative:

- (a) N or P
- (b) N or Ge
- (c) S or F
- (d) Cl or S
- (e) H or C
- (f) Se or P
- (g) C or Si

17. From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:

- (a) C, F, H, N, O
- (b) Br, Cl, F, H, I
- (c) F, H, O, P, S
- (d) Al, H, Na, O, P
- (e) Ba, H, N, O, As

18. From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:

- (a) As, H, N, P, Sb
- (b) Cl, H, P, S, Si
- (c) Br, Cl, Ge, H, Sr
- (d) Ca, H, K, N, Si
- (e) Cl, Cs, Ge, H, Sr

19. Which atoms can bond to sulfur so as to produce a positive partial charge on the sulfur atom?

20. Which is the most polar bond?

- (a) C–C
- (b) C–H
- (c) N–H
- (d) O–H
- (e) Se–H

21. Identify the more polar bond in each of the following pairs of bonds:

- (a) HF or HCl
- (b) NO or CO
- (c) SH or OH
- (d) PCl or SCl
- (e) CH or NH
- (f) SO or PO
- (g) CN or NN

22. Which of the following molecules or ions contain polar bonds?

- (a) O₃
- (b) S₈
- (c) O₂²⁻
- (d) NO₃⁻
- (e) CO₂
- (f) H₂S
- (g) BH₄⁻

4.3 Chemical Nomenclature

23. Name the following compounds:

- (a) CsCl
- (b) BaO
- (c) K₂S
- (d) BeCl₂
- (e) HBr
- (f) AlF₃

24. Name the following compounds:

- (a) NaF
- (b) Rb₂O
- (c) BCl₃
- (d) H₂Se
- (e) P₄O₆
- (f) ICl₃

25. Write the formulas of the following compounds:

- (a) rubidium bromide
- (b) magnesium selenide
- (c) sodium oxide
- (d) calcium chloride
- (e) hydrogen fluoride
- (f) gallium phosphide
- (g) aluminum bromide
- (h) ammonium sulfate

26. Write the formulas of the following compounds:

- (a) lithium carbonate
- (b) sodium perchlorate
- (c) barium hydroxide
- (d) ammonium carbonate
- (e) sulfuric acid
- (f) calcium acetate
- (g) magnesium phosphate
- (h) sodium sulfite

27. Write the formulas of the following compounds:

- (a) chlorine dioxide
- (b) dinitrogen tetroxide
- (c) potassium phosphide
- (d) silver(I) sulfide
- (e) aluminum fluoride trihydrate
- (f) silicon dioxide

28. Write the formulas of the following compounds:

- (a) barium chloride
- (b) magnesium nitride
- (c) sulfur dioxide
- (d) nitrogen trichloride
- (e) dinitrogen trioxide
- (f) tin(IV) chloride

29. Each of the following compounds contains a metal that can exhibit more than one ionic charge. Name these compounds:

- (a) Cr_2O_3
- (b) FeCl_2
- (c) CrO_3
- (d) TiCl_4
- (e) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$
- (f) MoS_2

30. Each of the following compounds contains a metal that can exhibit more than one ionic charge. Name these compounds:

- (a) NiCO_3
- (b) MoO_3
- (c) $\text{Co}(\text{NO}_3)_2$
- (d) V_2O_5
- (e) MnO_2
- (f) Fe_2O_3

31. The following ionic compounds are found in common household products. Write the formulas for each compound:

- (a) potassium phosphate
- (b) copper(II) sulfate
- (c) calcium chloride
- (d) titanium dioxide
- (e) ammonium nitrate
- (f) sodium bisulfate (the common name for sodium hydrogen sulfate)

32. The following ionic compounds are found in common household products. Name each of the compounds:

- (a) $\text{Ca}(\text{H}_2\text{PO}_4)_2$
- (b) FeSO_4
- (c) CaCO_3
- (d) MgO
- (e) NaNO_2
- (f) KI

33. What are the IUPAC names of the following compounds?

- (a) manganese dioxide
- (b) mercurous chloride (Hg_2Cl_2)
- (c) ferric nitrate [$\text{Fe}(\text{NO}_3)_3$]
- (d) titanium tetrachloride
- (e) cupric bromide (CuBr_2)

4.4 Lewis Symbols and Structures

34. Write the Lewis symbols for each of the following ions:

- (a) As^{3-}
- (b) I^-
- (c) Be^{2+}
- (d) O^{2-}
- (e) Ga^{3+}
- (f) Li^+
- (g) N^{3-}

35. Many monatomic ions are found in seawater, including the ions formed from the following list of elements. Write the Lewis symbols for the monatomic ions formed from the following elements:

- (a) Cl
- (b) Na
- (c) Mg
- (d) Ca
- (e) K
- (f) Br
- (g) Sr
- (h) F

36. Write the Lewis symbols of the ions in each of the following ionic compounds and the Lewis symbols of the atom from which they are formed:

- (a) MgS
- (b) Al_2O_3
- (c) GaCl_3
- (d) K_2O
- (e) Li_3N
- (f) KF

40. Write Lewis structures for the following:

- (a) O_2
- (b) H_2CO
- (c) AsF_3
- (d) $ClNO$
- (e) $SiCl_4$
- (f) H_3O^+
- (g) NH_4^+
- (h) BF_4^-
- (i) $HCCH$
- (j) $ClCN$
- (k) C_2^{2+}

41. Write Lewis structures for the following:

- (a) ClF_3
- (b) PCl_5
- (c) BF_3
- (d) PF_6^-

42. Write Lewis structures for the following:

- (a) SeF_6
- (b) XeF_4
- (c) $SeCl_3^+$
- (d) Cl_2BBCl_2 (contains a B–B bond)

43. Write Lewis structures for:

- (a) PO_4^{3-}
- (b) ICl_4^-
- (c) SO_3^{2-}
- (d) $HONO$

44. Correct the following statement: “The bonds in solid $PbCl_2$ are ionic; the bond in a HCl molecule is covalent. Thus, all of the valence electrons in $PbCl_2$ are located on the Cl^- ions, and all of the valence electrons in a HCl molecule are shared between the H and Cl atoms.”

45. Write Lewis structures for the following molecules or ions:

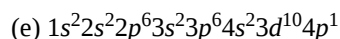
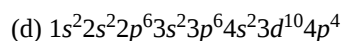
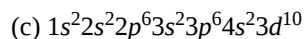
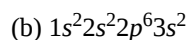
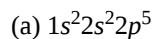
- (a) SbH_3
- (b) XeF_2
- (c) Se_8 (a cyclic molecule with a ring of eight Se atoms)

46. Methanol, H_3COH , is used as the fuel in some race cars. Ethanol, C_2H_5OH , is used extensively as motor fuel in Brazil. Both methanol and ethanol produce CO_2 and H_2O when they burn. Write the chemical equations for these combustion reactions using Lewis structures instead of chemical formulas.

47. Many planets in our solar system contain organic chemicals including methane (CH_4) and traces of ethylene (C_2H_4), ethane (C_2H_6), propyne (H_3CCCH), and diacetylene (HCCCCCH). Write the Lewis structures for each of these molecules.

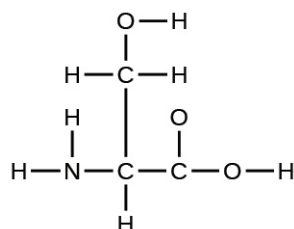
48. Carbon tetrachloride was formerly used in fire extinguishers for electrical fires. It is no longer used for this purpose because of the formation of the toxic gas phosgene, Cl_2CO . Write the Lewis structures for carbon tetrachloride and phosgene.

49. Identify the atoms that correspond to each of the following electron configurations. Then, write the Lewis symbol for the common ion formed from each atom:

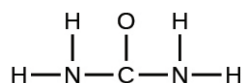


50. The arrangement of atoms in several biologically important molecules is given here. Complete the Lewis structures of these molecules by adding multiple bonds and lone pairs. Do not add any more atoms.

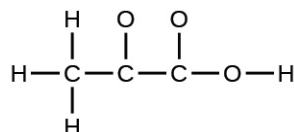
(a) the amino acid serine:



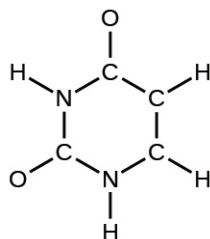
(b) urea:



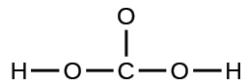
(c) pyruvic acid:



(d) uracil:



(e) carbonic acid:



51. A compound with a molar mass of about 28 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.

52. A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.

53. Two arrangements of atoms are possible for a compound with a molar mass of about 45 g/mol that contains 52.2% C, 13.1% H, and 34.7% O by mass. Write the Lewis structures for the two molecules.

54. How are single, double, and triple bonds similar? How do they differ?

4.5 Formal Charges and Resonance

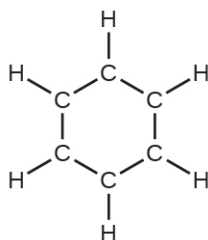
55. Write resonance forms that describe the distribution of electrons in each of these molecules or ions.

(a) selenium dioxide, OSeO

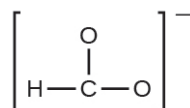
(b) nitrate ion, NO_3^-

(c) nitric acid, HNO_3 (N is bonded to an OH group and two O atoms)

(d) benzene, C_6H_6 :



(e) the formate ion:



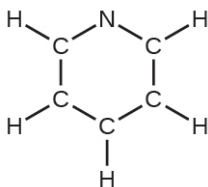
56. Write resonance forms that describe the distribution of electrons in each of these molecules or ions.

(a) sulfur dioxide, SO_2

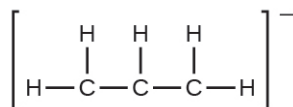
(b) carbonate ion, CO_3^{2-}

(c) hydrogen carbonate ion, HCO_3^- (C is bonded to an OH group and two O atoms)

(d) pyridine:



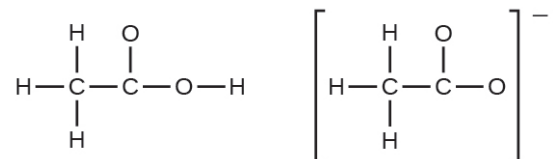
(e) the allyl ion:



57. Write the resonance forms of ozone, O_3 , the component of the upper atmosphere that protects the Earth from ultraviolet radiation.

58. Sodium nitrite, which has been used to preserve bacon and other meats, is an ionic compound. Write the resonance forms of the nitrite ion, NO_2^- .

59. In terms of the bonds present, explain why acetic acid, $\text{CH}_3\text{CO}_2\text{H}$, contains two distinct types of carbon-oxygen bonds, whereas the acetate ion, formed by loss of a hydrogen ion from acetic acid, only contains one type of carbon-oxygen bond. The skeleton structures of these species are shown:



60. Write the Lewis structures for the following, and include resonance structures where appropriate. Indicate which has the strongest carbon-oxygen bond.

(a) CO_2

(b) CO

61. Toothpastes containing sodium hydrogen carbonate (sodium bicarbonate) and hydrogen peroxide are widely used. Write Lewis structures for the hydrogen carbonate ion and hydrogen peroxide molecule, with resonance forms where appropriate.

62. Determine the formal charge of each element in the following:

(a) HCl

(b) CF_4

(c) PCl_3

(d) PF_5

63. Determine the formal charge of each element in the following:

(a) H_3O^+

(b) SO_4^{2-}

(c) NH_3

(d) O_2^{2-}

(e) H_2O_2

64. Calculate the formal charge of chlorine in the molecules Cl_2 , BeCl_2 , and ClF_5 .

65. Calculate the formal charge of each element in the following compounds and ions:

(a) F_2CO

(b) NO^-

(c) BF_4^-

(d) SnCl_3^-

(e) H_2CCH_2

(f) ClF_3

(g) SeF_6

(h) PO_4^{3-}

66. Draw all possible resonance structures for each of these compounds. Determine the formal charge on each atom in each of the resonance structures:

- (a) O_3
- (b) SO_2
- (c) NO_2^-
- (d) NO_3^-

67. Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in nitrosyl chloride: ClNO or ClON?

68. Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in hypochlorous acid: HOCl or OClH?

69. Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in sulfur dioxide: OSO or SOO?

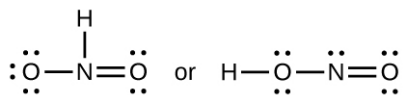
70. Draw the structure of hydroxylamine, H_3NO , and assign formal charges; look up the structure. Is the actual structure consistent with the formal charges?

71. Iodine forms a series of fluorides (listed here). Write Lewis structures for each of the four compounds and determine the formal charge of the iodine atom in each molecule:

- (a) IF
- (b) IF_3
- (c) IF_5
- (d) IF_7

72. Write the Lewis structure and chemical formula of the compound with a molar mass of about 70 g/mol that contains 19.7% nitrogen and 80.3% fluorine by mass, and determine the formal charge of the atoms in this compound.

73. Which of the following structures would we expect for nitrous acid? Determine the formal charges:



74. Sulfuric acid is the industrial chemical produced in greatest quantity worldwide. About 90 billion pounds are produced each year in the United States alone. Write the Lewis structure for sulfuric acid, H_2SO_4 , which has two oxygen atoms and two OH groups bonded to the sulfur.

4.6 Molecular Structure and Polarity

75. Explain why the HOH molecule is bent, whereas the HBeH molecule is linear.

76. What feature of a Lewis structure can be used to tell if a molecule's (or ion's) electron-pair geometry and molecular structure will be identical?

77. Explain the difference between electron-pair geometry and molecular structure.

78. Why is the H–N–H angle in NH_3 smaller than the H–C–H bond angle in CH_4 ? Why is the H–N–H angle in NH_4^+ identical to the H–C–H bond angle in CH_4 ?

79. Explain how a molecule that contains polar bonds can be nonpolar.

80. As a general rule, MX_n molecules (where M represents a central atom and X represents terminal atoms; $n = 2 - 5$) are polar if there is one or more lone pairs of electrons on M. NH_3 (M = N, X = H, $n = 3$) is an example. There are two molecular structures with lone pairs that are exceptions to this rule. What are they?

81. Predict the electron pair geometry and the molecular structure of each of the following molecules or ions:

- (a) SF_6
- (b) PCl_5
- (c) BeH_2
- (d) CH_3^+

82. Identify the electron pair geometry and the molecular structure of each of the following molecules or ions:

- (a) IF_6^+
- (b) CF_4
- (c) BF_3
- (d) SiF_5^-
- (e) BeCl_2

83. What are the electron-pair geometry and the molecular structure of each of the following molecules or ions?

- (a) ClF_5
- (b) ClO_2^-
- (c) TeCl_4^{2-}
- (d) PCl_3
- (e) SeF_4
- (f) PH_2^-

84. Predict the electron pair geometry and the molecular structure of each of the following ions:

- (a) H_3O^+
- (b) PCl_4^-
- (c) SnCl_3^-
- (d) BrCl_4^-
- (e) ICl_3
- (f) XeF_4
- (g) SF_2

85. Identify the electron pair geometry and the molecular structure of each of the following molecules:

- (a) ClNO (N is the central atom)
- (b) CS_2
- (c) Cl_2CO (C is the central atom)
- (d) Cl_2SO (S is the central atom)
- (e) SO_2F_2 (S is the central atom)
- (f) XeO_2F_2 (Xe is the central atom)
- (g) ClOF_2^+ (Cl is the central atom)

86. Predict the electron pair geometry and the molecular structure of each of the following:

- (a) IOF₅ (I is the central atom)
- (b) POCl₃ (P is the central atom)
- (c) Cl₂SeO (Se is the central atom)
- (d) ClSO⁺ (S is the central atom)
- (e) F₂SO (S is the central atom)
- (f) NO₂⁻
- (g) SiO₄⁴⁻

87. Which of the following molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?

- (a) ClF₅
- (b) ClO₂⁻
- (c) TeCl₄²⁻
- (d) PCl₃
- (e) SeF₄
- (f) PH₂⁻
- (g) XeF₂

88. Which of these molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?

- (a) H₃O⁺
- (b) PCl₄⁻
- (c) SnCl₃⁻
- (d) BrCl₄⁻
- (e) ICl₃
- (f) XeF₄
- (g) SF₂

89. Which of the following molecules have dipole moments?

- (a) CS₂
- (b) SeS₂
- (c) CCl₂F₂
- (d) PCl₃ (P is the central atom)
- (e) ClNO (N is the central atom)

90. Identify the molecules with a dipole moment:

- (a) SF₄
- (b) CF₄
- (c) Cl₂CCBr₂
- (d) CH₃Cl
- (e) H₂CO

91. The molecule XF₃ has a dipole moment. Is X boron or phosphorus?

92. The molecule XCl₂ has a dipole moment. Is X beryllium or sulfur?

93. Is the Cl₂BBCl₂ molecule polar or nonpolar?

94. There are three possible structures for PCl₂F₃ with phosphorus as the central atom. Draw them and discuss how measurements of dipole moments could help distinguish among them.

95. Describe the molecular structure around the indicated atom or atoms:

- (a) the sulfur atom in sulfuric acid, H₂SO₄ [(HO)₂SO₂]
- (b) the chlorine atom in chloric acid, HClO₃ [HOClO₂]
- (c) the oxygen atom in hydrogen peroxide, HOOH
- (d) the nitrogen atom in nitric acid, HNO₃ [HONO₂]
- (e) the oxygen atom in the OH group in nitric acid, HNO₃ [HONO₂]
- (f) the central oxygen atom in the ozone molecule, O₃
- (g) each of the carbon atoms in propyne, CH₃CCH
- (h) the carbon atom in Freon, CCl₂F₂
- (i) each of the carbon atoms in allene, H₂CCCH₂

96. Draw the Lewis structures and predict the shape of each compound or ion:

- (a) CO₂
- (b) NO₂⁻
- (c) SO₃
- (d) SO₃²⁻

97. A molecule with the formula AB₂, in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion for each shape.

98. A molecule with the formula AB₃, in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion that has each shape.

99. Draw the Lewis electron dot structures for these molecules, including resonance structures where appropriate:

- (a) CS₃²⁻
- (b) CS₂
- (c) CS

(d) predict the molecular shapes for CS₃²⁻ and CS₂ and explain how you arrived at your predictions

100. What is the molecular structure of the stable form of FNO₂? (N is the central atom.)

101. A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen. What is its molecular structure?

102. Use the **simulation (<http://openstaxcollege.org//16MolecPolarity>)** to perform the following exercises for a two-atom molecule:

- (a) Adjust the electronegativity value so the bond dipole is pointing toward B. Then determine what the electronegativity values must be to switch the dipole so that it points toward A.
- (b) With a partial positive charge on A, turn on the electric field and describe what happens.
- (c) With a small partial negative charge on A, turn on the electric field and describe what happens.
- (d) Reset all, and then with a large partial negative charge on A, turn on the electric field and describe what happens.

103. Use the **simulation (<http://openstaxcollege.org//16MolecPolarity>)** to perform the following exercises for a real molecule. You may need to rotate the molecules in three dimensions to see certain dipoles.

- (a) Sketch the bond dipoles and molecular dipole (if any) for O_3 . Explain your observations.
- (b) Look at the bond dipoles for NH_3 . Use these dipoles to predict whether N or H is more electronegative.
- (c) Predict whether there should be a molecular dipole for NH_3 and, if so, in which direction it will point. Check the molecular dipole box to test your hypothesis.

104. Use the **Molecule Shape simulator (<http://openstaxcollege.org//16MolecShape>)** to build a molecule. Starting with the central atom, click on the double bond to add one double bond. Then add one single bond and one lone pair. Rotate the molecule to observe the complete geometry. Name the electron group geometry and molecular structure and predict the bond angle. Then click the check boxes at the bottom and right of the simulator to check your answers.

105. Use the **Molecule Shape simulator (<http://openstaxcollege.org//16MolecShape>)** to explore real molecules. On the Real Molecules tab, select H_2O . Switch between the “real” and “model” modes. Explain the difference observed.

106. Use the **Molecule Shape simulator (<http://openstaxcollege.org//16MolecShape>)** to explore real molecules. On the Real Molecules tab, select “model” mode and S_2O . What is the model bond angle? Explain whether the “real” bond angle should be larger or smaller than the ideal model angle.

Chapter 5

Advanced Theories of Bonding

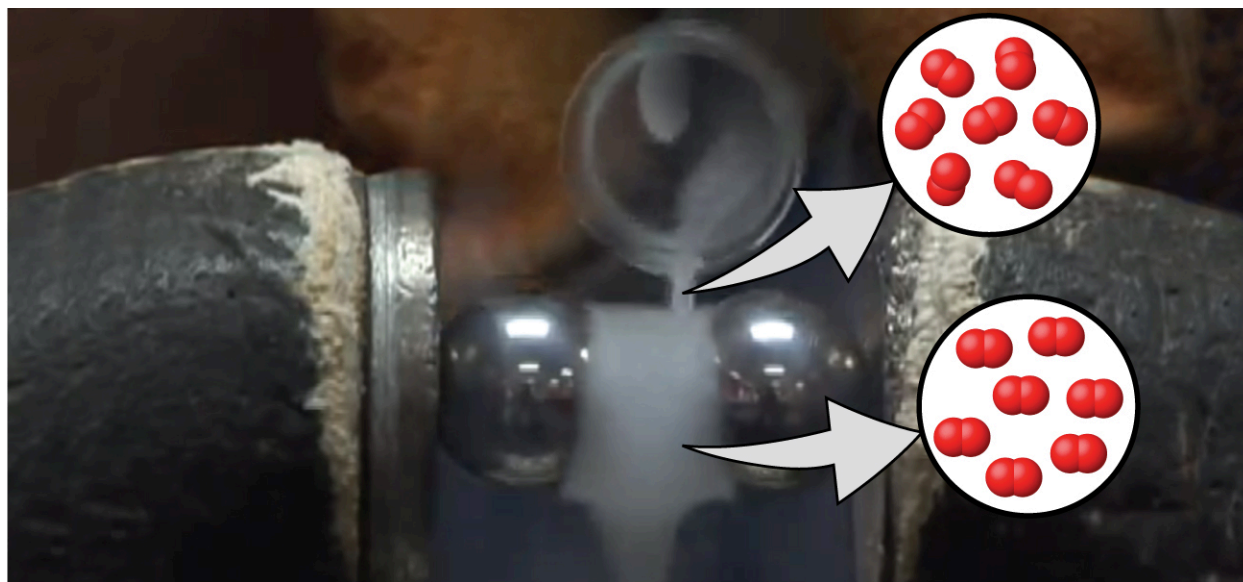


Figure 5.1 Oxygen molecules orient randomly most of the time, as shown in the top magnified view. However, when we pour liquid oxygen through a magnet, the molecules line up with the magnetic field, and the attraction allows them to stay suspended between the poles of the magnet where the magnetic field 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. (credit: modification of work by Jefferson Lab)

Chapter Outline

- 5.1 Valence Bond Theory
- 5.2 Hybrid Atomic Orbitals
- 5.3 Multiple Bonds
- 5.4 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_2 and O_2 have fairly similar Lewis structures that contain lone pairs of electrons.



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.

5.1 Valence Bond Theory

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 σ and π bonds

As we know, a scientific theory is a strongly supported explanation for observed natural laws or large bodies of experimental data. For a theory to be accepted, it must explain experimental data and be able to predict behavior. For example, VSEPR theory has gained widespread acceptance because it predicts three-dimensional molecular shapes that are consistent with experimental data collected for thousands of different molecules. However, VSEPR theory does not provide an explanation of chemical bonding.

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 5.2** illustrates how the sum of the energies of two hydrogen atoms (the colored curve) changes as they approach each other. When the atoms are far apart there is no overlap, and by convention we set the sum of the energies at zero. As the atoms move together, their orbitals begin to overlap. Each electron begins to feel the attraction of the nucleus in the other atom. In addition, the electrons begin to repel each other, as do the nuclei. While the atoms are still widely separated, the attractions are slightly stronger than the repulsions, and the energy of the system decreases. (A bond begins to form.) As the atoms move closer together, the overlap increases, so the attraction of the nuclei for the electrons continues to increase (as do the repulsions among electrons and between the nuclei). At some specific distance between the atoms, which varies depending on the atoms involved, the energy reaches its lowest (most stable) value. This optimum distance between the two bonded nuclei is the bond distance between the two atoms. The bond is stable because at this point, the attractive and repulsive forces combine to create the lowest possible energy configuration. If the distance between the nuclei were to decrease further, the repulsions between nuclei and the repulsions as electrons are confined in closer proximity to each other would become stronger than the attractive forces. The energy of the system would then rise (making the system destabilized), as shown at the far left of **Figure 5.2**.

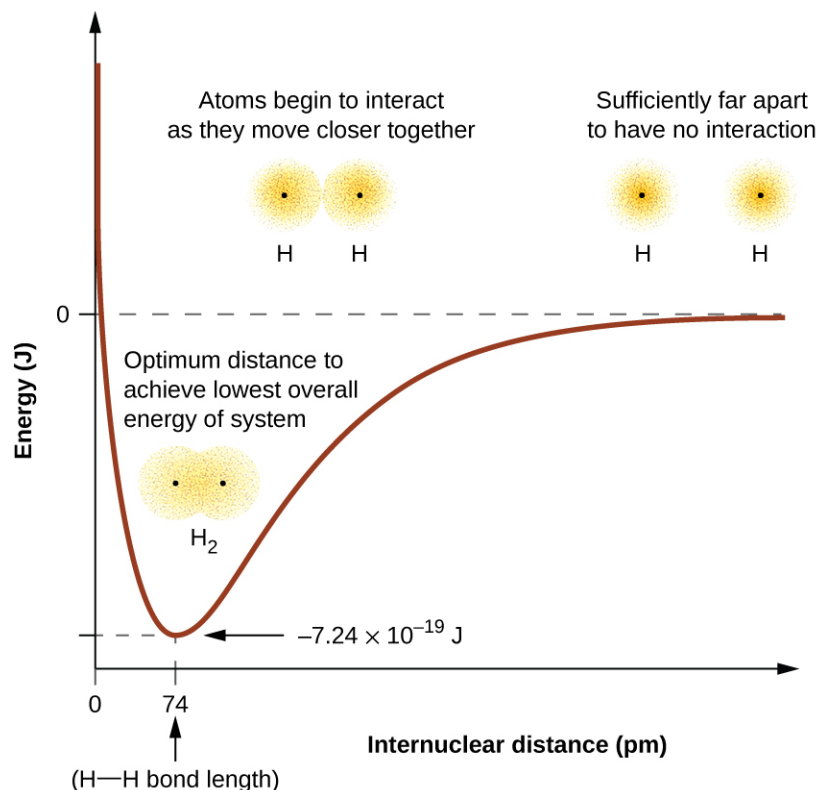


Figure 5.2 (a) The interaction of two hydrogen atoms changes as a function of distance. (b) The energy of the system changes as the atoms interact. The lowest (most stable) energy occurs at a distance of 74 pm, which is the bond length observed for the H_2 molecule.

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 5.3** 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.

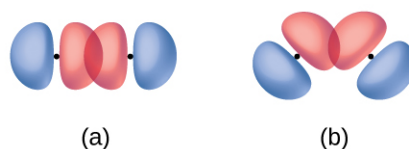


Figure 5.3 (a) The overlap of two p orbitals is greatest when the orbitals are directed end to end. (b) Any other arrangement results in less overlap. The dots indicate the locations of the nuclei.

The overlap of two s orbitals (as in H_2), the overlap of an s orbital and a p orbital (as in HCl), and the end-to-end overlap of two p orbitals (as in Cl_2) all produce **sigma bonds (σ bonds)**, as illustrated in **Figure 5.4**. A σ bond is a covalent bond in which the electron density is concentrated in the region along the internuclear axis; that is, a line between the nuclei would pass through the center of the overlap region. Single bonds in Lewis structures are described as σ bonds in valence bond theory.

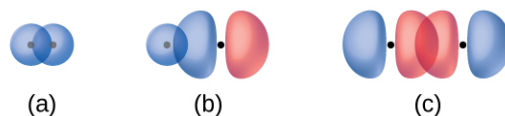


Figure 5.4 Sigma (σ) bonds form from the overlap of the following: (a) two s orbitals, (b) an s orbital and a p orbital, and (c) two p orbitals. The dots indicate the locations of the nuclei.

A **pi bond (π bond)** is a type of covalent bond that results from the side-by-side overlap of two p orbitals, as illustrated in **Figure 5.5**. In a π bond, the regions of orbital overlap lie on opposite sides of the internuclear axis. Along the axis itself, there is a **node**, that is, a plane with no probability of finding an electron.

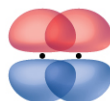
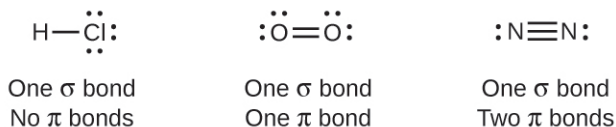


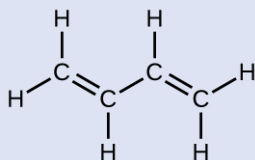
Figure 5.5 Pi (π) bonds form from the side-by-side overlap of two p orbitals. The dots indicate the location of the nuclei.

While all single bonds are σ bonds, multiple bonds consist of both σ and π bonds. As the Lewis structures below suggest, O_2 contains a double bond, and N_2 contains a triple bond. The double bond consists of one σ bond and one π bond, and the triple bond consists of one σ bond and two π bonds. Between any two atoms, the first bond formed will always be a σ bond, but there can only be one σ bond in any one location. In any multiple bond, there will be one σ bond, and the remaining one or two bonds will be π bonds. These bonds are described in more detail later in this chapter.



Example 5.1

Counting σ and π Bonds



Butadiene, C_4H_6 , is used to make synthetic rubber. Identify the number of σ and π bonds contained in this molecule.

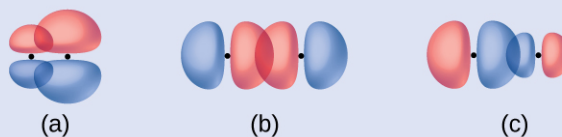
Solution

There are six σ C–H bonds and one σ C–C bond, for a total of seven from the single bonds. There are two double bonds that each have a π bond in addition to the σ bond. This gives a total nine σ and two π bonds overall.

Check Your Learning

Identify each illustration as depicting a σ or π 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



Answer: (a) is a π bond with a node along the axis connecting the nuclei while (b) and (c) are σ bonds that overlap along the axis.

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 1.60218×10^{-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 $(1.60218 \times 10^{19} \text{ C})(0.127 \times 10^{-9} \text{ m})$ or $2.03 \times 10^{-29} \text{ C}\cdot\text{m}$. Converted to D, this is $\left(2.03 \times 10^{-29} \text{ C}\cdot\text{m}\right) \left(\frac{1 \text{ Debye}}{3.336 \times 10^{-30} \text{ C}\cdot\text{m}}\right)$ or 6.09 D. Were HCl completely ionic, this would be its molecular dipole moment. To get the partial ionic character, we divide. This means the bond is about 17% ionic – or, put another way, the positive charge in H is +0.17 and the partial negative charge on chlorine, –0.17.

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.

5.2 Hybrid Atomic Orbitals

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° , as shown in **Figure 5.6**, because p orbitals are perpendicular to each other. Experimental evidence shows that the bond angle is 104.5° , not 90° . The prediction of the valence bond theory model does not match the real-world observations of a water molecule; a different model is needed.

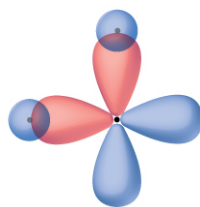


Figure 5.6 The hypothetical overlap of two of the $2p$ orbitals on an oxygen atom (red) with the $1s$ orbitals of two hydrogen atoms (blue) would produce a bond angle of 90° . This is not consistent with experimental evidence.^[1]

Quantum-mechanical calculations suggest why the observed bond angles in H_2O differ from those predicted by the overlap of the $1s$ orbital of the hydrogen atoms with the $2p$ orbitals of the oxygen atom. The mathematical expression known as the wave function, ψ , contains information about each orbital and the wavelike properties of

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.

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 5.7). Consequently, the overlap of the O and H orbitals should result in a tetrahedral bond angle (109.5°). The observed angle of 104.5° is experimental evidence for which quantum-mechanical calculations give a useful explanation: Valence bond theory must include a hybridization component to give accurate predictions.

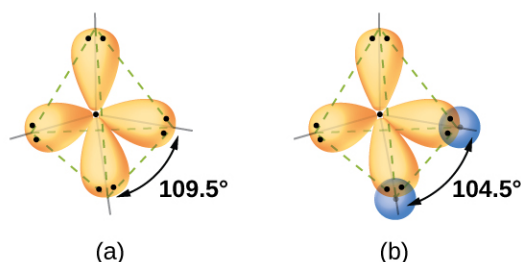


Figure 5.7 (a) A water molecule has four regions of electron density, so VSEPR theory predicts a tetrahedral arrangement of hybrid orbitals. (b) Two of the hybrid orbitals on oxygen contain lone pairs, and the other two overlap with the $1s$ orbitals of hydrogen atoms to form the O–H bonds in H_2O . This description is more consistent with the experimental structure.

The following ideas are important in understanding hybridization:

1. Hybrid orbitals do not exist in isolated atoms. They are formed only in covalently bonded atoms.
2. Hybrid orbitals have shapes and orientations that are very different from those of the atomic orbitals in isolated atoms.
3. A set of hybrid orbitals is generated by combining atomic orbitals. The number of hybrid orbitals in a set is equal to the number of atomic orbitals that were combined to produce the set.
4. All orbitals in a set of hybrid orbitals are equivalent in shape and energy.
5. The type of hybrid orbitals formed in a bonded atom depends on its electron-pair geometry as predicted by the VSEPR theory.
6. Hybrid orbitals overlap to form σ bonds. Unhybridized orbitals overlap to form π bonds.

In the following sections, we shall discuss the common types of hybrid orbitals.

sp Hybridization

The beryllium atom in a gaseous $BeCl_2$ molecule is an example of a central atom with no lone pairs of electrons in a linear arrangement of three atoms. There are two regions of valence electron density in the $BeCl_2$ molecule that correspond to the two covalent Be–Cl bonds. To accommodate these two electron domains, two of the Be atom's four valence orbitals will mix to yield two hybrid orbitals. This hybridization process involves mixing of the valence s orbital with one of the valence p orbitals to yield two equivalent **sp hybrid orbitals** that are oriented in a linear geometry (Figure 5.8). In this figure, the set of sp orbitals appears similar in shape to the original p orbital, but there is an important difference. The number of atomic orbitals combined always equals the number of hybrid orbitals formed. The p orbital is one orbital that can hold up to two electrons. The sp set is two equivalent orbitals that point

180° from each other. The two electrons that were originally in the s orbital are now distributed to the two sp orbitals, which are half filled. In gaseous BeCl_2 , these half-filled hybrid orbitals will overlap with orbitals from the chlorine atoms to form two identical σ bonds.

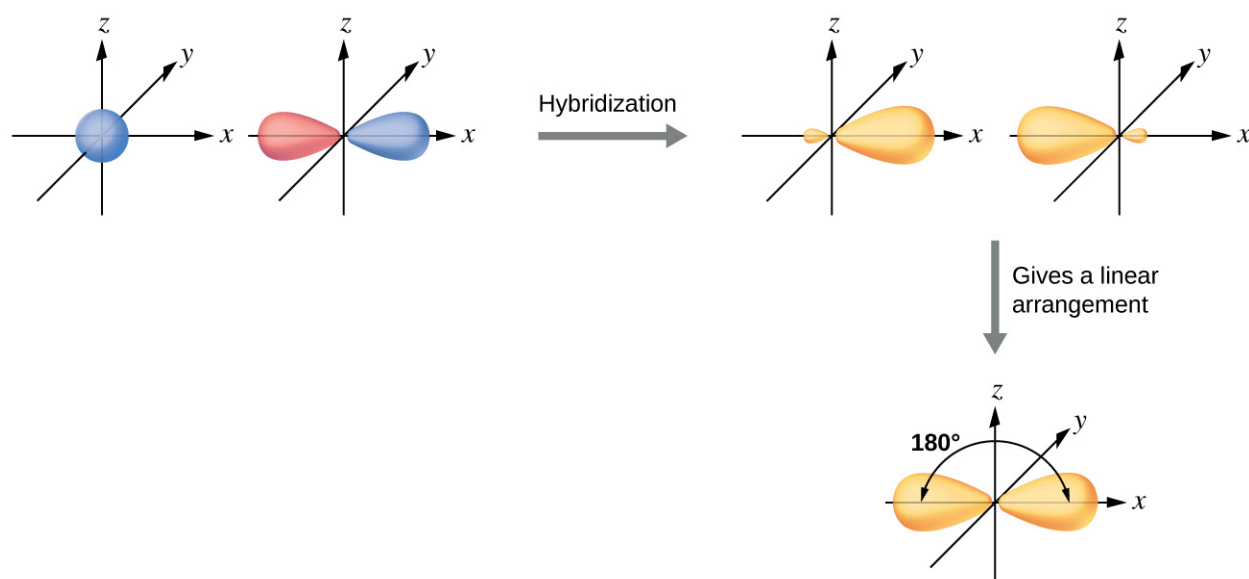


Figure 5.8 Hybridization of an s orbital (blue) and a p orbital (red) of the same atom produces two sp hybrid orbitals (yellow). Each hybrid orbital is oriented primarily in just one direction. Note that each sp orbital contains one lobe that is significantly larger than the other. The set of two sp orbitals are oriented at 180° , which is consistent with the geometry for two domains.

We illustrate the electronic differences in an isolated Be atom and in the bonded Be atom in the orbital energy-level diagram in **Figure 5.9**. 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.

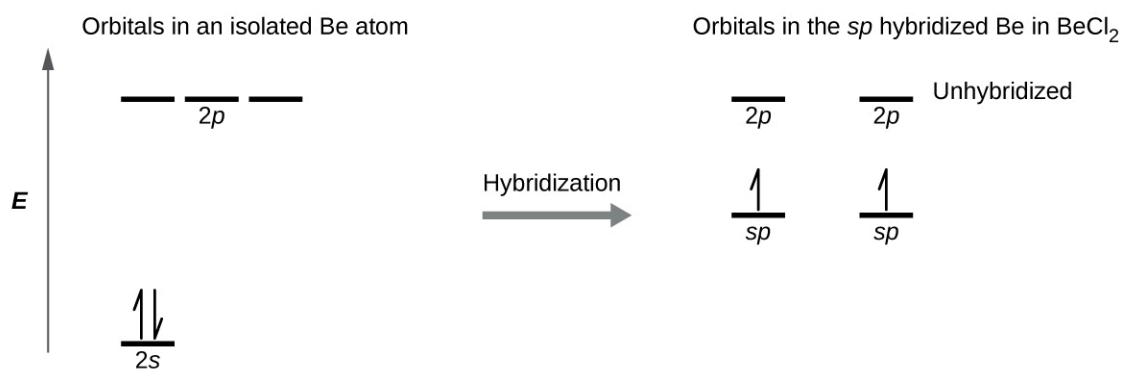


Figure 5.9 This orbital energy-level diagram shows the sp hybridized orbitals on Be in the linear BeCl_2 molecule. Each of the two sp hybrid orbitals holds one electron and is thus half filled and available for bonding via overlap with a Cl $3p$ orbital.

When atomic orbitals hybridize, the valence electrons occupy the newly created orbitals. The Be atom had two valence electrons, so each of the sp orbitals gets one of these electrons. Each of these electrons pairs up with the

unpaired electron on a chlorine atom when a hybrid orbital and a chlorine orbital overlap during the formation of the Be–Cl bonds.

Any central atom surrounded by just two regions of valence electron density in a molecule will exhibit sp hybridization. Other examples include the mercury atom in the linear HgCl_2 molecule, the zinc atom in $\text{Zn}(\text{CH}_3)_2$, which contains a linear C–Zn–C arrangement, and the carbon atoms in HCCH and CO_2 .

Link to Learning

Check out the University of Wisconsin-Oshkosh [website \(http://openstaxcollege.org/l/16hybridorbital\)](http://openstaxcollege.org/l/16hybridorbital) 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 5.10).

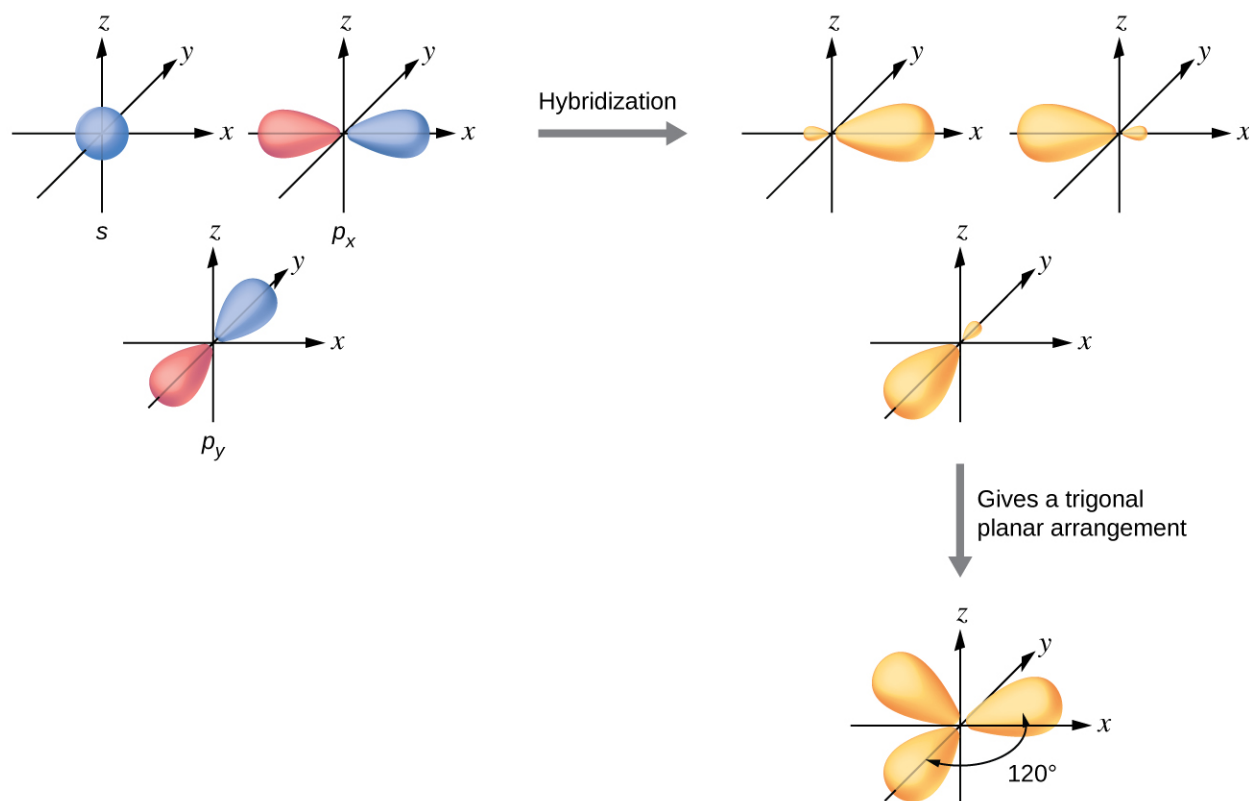


Figure 5.10 The hybridization of an s orbital (blue) and two p orbitals (red) produces three equivalent sp^2 hybridized orbitals (yellow) oriented at 120° with respect to each other. The remaining unhybridized p orbital is not shown here, but is located along the z axis.

Although quantum mechanics yields the “plump” orbital lobes as depicted in **Figure 5.10**, sometimes for clarity these orbitals are drawn thinner and without the minor lobes, as in **Figure 5.11**, 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.

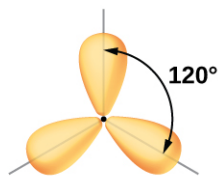


Figure 5.11 This alternate way of drawing the trigonal planar sp^2 hybrid orbitals is sometimes used in more crowded figures.

The observed structure of the borane molecule, BH_3 , suggests sp^2 hybridization for boron in this compound. The molecule is trigonal planar, and the boron atom is involved in three bonds to hydrogen atoms (**Figure 5.12**). 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 5.13**. 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.

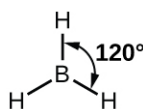


Figure 5.12 BH_3 is an electron-deficient molecule with a trigonal planar structure.

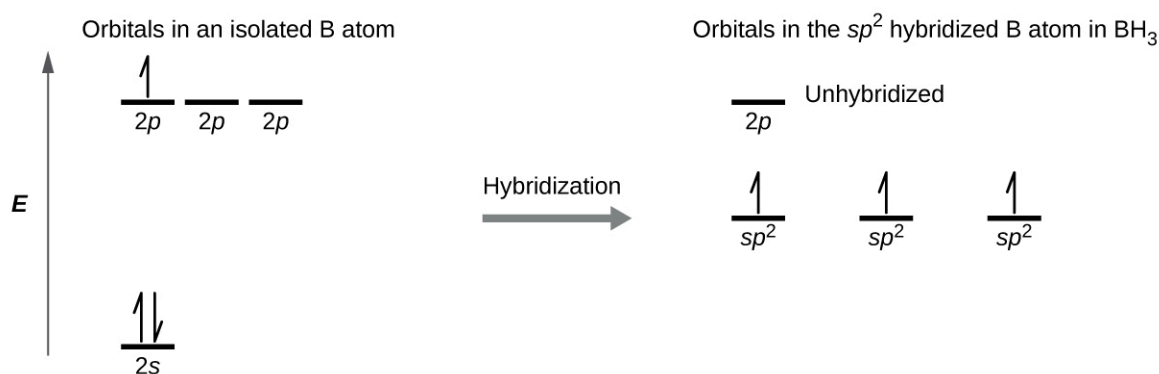


Figure 5.13 In an isolated B atom, there are one $2s$ and three $2p$ valence orbitals. When boron is in a molecule with three regions of electron density, three of the orbitals hybridize and create a set of three sp^2 orbitals and one unhybridized $2p$ orbital. The three half-filled hybrid orbitals each overlap with an orbital from a hydrogen atom to form three σ bonds in BH_3 .

Any central atom surrounded by three regions of electron density will exhibit sp^2 hybridization. This includes molecules with a lone pair on the central atom, such as $CINO$ (**Figure 5.14**), 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 .

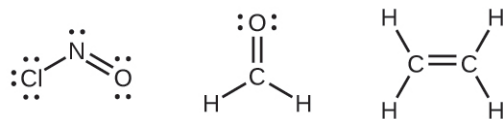


Figure 5.14 The central atom(s) in each of the structures shown contain three regions of electron density and are sp^2 hybridized. As we know from the discussion of VSEPR theory, a region of electron density contains all of the electrons that point in one direction. A lone pair, an unpaired electron, a single bond, or a multiple bond would each count as one region of electron density.

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 5.15**). Each of these hybrid orbitals points toward a different corner of a tetrahedron.

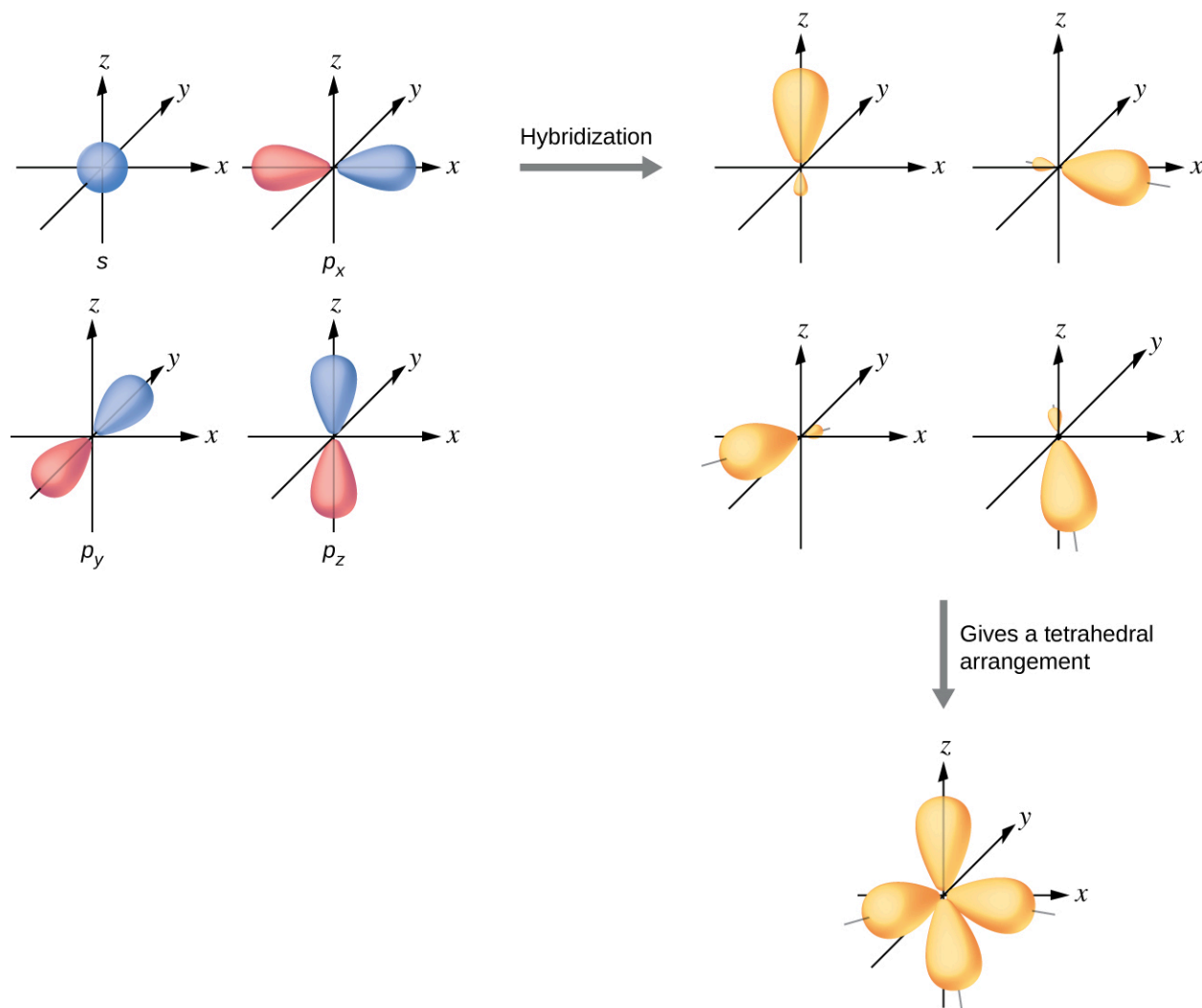


Figure 5.15 The hybridization of an s orbital (blue) and three p orbitals (red) produces four equivalent sp^3 hybridized orbitals (yellow) oriented at 109.5° with respect to each other.

A molecule of methane, CH_4 , consists of a carbon atom surrounded by four hydrogen atoms at the corners of a tetrahedron. The carbon atom in methane exhibits sp^3 hybridization. We illustrate the orbitals and electron distribution in an isolated carbon atom and in the bonded atom in CH_4 in **Figure 5.16**. 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.

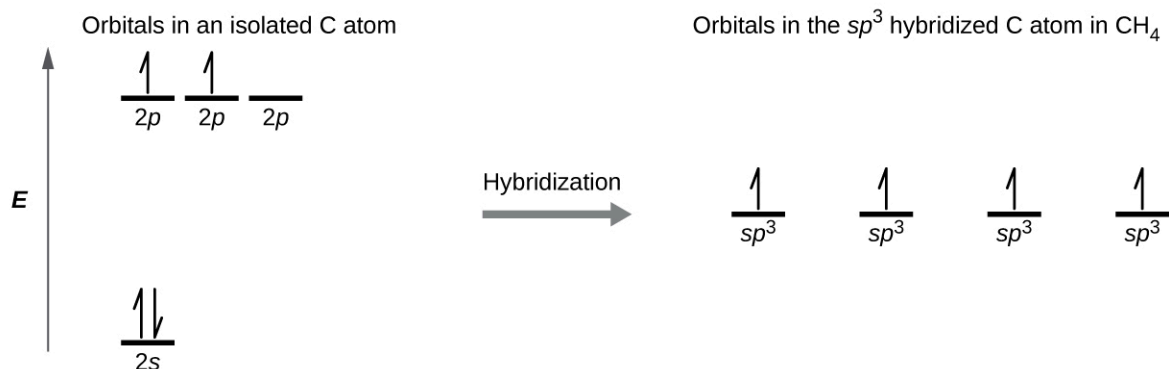


Figure 5.16 The four valence atomic orbitals from an isolated carbon atom all hybridize when the carbon bonds in a molecule like CH_4 with four regions of electron density. This creates four equivalent sp^3 hybridized orbitals. Overlap of each of the hybrid orbitals with a hydrogen orbital creates a C–H σ bond.

In a methane molecule, the $1s$ 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 (σ) bond. This results in the formation of four strong, equivalent covalent bonds between the carbon atom and each of the hydrogen atoms to produce the methane molecule, CH_4 .

The structure of ethane, C_2H_6 , is similar to that of methane in that each carbon in ethane has four neighboring atoms arranged at the corners of a tetrahedron—three hydrogen atoms and one carbon atom (**Figure 5.17**). However, in ethane an sp^3 orbital of one carbon atom overlaps end to end with an sp^3 orbital of a second carbon atom to form a σ bond between the two carbon atoms. Each of the remaining sp^3 hybrid orbitals overlaps with an s orbital of a hydrogen atom to form carbon–hydrogen σ bonds. The structure and overall outline of the bonding orbitals of ethane are shown in **Figure 5.17**. The orientation of the two CH_3 groups is not fixed relative to each other. Experimental evidence shows that rotation around σ bonds occurs easily.

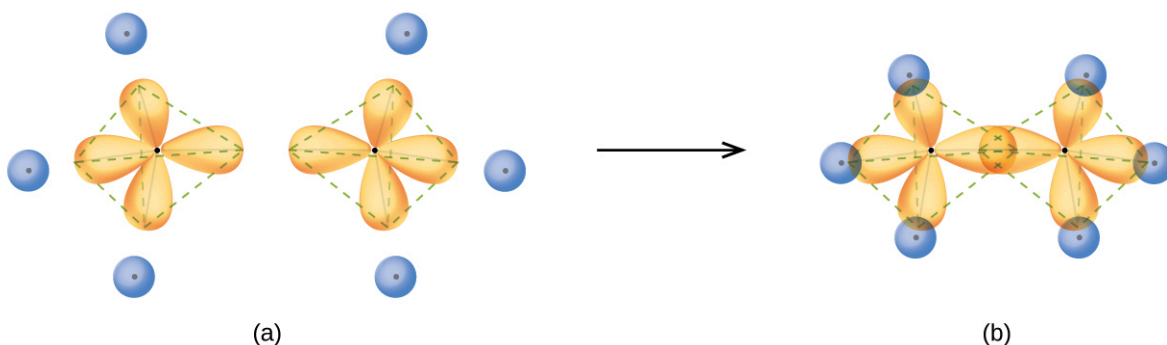


Figure 5.17 (a) In the ethane molecule, C_2H_6 , each carbon has four sp^3 orbitals. (b) These four orbitals overlap to form seven σ bonds.

An sp^3 hybrid orbital can also hold a lone pair of electrons. For example, the nitrogen atom in ammonia is surrounded by three bonding pairs and a lone pair of electrons directed to the four corners of a tetrahedron. The nitrogen atom is sp^3 hybridized with one hybrid orbital occupied by the lone pair.

The molecular structure of water is consistent with a tetrahedral arrangement of two lone pairs and two bonding pairs of electrons. Thus we say that the oxygen atom is sp^3 hybridized, with two of the hybrid orbitals occupied by lone pairs and two by bonding pairs. Since lone pairs occupy more space than bonding pairs, structures that contain lone pairs have bond angles slightly distorted from the ideal. Perfect tetrahedra have angles of 109.5° , but the observed angles in ammonia (107.3°) and water (104.5°) are slightly smaller. Other examples of sp^3 hybridization include CCl_4 ,

PCl_3 , and 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, 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 5.19) that are involved in the P–Cl bonds. Other atoms that exhibit sp^3d hybridization include the sulfur atom in SF_4 and the chlorine atoms in ClF_3 and in ClF_4^+ . (The electrons on fluorine atoms are omitted for clarity.)

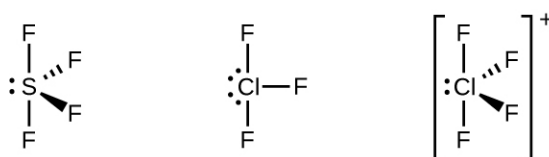


Figure 5.18 The three compounds pictured exhibit sp^3d hybridization in the central atom and a trigonal bipyramidal form. SF_4 and ClF_4^+ have one lone pair of electrons on the central atom, and ClF_3 has two lone pairs giving it the T-shape shown.

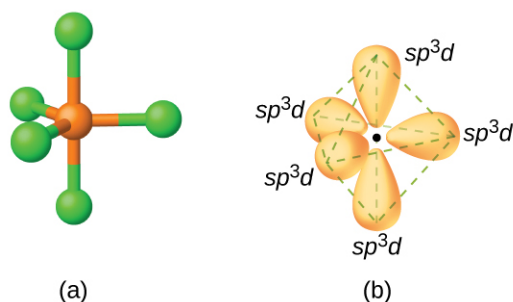


Figure 5.19 (a) The five regions of electron density around phosphorus in PCl_5 require five hybrid sp^3d orbitals. (b) These orbitals combine to form a trigonal bipyramidal structure with each large lobe of the hybrid orbital pointing at a vertex. As before, there are also small lobes pointing in the opposite direction for each orbital (not shown for clarity).

The sulfur atom in sulfur hexafluoride, SF_6 , exhibits sp^3d^2 hybridization. A molecule of sulfur hexafluoride has six bonding pairs of electrons connecting six fluorine atoms to a single sulfur atom. There are no lone pairs of electrons on the central atom. To bond six fluorine atoms, the $3s$ 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 PCl_6^- , the iodine atom in the interhalogens IF_6^+ , IF_5 , ICl_4^- , IF_4^- and the xenon atom in XeF_4 .

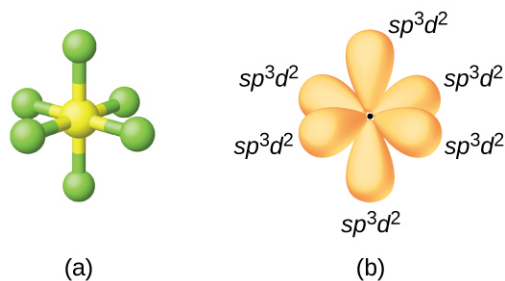


Figure 5.20 (a) Sulfur hexafluoride, SF_6 , has an octahedral structure that requires sp^3d^2 hybridization. (b) The six sp^3d^2 orbitals form an octahedral structure around sulfur. Again, the minor lobe of each orbital is not shown for clarity.

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 5.21**. 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 5.21** that corresponds to this geometry.


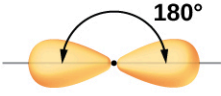

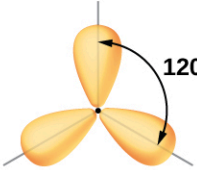
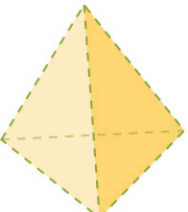
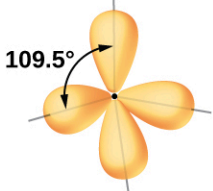

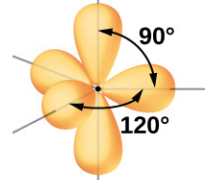

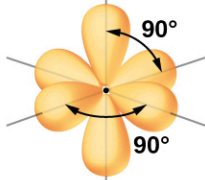
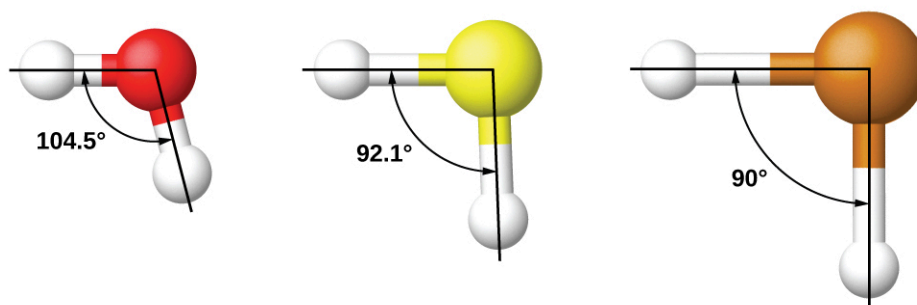
Regions of Electron Density	Arrangement		Hybridization	
2		linear	sp	
3		trigonal planar	sp^2	
4		tetrahedral	sp^3	
5		trigonal bipyramidal	sp^3d	
6		octahedral	sp^3d^2	

Figure 5.21 The shapes of hybridized orbital sets are consistent with the electron-pair geometries. For example, an atom surrounded by three regions of electron density is sp^2 hybridized, and the three sp^2 orbitals are arranged in a trigonal planar fashion.

It is important to remember that hybridization was devised to rationalize experimentally observed molecular geometries. 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° , which is more consistent with sp^3 hybrid orbitals (109.5°) on the central atom than with $2p$ orbitals (90°). Sulfur is in the same group as oxygen, and H_2S has a similar Lewis structure. However, it has a much smaller bond angle (92.1°), which indicates much less hybridization on sulfur than oxygen. Continuing down the group, tellurium is even larger than sulfur, and for H_2Te , the observed bond angle (90°) is consistent with overlap of the $5p$ orbitals, without invoking hybridization. We invoke hybridization where it is necessary to explain the observed structures.



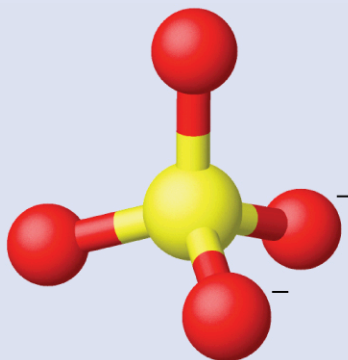
Example 5.3

Assigning Hybridization

Ammonium sulfate is important as a fertilizer. What is the hybridization of the sulfur atom in the sulfate ion, SO_4^{2-} ?

Solution

The Lewis structure of sulfate shows there are four regions of electron density. The hybridization is sp^3 .



Check Your Learning

What is the hybridization of the selenium atom in SeF_4 ?



Answer: The selenium atom is sp^3d hybridized.

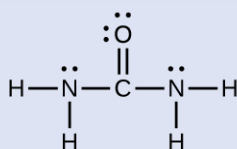
Example 5.4

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 each nitrogen and carbon atom in urea?

Solution

The Lewis structure of urea is

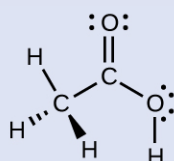


The nitrogen atoms are surrounded by four regions of electron density, which arrange themselves in a tetrahedral electron-pair geometry. The hybridization in a tetrahedral arrangement is sp^3 (Figure 5.21). This is the hybridization of the nitrogen atoms in urea.

The carbon atom is surrounded by three regions of electron density, positioned in a trigonal planar arrangement. The hybridization in a trigonal planar electron pair geometry is sp^2 (Figure 5.21), 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?



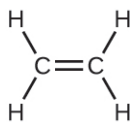
Answer: H_3C , sp^3 ; $\text{C}(\text{O})\text{OH}$, sp^2

5.3 Multiple Bonds

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 π -bonding and electron delocalization

The hybrid orbital model appears to account well for the geometry of molecules involving single covalent bonds. Is it also capable of describing molecules containing double and triple bonds? We have already discussed that multiple bonds consist of σ and π bonds. Next we can consider how we visualize these components and how they relate to hybrid orbitals. The Lewis structure of ethene, C_2H_4 , shows us that each carbon atom is surrounded by one other carbon atom and two hydrogen atoms.



The three bonding regions form a trigonal planar electron-pair geometry. Thus we expect the σ bonds from each carbon atom are formed using a set of sp^2 hybrid orbitals that result from hybridization of two of the $2p$ orbitals and the $2s$ orbital (Figure 5.22). These orbitals form the C–H single bonds and the σ bond in the $\text{C}=\text{C}$ double bond (Figure 5.23). The π bond in the $\text{C}=\text{C}$ 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 5.23) 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 5.23) and form a π bond.

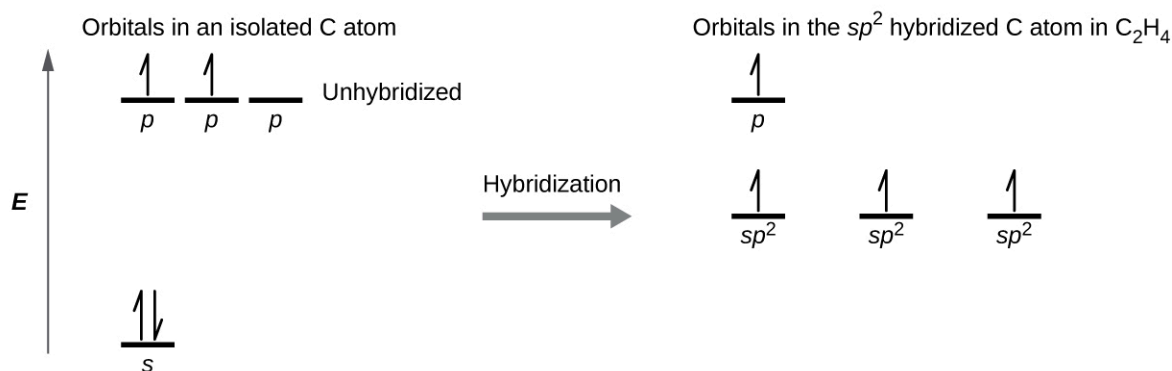


Figure 5.22 In ethene, each carbon atom is sp^2 hybridized, and the sp^2 orbitals and the p orbital are singly occupied. The hybrid orbitals overlap to form σ bonds, while the p orbitals on each carbon atom overlap to form a π bond.

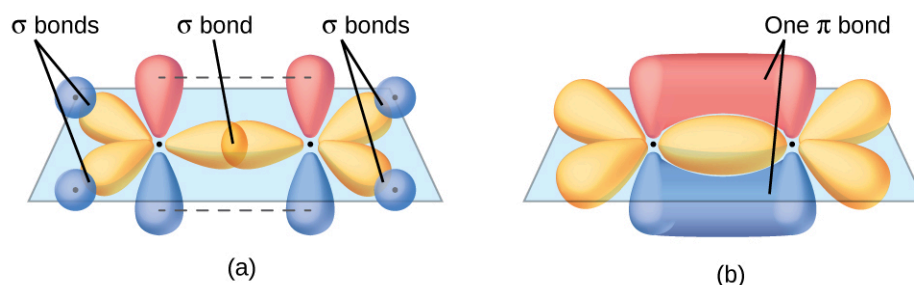


Figure 5.23 In the ethene molecule, C_2H_4 , there are (a) five σ bonds. One C–C σ bond results from overlap of sp^2 hybrid orbitals on the carbon atom with one sp^2 hybrid orbital on the other carbon atom. Four C–H bonds result from the overlap between the C atoms' sp^2 orbitals with s orbitals on the hydrogen atoms. (b) The π bond is formed by the side-by-side overlap of the two unhybridized p orbitals in the two carbon atoms. The two lobes of the π bond are above and below the plane of the σ system.

In an ethene molecule, the four hydrogen atoms and the two carbon atoms are all in the same plane. If the two planes of sp^2 hybrid orbitals tilted relative to each other, the p orbitals would not be oriented to overlap efficiently to create the π bond. The planar configuration for the ethene molecule occurs because it is the most stable bonding arrangement. This is a significant difference between σ and π bonds; rotation around single (σ) bonds occurs easily because the end-to-end orbital overlap does not depend on the relative orientation of the orbitals on each atom in the bond. In other words, rotation around the internuclear axis does not change the extent to which the σ bonding orbitals overlap because the bonding electron density is symmetric about the axis. Rotation about the internuclear axis is much more difficult for multiple bonds; however, this would drastically alter the off-axis overlap of the π bonding orbitals, essentially breaking the π bond.

In molecules with sp hybrid orbitals, two unhybridized p orbitals remain on the atom (**Figure 5.24**). We find this situation in acetylene, $H-C\equiv C-H$, which is a linear molecule. The sp hybrid orbitals of the two carbon atoms overlap end to end to form a σ bond between the carbon atoms (**Figure 5.25**). The remaining sp orbitals form σ bonds with hydrogen atoms. The two unhybridized p orbitals per carbon are positioned such that they overlap side by side and, hence, form two π bonds. The two carbon atoms of acetylene are thus bound together by one σ bond and two π bonds, giving a triple bond.

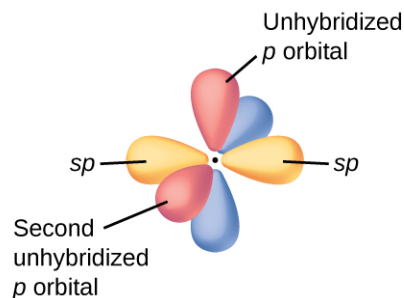


Figure 5.24 Diagram of the two linear sp hybrid orbitals of a carbon atom, which lie in a straight line, and the two unhybridized p orbitals at perpendicular angles.

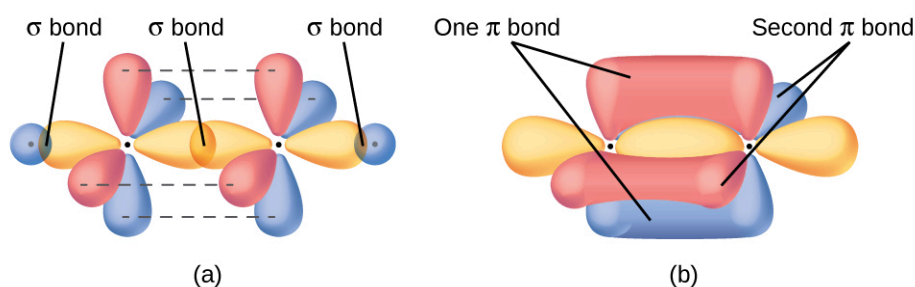


Figure 5.25 (a) In the acetylene molecule, C_2H_2 , there are two C–H σ bonds and a $C \equiv C$ triple bond involving one C–C σ bond and two C–C π bonds. The dashed lines, each connecting two lobes, indicate the side-by-side overlap of the four unhybridized p orbitals. (b) This shows the overall outline of the bonds in C_2H_2 . The two lobes of each of the π bonds are positioned across from each other around the line of the C–C σ bond.

Hybridization involves only σ bonds, lone pairs of electrons, and single unpaired electrons (radicals). Structures that account for these features describe the correct hybridization of the atoms. However, many structures also include resonance forms. Remember that resonance forms occur when various arrangements of π bonds are possible. Since the arrangement of π bonds involves only the unhybridized orbitals, resonance does not influence the assignment of hybridization.

For example, molecule benzene has two resonance forms (**Figure 5.26**). We can use either of these forms to determine that each of the carbon atoms is bonded to three other atoms with no lone pairs, so the correct hybridization is sp^2 . The electrons in the unhybridized p orbitals form π bonds. Neither resonance structure completely describes the electrons in the π bonds. They are not located in one position or the other, but in reality are delocalized throughout the ring. Valence bond theory does not easily address delocalization. Bonding in molecules with resonance forms is better described by molecular orbital theory. (See the next module.)

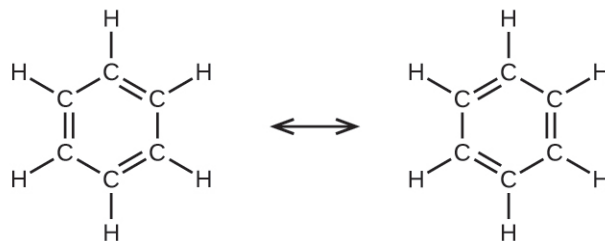


Figure 5.26 Each carbon atom in benzene, C_6H_6 , is sp^2 hybridized, independently of which resonance form is considered. The electrons in the π bonds are not located in one set of p orbitals or the other, but rather delocalized throughout the molecule.

Example 5.5

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



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, HNO_3 , which is produced by the reaction of nitrogen dioxide, NO_2 , with atmospheric water vapor. What is the hybridization of the nitrogen atom in NO_2 ? (Note: the lone electron on nitrogen occupies a hybridized orbital just as a lone pair would.)

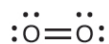
Answer: sp^2

5.4 Molecular Orbital Theory

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 :



This electronic structure adheres to all the rules governing Lewis theory. There is an O=O double bond, and each oxygen atom has eight electrons around it. However, this picture is at odds with the magnetic behavior of oxygen. By itself, O₂ 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 O₂ 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 5.27**), 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.

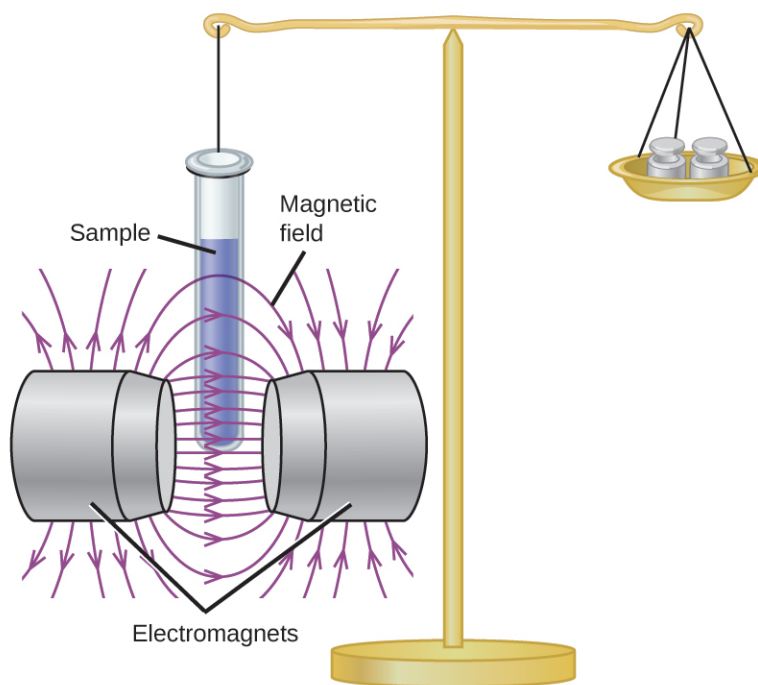


Figure 5.27 A Gouy balance compares the mass of a sample in the presence of a magnetic field with the mass with the electromagnet turned off to determine the number of unpaired electrons in a sample.

Experiments show that each O₂ 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 \(http://openstax.org//16diamagnetic\)](http://openstax.org//16diamagnetic) 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.

Comparison of Bonding Theories

Valence Bond Theory	Molecular Orbital Theory
considers bonds as localized between one pair of atoms	considers electrons delocalized throughout the entire molecule
creates bonds from overlap of atomic orbitals (<i>s</i> , <i>p</i> , <i>d</i> ...) and hybrid orbitals (<i>sp</i> , <i>sp</i> ² , <i>sp</i> ³ ...)	combines atomic orbitals to form molecular orbitals (σ , σ^* , π , π^*)
forms σ or π bonds	creates bonding and antibonding interactions based on which orbitals are filled
predicts molecular shape based on the number of regions of electron density	predicts the arrangement of electrons in molecules
needs multiple structures to describe resonance	

Table 5.1

Molecular orbital theory describes the distribution of electrons in molecules in much the same way that the distribution of electrons in atoms is described using atomic orbitals. Using quantum mechanics, the behavior of an electron in a molecule is still described by a wave function, Ψ , analogous to the behavior in an atom. Just like electrons around isolated atoms, electrons around atoms in molecules are limited to discrete (quantized) energies. The region of space in which a valence electron in a molecule is likely to be found is called a **molecular orbital (Ψ^2)**. Like an atomic orbital, a molecular orbital is full when it contains two electrons with opposite spin.

We will consider the molecular orbitals in molecules composed of two identical atoms (H_2 or Cl_2 , for example). Such molecules are called **homonuclear diatomic molecules**. In these diatomic molecules, several types of molecular orbitals occur.

The mathematical process of combining atomic orbitals to generate molecular orbitals is called the **linear combination of atomic orbitals (LCAO)**. The wave function describes the wavelike properties of an electron. Molecular orbitals are combinations of atomic orbital wave functions. Combining waves can lead to constructive interference, in which peaks line up with peaks, or destructive interference, in which peaks line up with troughs (**Figure 5.28**). 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.

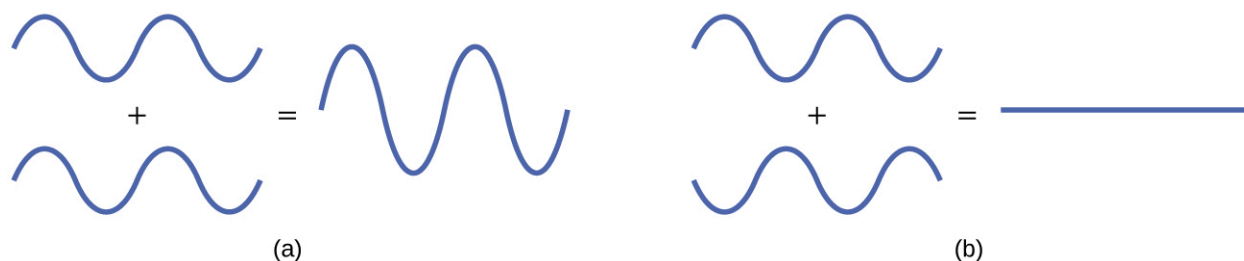


Figure 5.28 (a) When in-phase waves combine, constructive interference produces a wave with greater amplitude. (b) When out-of-phase waves combine, destructive interference produces a wave with less (or no) amplitude.

There are two types of molecular orbitals that can form from the overlap of two atomic s orbitals on adjacent atoms. The two types are illustrated in **Figure 5.29**. The in-phase combination produces a lower energy σ_s **molecular orbital** (read as "sigma-s") in which most of the electron density is directly between the nuclei. The out-of-phase addition (which can also be thought of as subtracting the wave functions) produces a higher energy **molecular orbital** (read as "sigma-s-star") molecular orbital in which there is a node between the nuclei. The asterisk signifies that the orbital is an antibonding orbital. Electrons in a σ_s orbital are attracted by both nuclei at the same time and are more stable (of lower energy) than they would be in the isolated atoms. Adding electrons to these orbitals creates a force that holds the two nuclei together, so we call these orbitals **bonding orbitals**. Electrons in the σ_s^* orbitals are located well away from the region between the two nuclei. The attractive force between the nuclei and these electrons pulls the two nuclei apart. Hence, these orbitals are called **antibonding orbitals**. Electrons fill the lower-energy bonding orbital before the higher-energy antibonding orbital, just as they fill lower-energy atomic orbitals before they fill higher-energy atomic orbitals.

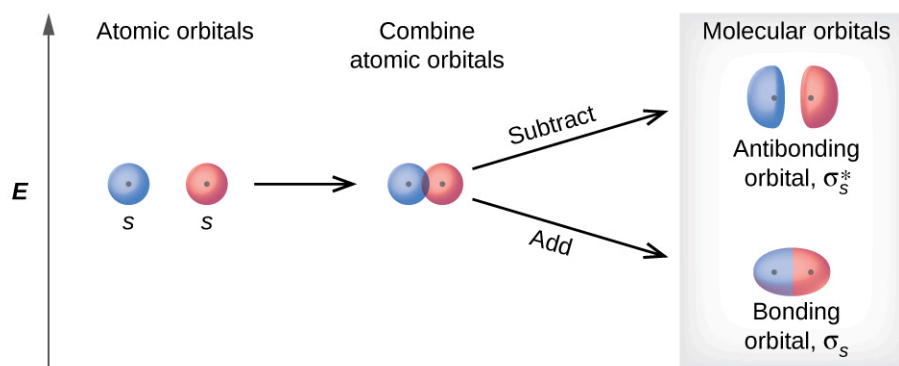


Figure 5.29 Sigma (σ) and sigma-star (σ^*) molecular orbitals are formed by the combination of two s atomic orbitals. The plus (+) signs indicate the locations of nuclei.

Link to Learning

You can watch **animations** (<http://openstax.org//16molecorbital>) 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 phase overlap, the destructive wave interference decreases electron density and creates nodes. When p orbitals overlap end to end, they create σ and σ^* orbitals (**Figure 5.30**). If two atoms are located along the x -axis in a Cartesian coordinate system, the two p_x orbitals overlap end to end and form σ_{px} (bonding) and σ_{px}^* (antibonding) (read as "sigma-p-x" and "sigma-p-x star," respectively). Just as with s -orbital overlap, the asterisk indicates the orbital with a node between the nuclei, which is a higher-energy, antibonding orbital.

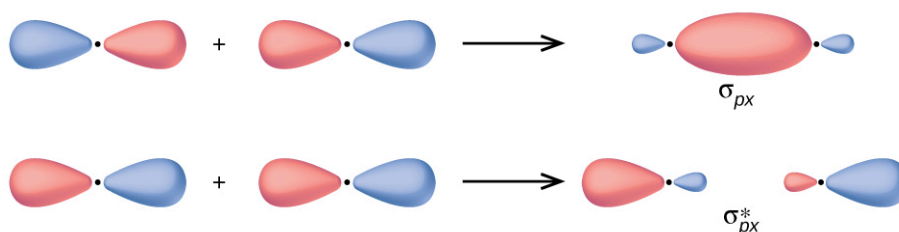


Figure 5.30 Combining wave functions of two p atomic orbitals along the internuclear axis creates two molecular orbitals, σ_p and σ_p^* .

The side-by-side overlap of two p orbitals gives rise to a **pi (π) bonding molecular orbital** and a **π^* antibonding molecular orbital**, as shown in **Figure 5.31**. In valence bond theory, we describe π bonds as containing a nodal plane containing the internuclear axis and perpendicular to the lobes of the p orbitals, with electron density on either side of the node. In molecular orbital theory, we describe the π orbital by this same shape, and a π bond exists when this orbital contains electrons. Electrons in this orbital interact with both nuclei and help hold the two atoms together, making it a bonding orbital. For the out-of-phase combination, there are two nodal planes created, one along the internuclear axis and a perpendicular one between the nuclei.

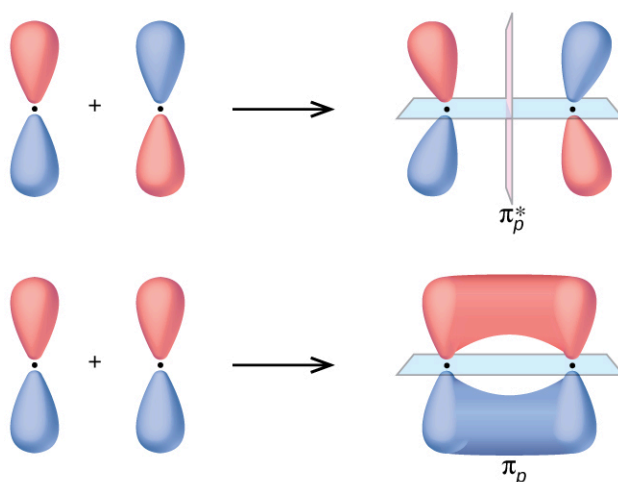


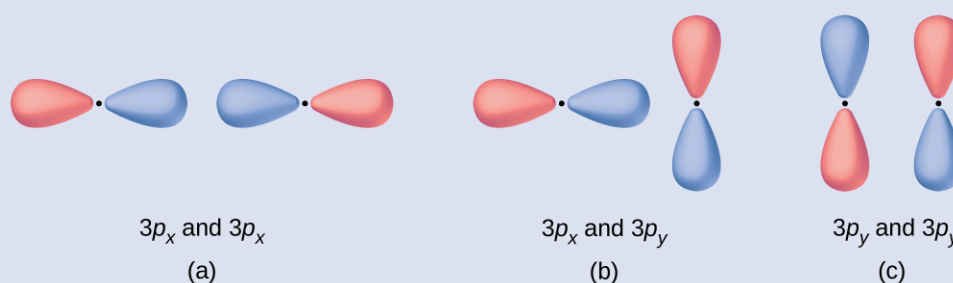
Figure 5.31 Side-by-side overlap of each two p orbitals results in the formation of two π molecular orbitals. Combining the out-of-phase orbitals results in an antibonding molecular orbital with two nodes. One contains the internuclear axis, and one is perpendicular to the axis. Combining the in-phase orbitals results in a bonding orbital. There is a node (blue) containing the internuclear axis with the two lobes of the orbital located above and below this node.

In the molecular orbitals of diatomic molecules, each atom also has two sets of p orbitals oriented side by side (p_y and p_z), so these four atomic orbitals combine pairwise to create two π orbitals and two π^* orbitals. The π_{py} and π_{pz}^* orbitals are oriented at right angles to the π_{pz} and π_{py}^* orbitals. Except for their orientation, the π_{py} and π_{pz} orbitals are identical and have the same energy; they are **degenerate orbitals**. The π_{py}^* and π_{pz}^* antibonding orbitals are also degenerate and identical except for their orientation. A total of six molecular orbitals results from the combination of the six atomic p orbitals in two atoms: σ_{px} and σ_{px}^* , π_{py} and π_{py}^* , π_{pz} and π_{pz}^* .

Example 5.6

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.



Solution

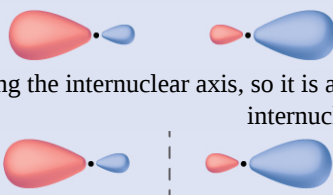
(a) is an in-phase combination, resulting in a σ_{3p} orbital

(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 π_{3p}^* orbital.

Check Your Learning

Label the molecular orbital shown as σ or π , bonding or antibonding and indicate where the node occurs.



Answer: The orbital is located along the internuclear axis, so it is a σ orbital. There is a node bisecting the internuclear axis, so it is an antibonding orbital.

Portrait of a Chemist

Walter Kohn: Nobel Laureate

Walter Kohn (Figure 5.32) 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 5.32 Walter Kohn developed methods to describe molecular orbitals. (credit: image courtesy of Walter Kohn)

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. Although he is now an emeritus professor, he is still actively working on projects involving global warming and renewable energy.

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 5.33**). 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.