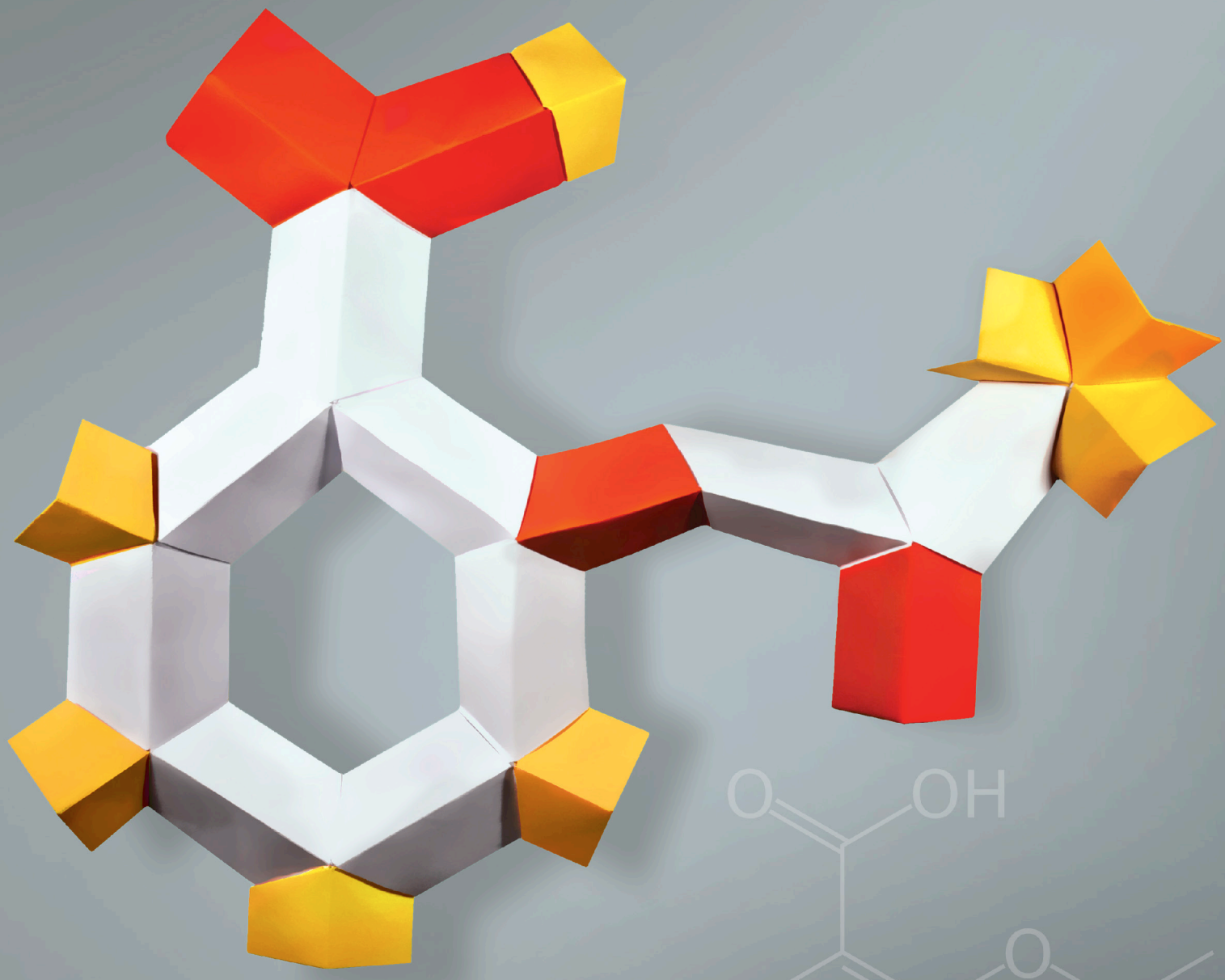
Organic Chemistry

PRINCIPLES AND MECHANISMS



JOEL KARTY

Organic Chemistry

Principles and Mechanisms

Joel M. Karty
Elon University

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To Pnut, Fafa, and Jakers

About the Author

JOEL KARTY earned his B.S. in chemistry at the University of Puget Sound and his Ph.D. at Stanford University. He joined the faculty of Elon University in 2001, where he currently holds the rank of associate professor. He teaches primarily the organic chemistry sequence and also teaches general chemistry. In the summer, Joel teaches at the Summer Medical and Dental Education Program through the Duke University medical center. His research interests include investigating the roles of resonance and inductive effects in fundamental chemical systems and studying the mechanism of pattern formation in Liesegang reactions. He has written a very successful student supplement, *Get Ready for Organic Chemistry*, Second Edition (formerly called *The Nuts and Bolts of Organic Chemistry*).

Brief Contents

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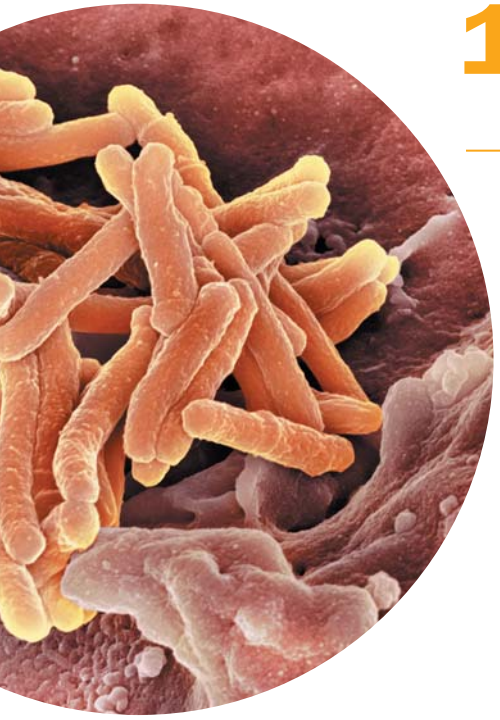
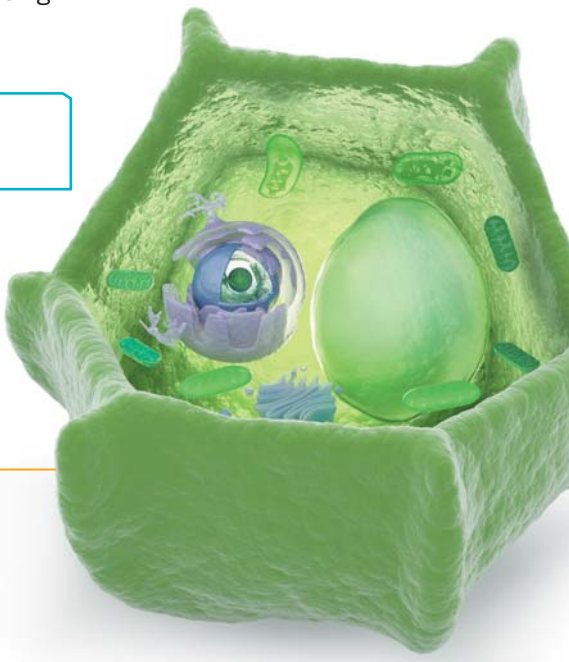
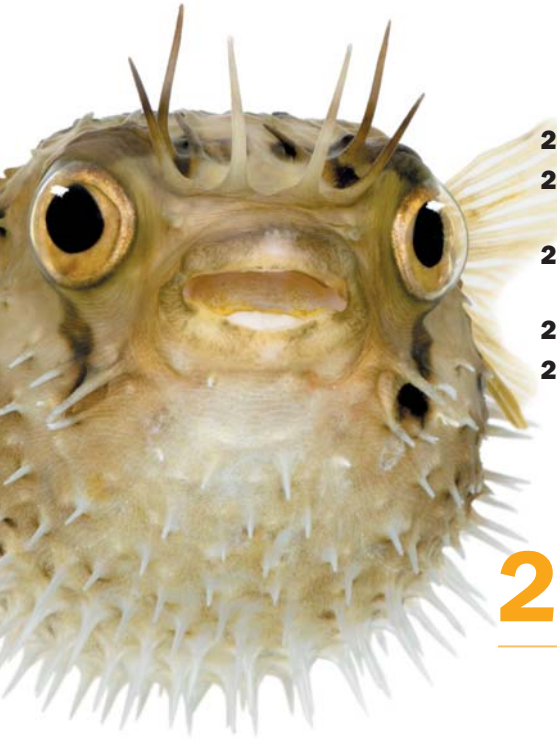






List of Interest Boxes

List of Mechanisms

Preface

More Than an *Emphasis* on Mechanisms: *Organized* by Mechanism

During my first year of teaching organic chemistry, I taught what I have come to learn is a traditional approach. I organized the course the way that most textbooks are organized, with reactions pulled together according to the functional groups involved. Moreover, because I wanted my students to understand and not just memorize the material, I emphasized mechanisms very heavily. Despite my best efforts, the majority of my students struggled with even the basics of mechanisms and, consequently, turned to flashcards as their primary study tool. They tried to memorize their way through the course, which made matters worse.

My goal in writing this book was to solve the problem of memorization by grouping reactions according to similarities in their *mechanisms*. Thus, while the content of this book is the same as in other mainstream textbooks, the different *organization* establishes a coherent story of chemical reactivity. The story begins with molecular structure and energetics, and then guides students into reaction mechanisms with a few transitional chapters. Thereafter, students study how and why reactions take place as they do, focusing on one type of mechanism at a time. Ultimately, students learn how to intuitively use reactions in synthesis.

As mechanisms are central to the story of the book, students are naturally deterred from overlooking them. Students are made to feel more comfortable with mechanisms, and are clearly shown how the material builds from one chapter to the next, providing the foundation for understanding mechanisms in later chapters. Consequently, early in the course, students naturally embrace mechanisms as a learning tool, which I believe is vital to their success throughout the entire course and later—including on admission exams such as the MCAT.

Advantages of a Mechanistic Organization

In terms of student success, an organization by mechanism type offers two main advantages over the traditional organization by functional group. First, it allows students to focus more on reaction mechanisms within each chapter. This is because, once students are introduced to a particular reaction type, they get to apply those mechanisms across various functional groups. For example, after learning nucleophilic substitution reactions, students see that the mechanism applies to alkyl halides, alcohols, ethers, ketones, aldehydes, amines, and carboxylic acids. Second, as students begin to see the mechanistic patterns that unfold in one chapter, they will develop a better toolbox of mechanisms to draw upon in subsequent chapters. Students will therefore be better able to predict what will happen and why.

An organization by functional group, on the other hand, makes it very difficult for students to recognize patterns because each functional group chapter presents disjointed pieces of information related to that functional group. A functional group chapter discusses aspects of nomenclature, physical properties, synthesis, and spectroscopy in addition to new reactions and mechanisms. As a result, students find themselves overwhelmed and most will see no option but to memorize. Specifically, they will memorize what they perceive to be most important—predicting products of reactions—and will typically ignore, or give short shrift to, fundamental concepts and mechanisms.

I have now taught organic chemistry using a mechanistic organization for nearly a decade, during which time I have seen student performance and outlook improve dramatically.[1] I believe it all begins with students having a better handle on concepts and reactions early on. In my experience, the greatest motivator for students to put forth effort is the feeling of *understanding* the material—the feeling of being in *control* over the material. Students who feel that they "get" it are vastly more motivated to put in an even greater effort. The better understanding that a mechanistic organization affords students at the outset, therefore, paves the way for their success throughout the entire course.

Details about the Organization

The book is divided into three major parts:

Part I: Atomic and molecular structure

- Chapter 1: Atomic structure, Lewis structures and the covalent bond, and resonance theory, culminating in an introduction to functional groups
- Chapter 2: Aspects of three-dimensional geometry and its impacts on intermolecular forces
- Chapter 3: Structure in terms of hybridization and molecular orbital (MO) theory
- Chapters 4 and 5: Isomerism in its entirety, including constitutional isomerism, conformational isomerism, and stereoisomerism

Part II: Developing a toolbox for working with mechanisms

- Chapters 6 and 7: Ten elementary steps of mechanisms are examined.
- Chapter 8: Beginnings of multistep mechanisms using S_N1 and E1 reactions as examples

Part II provides a transition into Part III, which deals more intently with reactions.

Part III: Major reaction types

- Chapters 9 and 10: Nucleophilic substitution and elimination
- Chapters 11 and 12: Electrophilic addition
- Chapters 17 and 18: Nucleophilic addition
- Chapters 20 and 21: Nucleophilic addition–elimination
- Chapters 22 and 23: Electrophilic aromatic substitution
- Chapter 24: Diels–Alder reactions and other pericyclic reactions
- Chapter 25: Radical reactions
- Chapter 26: Polymerization

Notice that several of these chapters come in pairs. The first chapter in each pair is used to introduce key ideas about the reaction/mechanism and the second chapter explores the reaction/mechanism to greater depth and breadth.

Interspersed in Part III are chapters dealing with synthesis (Chapters 13 and 19), conjugation and aromaticity (Chapter 14), and spectroscopy (Chapters 15 and 16). The spectroscopy chapters are self contained and can be taught earlier, at the instructor's discretion.

Another major structural component of the book pertains to nomenclature. Nomenclature is separated out from the main chapters, in four relatively short units. Each unit focuses on specific rules of nomenclature, as opposed to specific functional groups. With each new nomenclature unit, new rules are introduced, which increases the complexity of the material discussed. These units can be covered in lecture or easily assigned for self study.

[1]Bowman, B. G.; Karty, J. M.; Gooch, G. "Teaching a Modified Hendrickson, Cram and Hammond Curriculum in Organic Chemistry." *J. Chem. Ed.* **2007**, *84*, 1209.

Finally, the application of MOs toward chemical reactions is separated from the main reaction chapters, and is presented, instead, as an optional, self-contained interchapter. This interchapter appears just after Chapter 7, the overview of the 10 most common elementary steps. Each elementary step from Chapter 7 is revisited from the perspective of MO theory—more specifically, frontier MO theory. Because this interchapter is optional, chapters later in the book do not rely on coverage of this material.

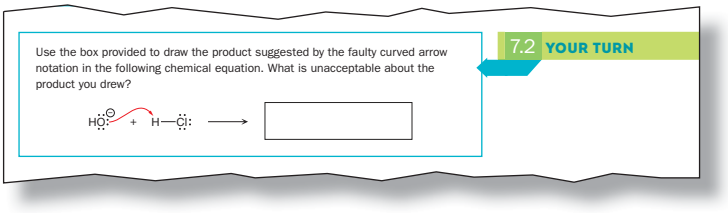
A Better Tool for Students

While the organization provides a coherent story, other aspects of the book make it an excellent learning tool for students.

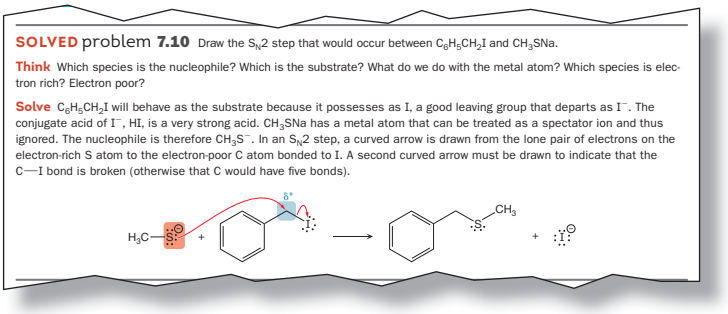
Extended coverage of general chemistry topics. The early chapters provide extended coverage of a variety of general chemistry topics. This is deliberate because I believe most students need a review of several of these topics upon entering organic chemistry. For example, I have found that most students do not have a firm grasp of Lewis structures, intermolecular forces, and equilibria and thermodynamics. Rather than assume that students will dive into their general chemistry textbook to review these topics, I have provided this additional material, with an organic focus, as a convenient student resource. Instructors can tailor their in-class coverage of this material as they deem necessary.

Strategies for Success. In addition to reviewing important general chemistry topics, I have provided Strategies for Success sections to help students build specific skills they need in this course. For example, Chapter 1 provides strategies for drawing all resonance structures of a given species, and sections in Chapters 2 and 3 are devoted to the importance of molecular modeling kits in working with the three-dimensional aspects of molecules and also with the different rotational characteristics of σ and π bonds. In Chapter 4, students are shown how to draw chair conformations and how to draw all constitutional isomers of a given formula. Chapter 5 provides help with drawing mirror images of molecules. One Strategies for Success section in Chapter 6 helps students estimate pK_a values and another helps students rank acid and base strengths based only on their Lewis structures. In Chapter 14, I include a section that shows students how to use the Lewis structure to assess conjugation and aromaticity, and Chapter 16 has a section that teaches students the chemical distinction test for nuclear magnetic resonance.

Your Turn exercises. Getting students to read *actively* can be challenging, so I wrote the Your Turns in each chapter to motivate this type of behavior. Your Turns are basic exercises that ask students to either answer a question, look something up in a table from a previous chapter, construct a molecule using a model kit, use a table in the chapter, or interact with art in a figure or data in a plot. In addition to getting students active when they read, these exercises are intended to be "reality checks" for students as they read. Your Turns should be used as indicators to students as to whether they understand what they have just read. If they cannot solve/answer a Your Turn exercise easily, students should interpret this as a signal that they need to either reread the previous section(s) or seek help. Short answers to all Your Turns are provided in the back of the book and complete solutions to these exercises are provided in the Study Guide and Solutions Manual.



Consistent and effective problem-solving approach. Helping students become expert problem-solvers, in this course and beyond, is one of my major goals. I have developed the Solved Problems in the book to train students how to think as they approach a problem. On average, there are seven Solved Problems per chapter and each one is broken down into two parts: *Think* and *Solve*.



In the Think part, students are provided a handful of *questions* that I want them to be asking as they approach the problem. In the Solve part, those questions are answered and the problem is solved. This mirrors the strategy I use to help students during office hours, and we have used these same steps for *every* problem in the Solutions Manual that accompanies the book.

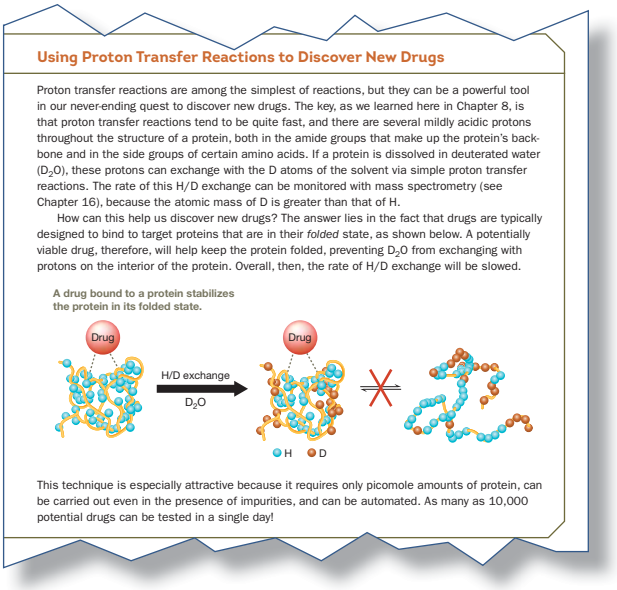
Another excellent training tool is SmartWork, Norton's online tutorial and homework system. SmartWork allows students to practice their problem-solving skills and receive hints and answer-specific feedback that reinforce what students see in the book.

Developing a toolbox of mechanisms. Understanding the common elementary steps that make up mechanisms is a crucial part of solving organic chemistry problems. The elementary steps introduced in Chapters 6 and 7 effectively provide students a toolbox for working comfortably with mechanisms later on. Moreover, students will find that many reactions they encounter throughout the course have mechanisms that comprise just these steps. This makes it more transparent to students how seemingly different reactions can, in fact, be very closely related—through the mechanism.

Separating nomenclature. As I discussed earlier, nomenclature is presented in four separate units, interspersed between chapters in the first half of the book. These units are self-contained and they can be covered where they are located in the textbook or any point after. One of the main reasons for presenting nomenclature separately is that it helps minimize distractions. A second reason for separate coverage of nomenclature is that nomenclature is among the most straightforward topics students will encounter. Naming a molecule requires memorizing certain rules and then practicing applying those rules. This is something that students are quite comfortable with, so instructors have the option of holding students accountable for learning nomenclature on their own or covering it in class.

Biochemistry and MCAT 2015. Most organic chemistry students are biology majors and/or are seeking a career in a health profession. They appreciate seeing how organic chemistry relates to their interests and look for ways in which this course will prepare them for the admissions exams (such as the MCAT) that may determine their future.

Rather than relegating biochemistry to the end of the book, I have placed the Organic Chemistry of Biomolecules in self-contained sections at the ends of several chapters, beginning with Chapter 1. The topics chosen for these sections cover many of the topics outlined in the MCAT 2015 Preview Guide, which means that the Organic Chemistry of Biomolecules sections are not *in addition to* what students are expected to know for the MCAT; they are topics that students *should know* for the test. In even the earliest of chapters, students have the tools to start learning aspects of this traditional biochemistry coverage. More importantly, these sections provide reinforcement of topics. In each biomolecules section, the material is linked directly back to concepts encountered earlier in the chapter.



These Organic Chemistry of Biomolecules sections are both optional and flexible. Instructors can decide to cover only a few of these topics or none at all, and can do so either as they appear in the book or as special topics at the end of the second semester.

A range of interesting applications. In addition to the Organic Chemistry of Biomolecules sections, most chapters have two special interest boxes. These boxes apply a concept in the chapter to a discovery or process that students can relate to. In addition to reinforcing concepts from the chapter, these boxes are intended to provide *meaning* to what students are learning, and to motivate students to dig deeper.

A focus on synthesis. Synthesis problems represent one of the greatest challenges undergraduates face in this course. Not only must students have a command of the reactions they have learned, but they must also be able to think critically to find the right combination of those reactions that will transform the starting mate-

rial into the desired compound. I provide a thorough introduction to organic synthesis in two chapters—Chapters 13 and 19. Chapter 13 discusses introductory topics in synthesis, including the basics of retrosynthetic analysis and the idea of cataloging reactions according to what they accomplish. Chapter 19 presents more challenging topics in synthesis, such as the use of protecting groups and how to place functional groups strategically within a carbon backbone. Therefore, whereas Chapter 13 ought to be covered by most mainstream classes, instructors can choose to cover only certain sections of Chapter 19 or skip it entirely.

I have found that treating synthesis in dedicated chapters makes it more meaningful to students. When I taught synthesis under a traditional functional group organization, it became a distraction to the reactions that students are simultaneously learning. I also found that students often associated a synthetic strategy only with the functional group for which it was introduced. For example, when the idea of protecting groups is introduced in the ketones/aldehydes chapter of a textbook traditionally organized by functional group, students tend to associate protecting groups with ketones/aldehydes *only*. My dedicated synthesis chapters help students focus on synthesis without compromising their focus on reactions. Furthermore, synthesis strategies are discussed more holistically, so students can appreciate them in a much broader context rather than being applicable to a single functional group.

Optional interchapter on the application of MO theory toward reactions. Under an organization according to functional group, the roles of MOs in chemical reactions typically appear integrated into several different functional group chapters. For example, the role of orbitals in an S_N2 reaction is typically integrated in an alkyl halides chapter, and the role of orbitals in a nucleophilic addition reaction is typically integrated into the ketones/aldehydes chapter. For instructors who do not teach this aspect of MOs in their course, these discussions can represent distractions and are potentially counterproductive to student learning.

Presenting this material together in an optional interchapter, as I have done in this book, offers two main advantages to students. One is that it removes a potential distraction from the main reaction chapters and, being optional, instructors have the choice of not covering it at all. Another advantage comes from the fact that the MO pictures of all 10 common elementary steps appear together in the interchapter. Therefore, instructors who wish to cover this interchapter can expect their students to come away with a better understanding of the bigger picture of MO theory as it pertains to chemical reactions.

Acknowledgments

There are many people who have been a part of or impacted by my work on this textbook, and my gratitude for all of them is immense. First and foremost, however, I must acknowledge my family—Valerie, Joshua, and Jacob. When I began work on this book, Joshua wasn't even walking; now he's 11 and Jacob is 9. It has been a long and arduous endeavor. But it is also one that has been worthwhile and has helped shape who I am today. Thank you for your love and support and for standing by me the entire way.

I must also acknowledge my parents, Alec and Maraline, who instilled in me the importance of academics and the love of learning. My thanks goes out to them especially for the numerous sacrifices they made so that I could have the best in education and the best in life.

I owe a lot to my brothers and sister, too—Ben, Kevin, and Sarah. Those sibling rivalries we had growing up certainly brought out the best in me. More recently, thank you for tolerating me throughout this process.

Thanks must also go to my colleagues in the chemistry department here at Elon, for your support and understanding of how important this book has become. I especially must acknowledge Gene and Marcia Gooch. Gene was initially part of this project but died tragically in a bicycle accident.

To my teachers through the years, thank you for your wisdom and encouragement, as well as your friendship. Jack Howard, you got me started in chemistry in high school, and I still remember when you said: "I'm not a smart man, but I do know how to convert units." John Hanson and Bill Dasher, you "showed me the way" in organic chemistry, and Ken Rousslang, you taught me to appreciate the finer details in physical chemistry and turned me on to the world of research. Tim Hoyt, thank you for being the "Wiz" that you are. And to John Brauman, it is because of you that I can truly call myself a scientist.

My students deserve a lot of credit, too. Even though I am the teacher (technically), I continue to learn from my students year in and year out. Thank you, especially, for being guinea pigs at times, giving me the chance to learn how to become a better teacher.

To Maureen Cullins, thank you for letting me be creative. It was in my first year teaching at the Summer Medical and Dental Education Program that I "discovered" a better way to teach organic chemistry, and you have always been one of my biggest fans.

A tremendous amount of thanks goes to the many members of the Norton team. Erik Fahlgren, thank you for believing in me, and for taking on this project with as much passion as I have given it. Your balance of optimism and critique has truly brought the book to a whole new level of quality. John Murdzek, your help through the developmental editing process has been priceless, and your humor has helped me keep things in perspective. Renee Cotton and Christine D'Antonio, I continue to be amazed with your attention to detail and ability to stay on top of things. Jane Miller, I appreciate the hours you have spent researching photos and bearing with me when things are not precisely to my liking. And to Stacy Loyal, I admire the work you've done in marketing this book. Changing a paradigm that's over half a century old is no small task. Kudos to you.

A special thanks to Steve Pruett and Marie Melzer. Steve, your patience with me and with this book has been incredible, and your insights have been tremendously appreciated. Thank you, in particular, for your commitment through it all. Marie, I appreciate your help creating the Your Turn answers at the end of the book and greatly value the energy and the insight that you have brought to the Study Guide and Solutions Manual.

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Additional Resources

For Students

Study Guide and Solutions Manual

by Joel Karty, Elon University, and Marie Melzer, Old Dominion University

Written by two dedicated teachers, this guide provides students with fully worked solutions to all unworked problems in the text. Every solution follows the Think/Solve format used in the textbook, so the approach to problem-solving is modeled consistently.

SmartWork

Created by chemistry educators, SmartWork is the most intuitive online tutorial and homework system available for organic chemistry. A powerful engine supports and grades an unparalleled range of problems written for Karty's text, including numerous arrow-pushing problems. *Every* problem in SmartWork has hints and answer-specific feedback to coach students and provide the help they need, when they need it. Problems in SmartWork link directly to the appropriate page in the electronic version of Karty's text so students have an instant reference and are prompted to read.

Instructors can draw from Norton's bank of more than 2000 high-quality, class-tested problems, or use our innovative authoring tools to easily modify existing problems or write new ones. Instructors can sort problems by learning goal and create assignments to assess any learning goals, concepts, or skills that they choose.

The Karty SmartWork course also features:

- **An expert author team.** The organic SmartWork course was authored by instructors who teach at a diverse group of schools: Arizona State University, Florida State University, Brigham Young University, and Mesa Community College. The authors have translated their experience in teaching such a diverse student population by creating a library of problems that will appeal to instructors at all schools.

- **Pooled drawing and nomenclature problems.** SmartWork features sets of pooled problems for drawing and nomenclature to promote independent work. Groups of similar problems are "pooled" into one problem so different students receive different problems from the pool. Instructors can choose our preset pools or create their own.

For Instructors

Instructor's Guide

by Stephen R. Pruett, Jefferson Community and Technical College

Written by one of the first users of Joel's material, each chapter in the Instructor's Guide begins with a brief overview of the chapter, followed by a more detailed section-by-section discussion that includes information on differences between this book and textbooks with a functional group organization.

Pruett includes suggestions on how to present difficult concepts to students, and, incorporating his experiences teaching with the preliminary edition of the textbook, documents information about his and his students' experiences with the material. Suggested clicker questions from *Clickers in Action: Active Learning in Organic Chemistry* and a section on additional resources (such as specific websites, articles, or books) that instructors can incorporate into their course round out each chapter. The Instructor's Guide includes a chapter for each of the 26 chapters in the textbook, plus a chapter for the MO theory interchapter and a chapter for the nomenclature units.

Clickers in Action: Active Learning in Organic Chemistry

by Suzanne M. Ruder, Virginia Commonwealth University

This instructor-oriented resource provides information on implementing clickers in organic chemistry courses. Part I gives instructors information on how to choose and manage a classroom response system, develop effective questions, and integrate the questions into their courses. Part II contains 140 class-tested, lecture-ready questions. Most questions include histograms that show actual student response, generated in large classes with 200–300 students over multiple semesters. Each question also includes insights and suggestions for implementation. The 140 questions from the book and an additional 100 lecture-ready questions are available in PowerPoint, sorted to correspond to the chapters in the textbook, at wwnorton.com/instructors.

Test Bank

by Amy M. Deveau, University of New England; James Wollack, St. Catherine University; and Alexandra Jones, St. Catherine University

The Test Bank contains more than 1300 multiple-choice and short-answer questions. Questions are organized by chapter section, and each question is ranked by difficulty and type. Questions are further classified by learning objectives. The list of learning objectives provided at the beginning of each chapter makes it easy to find questions that test each objective.

The Test Bank is available in print, *ExamView* Assessment Suite, Word RTF, and PDF formats.

ExamView Test Generator Software

All Norton test banks are available with ExamView Test Generator software, allowing instructors to effortlessly create, administer, and manage assessments. The convenient and intuitive test-making wizard makes it easy to create customized exams with no software learning curve. Other key features include the ability to create paper exams with algorithmically generated variables and export files directly to Blackboard, WebCT, and Angel.

Instructor's Resource Disc

This helpful classroom presentation tool features:

- Select photographs and every piece of line art in JPEG format
- Select photographs and every piece of line art in PowerPoint
- Lecture PowerPoint slides with integrated figures from the book
- Clicker questions from *Clickers in Action: Active Learning in Organic Chemistry*

Downloadable Instructor's Resources (wwnorton.com/instructors)

This instructor-only, password-protected site features instructional content for use in lecture and distance education, including test-item files, PowerPoint lecture slides, images, figures, and more. The instructor's website includes:

- Select photographs and every piece of line art in JPEG format
- Select photographs and every piece of line art in PowerPoint
- Lecture PowerPoint slides with integrated figures from the book
- Clicker questions from *Clickers in Action: Active Learning in Organic Chemistry*
- Instructor's Guide in PDF format
- Test bank in PDF, Word RTF, and ExamView formats

Author Blog: www.teachthemechanism.com

Starting in July 2012, Joel Karty and Steve Pruett started blogging about Joel's approach and their experience teaching a course organized by mechanism. In addition to written posts, the blog includes videos of Joel discussing his approach and answering some of the questions he is frequently asked about teaching a mechanistically organized course. Guest bloggers, most of whom have adopted Karty's text, have also contributed their stories and insights about teaching a course organized by mechanism. You are encouraged to visit the blog and submit comments of your own.

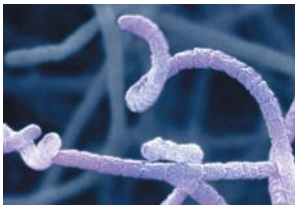
Preface for the Student

Organic Chemistry and You

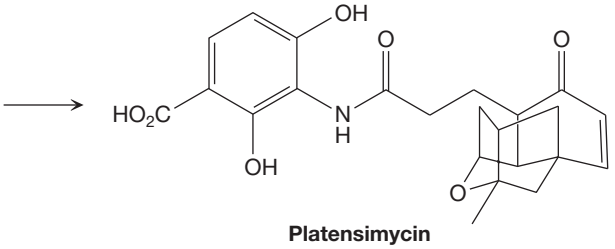
You are taking organic chemistry for a reason—you might be pursuing a career in which an understanding of organic chemistry is crucial, or the course might be required for your particular field of study, or both. You might even be taking the course simply out of interest. Regardless of the reason, organic chemistry impacts your life in significant ways.

Consider, for example, the growing concern about the increasing resistance of bacteria to antibiotics. Perhaps no germ has caused more alarm than methicillin-resistant *Staphylococcus aureus* (MRSA), a type of bacteria responsible for "staph" infections. Methicillin is a member of the penicillin family of antibiotics, and resistance to methicillin in these bacteria was first observed in 1961. Today MRSA, which has been called a "superbug," is resistant to most antibiotics, including *all* penicillin-derived antibiotics.

A breakthrough in the fight against MRSA occurred in 2006 with the discovery of a compound called platensimycin, isolated from *Streptomyces* spores.



***Streptomyces* spores**



Platensimycin

The way that platensimycin targets bacteria is different from that of any other antibiotic in use and, therefore, it is not currently susceptible to bacterial resistance.

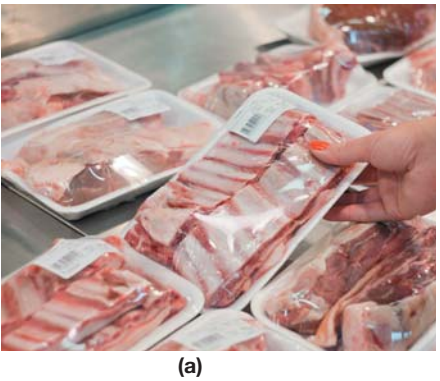
Platensimycin is found in a type of South African mushroom, *Streptomyces platensis*, and was discovered by screening 250,000 natural product extracts for antibacterial activity. Sheo B. Singh (Merck Research Laboratories) and coworkers determined the structure of platensimycin using a technique called nuclear magnetic resonance (NMR) spectroscopy, which we discuss in Chapter 16. Not long after, K.C. Nicolaou and coworkers from The Scripps Research Institute (La Jolla, California) and the University of California, San Diego, were the first to devise a synthesis of platensimycin from other readily available chemicals.

The story of platensimycin, from discovery to synthesis, involves several of the subdisciplines that make up the field of organic chemistry.

- **Biological chemistry (biochemistry):** The study of the behavior of biomolecules and the nature of chemical reactions that occur in living systems.
- **Structure determination:** The use of established experimental techniques to determine the structure of newly discovered compounds.
- **Organic synthesis:** The design of pathways for making new compounds from existing, readily available compounds by means of known organic reactions.

Because each of these areas typically focuses on solving existing and practical problems, they are considered to be *applied* areas of organic chemistry. However, other areas of organic chemistry, considered to be *theoretical* in nature, provide the foundations on which such applications rest. They focus on answering questions about the "how" and "why" of chemical processes. For example, an understanding of the basic principles of NMR spectroscopy (an analytical technique discussed in Chapter 16) underlies our ability to determine molecular structure. Understanding the principles that govern organic reactions (such as those involved in the synthesis of platensimycin) may allow us to enhance yields, not only by altering reaction conditions, but also perhaps by devising entirely new synthesis schemes. And understanding platensimycin's specific mode of attack on bacteria will likely guide us in modifying its chemical structure to make it even more effective.

The story of platensimycin showcases the importance of organic chemistry in the pharmaceutical industry, but organic chemistry is at the center of other high-profile areas as well, including the fabrication of new materials such as plastics (the topic of Chapter 26). The durability and chemical stability of plastics have made them excellent choices for use in food packaging (Fig. P.1a) and the fabrication of the artificial heart (Fig. P.1b). Plastics are the source of synthetic fibers such as nylon and polyester, which are often used in the clothing industry, as well as Kevlar®, which is used to make body armor (Fig. P.1c). Composite materials made from plastic and carbon fibers are so strong that some commercial jets are now constructed with a body made largely from plastics (Fig. P.1d).



(a)

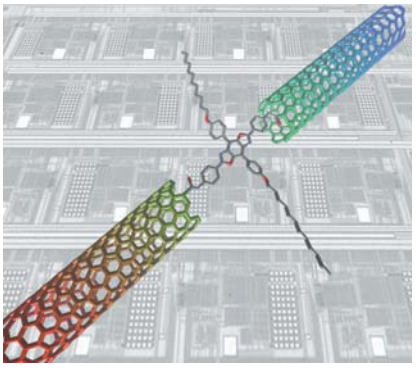
(b)

(c)

(d)

FIGURE P.1 Some uses of plastics Plastics, which are designed and created in the laboratories of organic chemists, are found in a wide range of products, such as (a) food packaging, (b) an artificial heart, (c) body armor made from Kevlar®, and (d) a Boeing 787, a commercial jet whose body consists largely of composite materials made from plastics and carbon fibers.

(a)



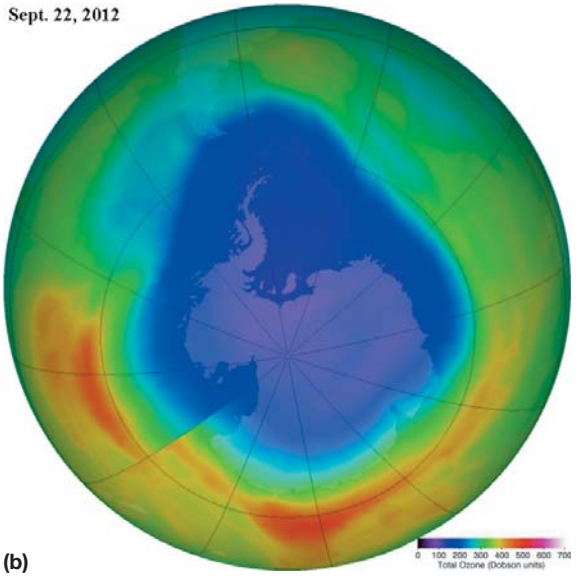
(b)

FIGURE P.2 Organic chemistry in the electronics industry (a) A full-color digital display made from organic light-emitting diodes. (b) A molecular switch in which an organic molecule joins together two carbon nanotubes—sheets of carbon in the form of cylinders with a diameter on the order of 10^{-9} meters.

Organic chemistry has also been at the forefront of generating new materials for electronic devices. Organic light-emitting diodes (OLEDs) are the main components of full-color electronic displays (Fig. P.2a), and single organic molecules can be used to make electronic switches tens of thousands of times smaller than those used in today's integrated circuits (Fig. P.2b).

Perhaps even more important to our lives is the impact that organic chemistry can have on our ability to understand, and solve, environmental problems, such as overflowing landfills (Fig. P.3a), the destruction of the stratospheric ozone layer (Fig. P.3b), and global warming (Fig. P.3c). Organic chemistry, for example, is helping

(a)



(b)

(c)

FIGURE P.3 Organic chemistry and the environment Organic chemistry continues to play a significant role in solving environmental problems, such as (a) overflowing landfills, (b) ozone depletion (the area in blue represents the "ozone hole" over Antarctica), and (c) global warming (the ice sheets in Montana's Glacier National Park have been melting at a dramatically accelerating rate over the past 90 years).

provide new ways to recycle waste materials. Additionally, organic chemistry has been used to engineer new coolants that are safer for the environment than the chlorofluorocarbons (CFCs) used in the late 20th century in refrigerators and air conditioners. Finally, organic chemistry may lead us to economically feasible processes by which we can synthesize hydrogen gas, a fuel whose combustion product is only water. This could be a welcome alternative to coal and oil, whose combustion products not only cause air and water pollution, but also generate carbon dioxide, one of several greenhouse gases responsible for global warming.

Because organic chemistry is important in so many ways, you will find interest boxes in each chapter, which show how the material in the chapter directly connects to issues that you might find more relevant or more interesting. Take the time to read those boxes, and consider researching them even further.

Some Suggestions for Studying

Perhaps you have heard that organic chemistry is difficult. Perhaps you have heard that it requires an enormous amount of *memorization*. Are these statements true? It depends on how you approach the course. What is true is that this book contains a lot of information—much more than you can memorize. There is a better way.

Organic chemistry can be *understood* through models and theories that are built upon *fundamental concepts*. Consider, for example, that when two compounds react under a given set of conditions, the outcome of that reaction is precisely the same each and every time. Is this because the reactant molecules have *memorized* what products they are supposed to make? No—they are obeying certain chemical laws, and those laws can be learned.

You will spend considerable effort throughout this course developing those models and theories. Reaction mechanisms—detailed steps that show how reactions take place—are among the most important ideas to develop. If you devote your time and energy to understanding them and learning how they are applied toward solving problems, you will find that much of organic chemistry can be conquered without rote memorization, and you will find the course to be quite rewarding and enjoyable. The skills you develop in organic chemistry will apply to complex situations you will face beyond this course.

If you are planning on a career in a health profession, it is particularly important for you to focus on understanding and applying concepts as opposed to memorizing. On standardized exams like the MCAT, you will often need to choose between answers that are designed to look equally good to students who have memorized the material. To a student who is well versed in applying concepts and mechanisms toward solving problems, on the other hand, those choices are more easily discernible.

In light of how important it is to understand concepts and mechanisms, your success in this course will demand a lot of time and devotion. The following are suggestions for using that time, and this book, most efficiently:

- **Read actively and diligently.** You should try to read the assigned sections before class if possible. Reading prior to lecture means that lecture is the second time you'll be presented the material. This will allow you to better process information and give you ample opportunity to ask pertinent questions. When you read, you should have a pen or pencil in hand so you can underline or highlight what you feel is important, and take notes about what you find enlightening or confusing. When the text refers to a figure or reaction mechanism, take that as a cue to study that figure now. Be sure that what the text is describing makes sense to you before you move on. If you are referred to a previous chapter, flip to the appropriate page to refresh your memory.
- **Your Turns.** The "Your Turn" exercises are relatively short activities that ask you to complete a task based on what you have just read. These exercises were developed to help you remain *actively engaged* while you read. They should also help you quickly

evaluate whether or not you understand the topic at hand. I encourage you to *work through all Your Turn exercises in each chapter* and quickly check the answers in the back of the book. Feedback from students who have used this book supports this advice.

- **Problems.** As with anything new you attempt, mastery requires practice. Most of your practice should come from solving problems. I have included nearly 2000 problems throughout this book. Many are integrated into the chapters, but most are gathered at the end of each chapter. Take the time to work through as many problems as possible, and use them to assess areas of strength and weakness.

That said, it's time to get started. Keep your focus on concepts and mechanisms, and work hard!

When Joel discusses his approach with instructors, he is frequently asked:

Q How does this book benefit preprofessional (premed, predent, prepharm) students?

A The mechanistic organization benefits preprofessional students in two major ways. First, students who are more competent with mechanisms will have better success in the course—a course for which a student's performance is considered by many medical, dental, and pharmacy school admissions committees. Second, students will be better poised for standardized exams like the MCAT. Many questions on these exams are written to make all the answer choices look correct to those who don't *understand* the material.

Moreover, in 2015 the MCAT will be expecting more biochemistry of students, and my Organic Chemistry of Biomolecules sections provide instructors a convenient and meaningful way to incorporate more biochemistry content throughout the year. The topics chosen for these sections cover many of the topics outlined in the MCAT 2015 Preview Guide, which means that the Organic Chemistry of Biomolecules sections are not *in addition to* what students are expected to know for the MCAT. They are topics that students *should know* for the test.

Q How do you handle a student who transfers and uses a traditionally organized book for the other semester?

A In my experience (and that of some class testers), transfer students have not been affected by the organization. When students enter my Organic II course having taken Organic I elsewhere, I ask them to read Chapters 6 and 7. When students who have used my book in Organic I transfer to a different institution for Organic II, they are well prepared to be successful no matter where they transfer. I have administered the first-semester ACS exam to my students each year of its existence, and my students routinely average significantly above the fiftieth percentile.

Q What is a specific example of reactions that are learned together in this book but not in textbooks organized according to functional groups?

A One example is in Chapter 10, where alpha alkylation and Hofmann elimination are discussed in the context of nucleophilic substitution and elimination reactions. Traditionally, the discussion of nucleophilic substitution and elimination is reserved for the alkyl halides chapter, alpha alkylation is discussed in a chapter on ketones and aldehydes, and Hofmann elimination is relegated to an amines chapter.

Q Can this book work with "flipping" the classroom?

A I have been using such an approach in my own classroom for several years. This textbook is well suited for flipping the classroom, for two main reasons. First, the organization helps students maintain focus on understanding as opposed to memorizing, so they are well poised to apply that understanding toward solving problems in class. Second, I have written the text to be accessible to students, and I have included pedagogical features to help keep students engaged as they read—including Your Turn exercises and Solved Problems, which pose questions in the *Think* step.

What your colleagues say . . .

On the mechanistic organization:

Barbora Morra, University of Toronto: "This approach will surely promote **more understanding and less memorization**."

Eric Finney, University of Washington: "I . . . would be excited to teach a course following this style of organization. I think the potential exists **to improve the way students learn organic chemistry using this different organizational method**."

Eugene Zubarev, Rice University: "This is a unique type of textbook. The idea to focus the entire course on mechanisms as opposed to memorization is not new, but it has never been implemented. If this book were published, it would be **a fresh breath of air**."

On Joel's writing style and in-text pedagogy:

Claudia Lucero, California State University, Sacramento: "The author understands that organic chemistry is an overwhelming subject and has seen the many mistakes that students make. The chapters that I have read are written in such a way that **the reader feels like the author can relate to them**."

Brad Chamberlain, Luther College: "**The biological applications chosen by the author are particularly apt in light of the revised MCAT exam** that will begin use in 2015."

Daniel Berger, Bluffton University: "It is by far **the clearest and best treatment of organic synthesis** that I have seen in a lower-level organic textbook, and I plan to steal from it shamelessly."

Jared Ashcroft, Pasadena City College: "I thought it was a great book and explained many tough concepts **better than other books I have used**."

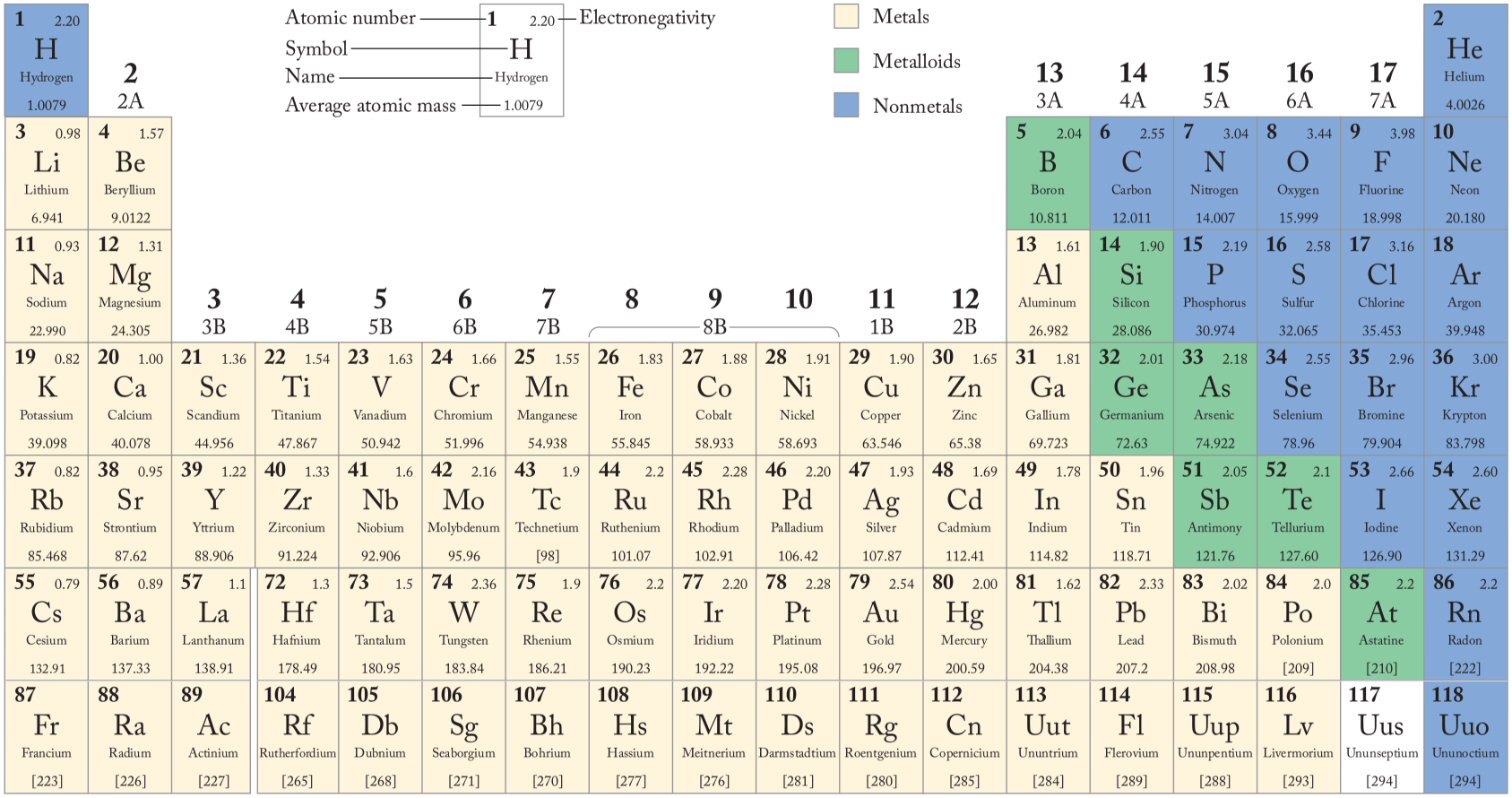
Tammy Davidson, University of Florida: "I like the way the author has continued to include the Your Turn exercises, especially how he follows up the Solved Problems with **a chance for the students to practice what they have seen**. I also like how he has drawn the structures for many of the reactions and the students need to show the mechanism arrows–this is good reinforcement of the ideas presented in the text, and it will give the students **many chances to learn the right habits for electron pushing**."

On the problems:

Brian Frink, Lakeland College: "**The Solved Problems in the chapters are great**. The idea that thinking is asking questions is often lost on the students. The students tend to believe that thinking is about information, not questions. These problems put the emphasis on the questions that the student needs to ask himself or herself in support of answering the question posed by the author (and later by his or her instructor on an exam). This Think/Solve model is truly revolutionary and great!"

Jason Lockin, University of Georgia: "The biggest complaint of students in our class has to do with end-of-chapter problems. They always say, 'The ones in the textbook were too easy compared to the ones on the exam.' With that being said, **the end-of-chapter problems in this textbook are very good**."

PERIODIC TABLE OF THE ELEMENTS



6 Lanthanides	58 Ce Cerium 140.12	59 Pr Praseodymium 140.91	60 Nd Neodymium 144.24	61 Pm Promethium [145]	62 Sm Samarium 150.36	63 Eu Europium 151.96	64 Gd Gadolinium 157.25	65 Tb Terbium 158.93	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93	68 Er Erbium 167.26	69 Tm Thulium 168.93	70 Yb Ytterbium 173.05	71 Lu Lutetium 174.97
7 Actinides	90 Th Thorium 232.04	91 Pa Protactinium 231.04	92 U Uranium 238.03	93 Np Neptunium [237]	94 Pu Plutonium [244]	95 Am Americium [243]	96 Cm Curium [247]	97 Bk Berkelium [247]	98 Cf Californium [251]	99 Es Einsteinium [252]	100 Fm Fermium [257]	101 Md Mendelevium [258]	102 No Nobelium [259]	103 Lr Lawrencium [262]

We have used the U.S. system as well as the system recommended by the International Union of Pure and Applied Chemistry (IUPAC) to label the groups in this periodic table. The system used in the United States includes a letter and a number (1A, 2A, 3B, 4B, etc.), which is close to the system developed by Mendeleev. The IUPAC system uses numbers 1–18 and has been recommended by the American Chemical Society (ACS). While we show both numbering systems here, we predominantly use the IUPAC system in the book.

CHAPTER 1

Atomic and Molecular Structure

Very likely you have heard that organic chemistry is "the chemistry of life." Inherent to this description is the idea that certain types of compounds, and the reactions they undergo, are suitable to sustain life, while others are not. If so, what are the characteristics of such compounds and what advantages do those compounds afford living organisms? Here in Chapter 1 we will begin to answer these questions.

We will review several aspects of atomic and molecular structure typically covered in a general chemistry course, including ionic and covalent bonding, the basics of Lewis structures, and resonance theory. With such a general foundation, we will then begin to tighten our focus on organic molecules. We will present various types of shorthand notation that organic chemists often use and we will introduce you to functional groups commonly encountered in organic chemistry.

Toward the end of this chapter, we will shift our focus to examining specific classes of biomolecules: amino acids, monosaccharides, and nucleotides. Not only will such a discussion provide insight into the relevance of organic chemistry to biological systems, but it will also reinforce specific topics discussed in the chapter, such as functional groups.

Organic chemistry is often referred to as the chemistry of life, because biological compounds such as DNA, proteins, and carbohydrates are themselves organic molecules. In this chapter, we will examine some of the bonding characteristics of these and other organic molecules, which are constructed primarily from carbon, hydrogen, nitrogen, and oxygen.

CHAPTER OBJECTIVES

Upon completing Chapter 1 you should be able to:

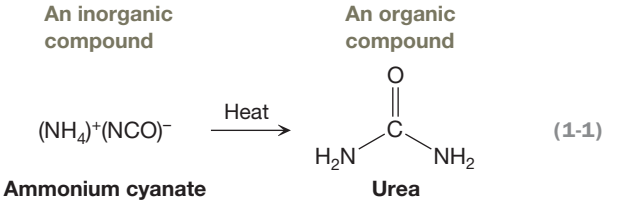
- Distinguish organic compounds from inorganic ones.
- Explain the advantages brought about by the fact that carbon is the basis of organic molecules.
- Describe the basic structure of an atom and understand that the vast majority of its volume is taken up by electrons.
- Determine the ground state electron configuration of any atom in the first three rows of the periodic table and distinguish valence electrons from core electrons.
- Define bond length and bond energy and understand how these two quantities change with increasing numbers of bonds between a given pair of atoms.
- Draw the Lewis structure of a species, given only its connectivity and total charge.
- Differentiate between a nonpolar covalent bond, a polar covalent bond, and an ionic bond, and distinguish a covalent compound from an ionic compound.
- Assign a formal charge and an oxidation state to any atom in a molecular species, given only its Lewis structure.
- Describe what a resonance structure is and explain the effect that resonance has on a species' stability.
- Draw all resonance structures of a given species, as well as its resonance hybrid, and determine the relative stabilities of resonance structures.
- Draw and interpret Lewis structures, condensed formulas, and line structures.
- Explain why functional groups are important and identify functional groups that are common in organic chemistry.

1.1 What Is Organic Chemistry?

Before beginning our study of organic chemistry, we ought to have an idea of what organic chemistry is. Very crudely, **organic chemistry** is the branch of chemistry involving *organic compounds*. What, then, is an organic compound?

In the late 1700s, scientists defined an **organic compound** as one that could be obtained from a *living* organism, whereas **inorganic compounds** encompassed everything else. It was believed that organic compounds could *not* be made in the laboratory; instead, only living systems could summon up a mysterious "vital force" needed to synthesize them. This belief was called **vitalism**. Using this definition, many familiar compounds, such as glucose (a sugar), testosterone (a hormone), and deoxyribonucleic acid (DNA) are *organic* (Fig. 1-1).

This definition of organic compounds broke down in 1828, when Friedrich Wöhler (1800–1882), a German physician and chemist, synthesized urea (an organic compound known to be a major component of mammalian urine) by heating a solution of ammonium cyanate (an inorganic compound; Equation 1-1).Within a couple of decades after Wöhler's discovery, vitalism was dead.

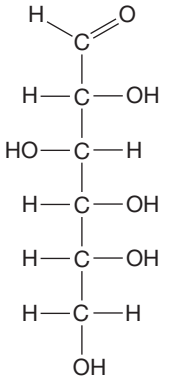


(1-1)

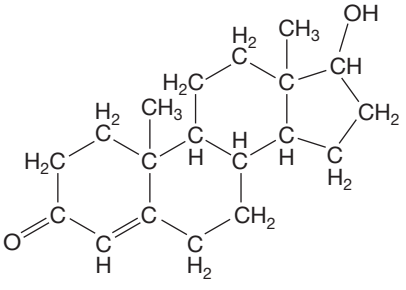
With the end of vitalism, another definition was needed to describe the many compounds that were already labeled as organic. Gradually, chemists arrived at our modern definition:

> An **organic compound** is composed primarily of carbon and hydrogen.

This definition, however, is still imperfect, because it leaves considerable room for interpretation. For example, many chemists would classify carbon dioxide (CO_2) as *inorganic* because it



Glucose

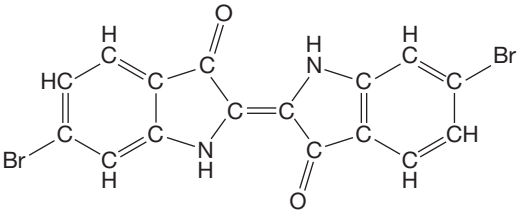


Testosterone


DNA

FIGURE 1-1 Some familiar organic compounds Glucose, testosterone, and DNA are organic compounds produced by living organisms.

Bolinus brandaris



"Royal purple"

FIGURE 1-2 Royal purple Ancient Phoenicians processed about 10,000 aquatic snails, *Bolinus brandaris* (left), to yield 1 g of "royal purple" dye. The structure of the molecule responsible for the dye's color is shown at right.

does not contain any hydrogen atoms, whereas others would argue that it is *organic* because it contains carbon and is critical in living systems. In plants, it is a starting material in photosynthesis, and in animals, it is a byproduct of respiration. Similarly, tetrachloromethane (carbon tetrachloride, CCl_4) contains no hydrogen, but many would classify it as an organic compound. Butyllithium (C_4H_9Li), on the other hand, is considered by many to be inorganic, despite the fact that 13 of its 14 atoms are carbon or hydrogen. (In Chapter 17, we will learn that the behavior of such compounds containing metal atoms, called *organometallic* compounds, is substantially different from that of typical organic compounds.) Rest assured that although this definition of an organic compound has its inadequacies, it does allow chemists to agree on the classification of most molecules.

Historians place the birth of organic chemistry as a distinct field around the time that vitalism was dismissed, thus making the discipline less than 200 years old. However, humans have taken advantage of organic reactions and the properties of organic compounds for thousands of years! Since about 6000 B.C., for example, civilizations have fermented grapes to make wine. Some evidence suggests that Babylonians, as early as 2800 B.C., could convert oils into soaps.

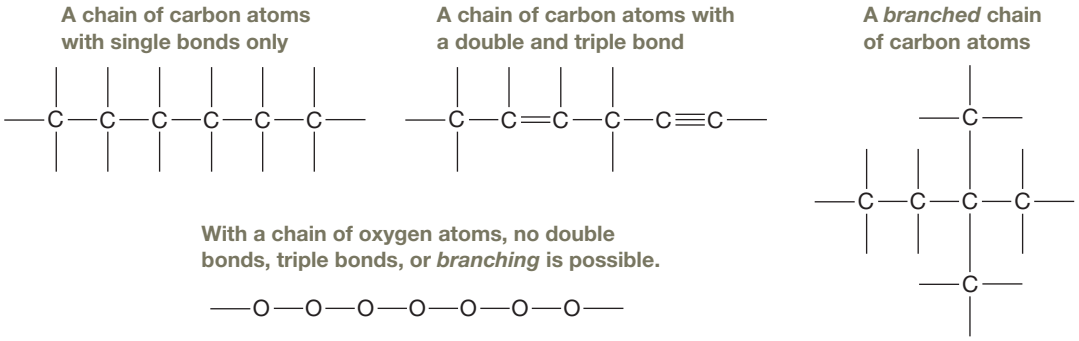
Many clothing dyes are organic compounds. Among the most notable of these dyes is **royal purple**, which was obtained by ancient Phoenicians from a type of aquatic snail called *Bolinus brandaris* (Fig. 1-2). These organisms produced the compound in such small amounts, however, that an estimated 10,000 of them had to be processed to obtain a single gram of dye. This effectively limited the availability of the dye only to those who had substantial wealth and resources—royalty.

Organic chemistry has matured tremendously since its inception. Today, we can not only use organic reactions to reproduce complex molecules found in nature, but also engineer new molecules never before seen.

1.2 Why Carbon?

There is no question that the chemistry of life is centered primarily around the carbon atom. The backbones of familiar biomolecules like DNA, proteins, and carbohydrates are all composed primarily of carbon. Why does the carbon atom play this central role and what is so special about it?

One of the main reasons must be the *diversity* of compounds possible when carbon is their chief structural component. As we will see in Section 1.6, the carbon atom is capable of forming four covalent bonds to other atoms—especially other carbon atoms. Consequently, carbon atoms can link together in chains of almost any length, allowing for an enormous range in molecular size. Moreover, the ability to form four bonds means there is potential for *branching* at each carbon in the chain. And each carbon atom is capable of forming not only single bonds, but double and triple bonds as well. These characteristics make possible a tremendous number of compounds, even with a relatively small number of carbon atoms. Indeed, to date, tens of millions of organic compounds are known, and the list is growing rapidly as we continue to discover or synthesize new compounds.



This same kind of diversity would not be possible in compounds based on another element, such as oxygen. Oxygen atoms are most stable when they form two covalent bonds, so they could form a linear chain only (as shown in the hypothetical example above). No branching could occur, nor could other groups or atoms be attached to the chain except at the ends. Furthermore, the atoms along the chain could not participate in either double or triple bonds.

If carbon works so well, then why *not* silicon, which appears just below carbon in the periodic table? Elements in the same group (column) of the periodic table tend to exhibit similar chemical properties, so silicon, too, can form four covalent bonds, giving it the same potential for diversity as carbon.

The answer is *stability*. As we will see in Section 1.4, the carbon atom tends to form rather strong bonds with a variety of atoms, including other carbon atoms. For example, it takes 339 kJ/mol (81 kcal/mol) to break an average C—C single bond, and 418 kJ/mol (100 kcal/mol) to break an average C—H bond. By contrast, it takes only 223 kJ/mol (53 kcal/mol) to break a typical Si—Si bond. The strength of typical bonds involving carbon atoms goes a long way toward keeping biomolecules intact—an essential characteristic for molecules whose job it is to store information or provide cellular structure.

Even though organic molecules are based on the carbon atom, what would life be like if silicon atoms were to replace carbon atoms in biomolecules such as glucose ($C_6H_{12}O_6$)? Glucose is broken down by our bodies through respiration to extract energy, according to the overall reaction in Equation 1-2. One of the byproducts is carbon dioxide, a gas, which is exhaled from the lungs. In a world in which life is based on silicon, glucose would be $Si_6H_{12}O_6$, and its byproduct would be silicon dioxide (SiO_2), as shown in Equation 1-3. Silicon dioxide, a solid, is the main component of sand; in its crystalline form, it is known as quartz (Fig. 1-3).

FIGURE 1-3 Quartz crystal Quartz (silicon dioxide) is the silicon analog of carbon dioxide. Whereas carbon dioxide is gaseous, silicon dioxide is a solid.

$$C_6H_{12}O_6 + 6\ O_2 \longrightarrow 6\ CO_2 + 6\ H_2O \qquad (1\text{-}2)$$

$$Si_6H_{12}O_6 + 6\ O_2 \longrightarrow 6\ SiO_2 + 6\ H_2O \qquad (1\text{-}3)$$

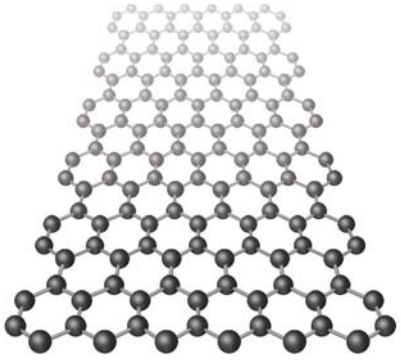
1.3 Atomic Structure and Ground State Electron Configurations

In Section 1.2, we saw that carbon's bonding characteristics are what give rise to the large variety of organic molecules. Those bonding characteristics, and the bonding characteristics of all atoms, are governed by the electrons that the atom has.

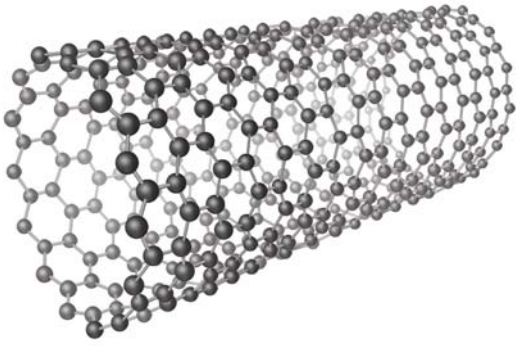
With this in mind, Section 1.3 is devoted to the nature of electrons in atoms. We first review the basic structure of an atom, followed by a discussion of orbitals and shells. Finally, we review electron configurations, distinguishing between *valence electrons*—electrons that can be used for bonding—and *core electrons*.

Chemistry with Chicken Wire

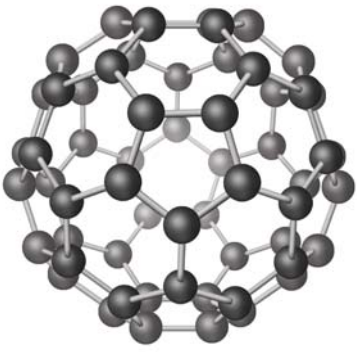
Even though carbon takes center stage in organic chemistry, organic molecules invariably include other atoms as well, such as hydrogen, nitrogen, oxygen, and halogen atoms. Some of the most exciting chemistry today, however, involves extended frameworks of *only* carbon. A single flat sheet of such a framework is called **graphene**, and resembles molecular chicken wire. Wrapped around to form a cylinder, a graphene sheet forms what is called a **carbon nanotube**. Pure carbon can even take the form of a soccer ball—the so-called **buckminsterfullerene**.



A sheet of graphene



A carbon nanotube



Buckminsterfullerene

These structures themselves have quite interesting electronic properties, giving them a bright future in nanoelectronics. Carbon nanotubes and buckminsterfullerenes have high tensile strength, moreover, giving them potential use for structural reinforcement in concrete, sports equipment, and body armor. Chemical modification gives these structures an even wider variety of potential uses. Graphene oxide, for example, has promising antimicrobial activity, and attaching certain molecular groups to the surface of a carbon nanotube or buckminsterfullerene has potential for use as drug carriers for cancer therapeutics.

1.3a The Structure of the Atom

At the center of an atom (Fig. 1-4) is a positively charged nucleus, composed of *protons* and *neutrons*. Surrounding the nucleus is a cloud of negatively charged *electrons*, attracted to the nucleus by simple **electrostatic forces** (the forces by which opposite charges attract one another and like charges repel one another). It is important to realize that individual electrons are incredibly small, even much smaller than the nucleus.

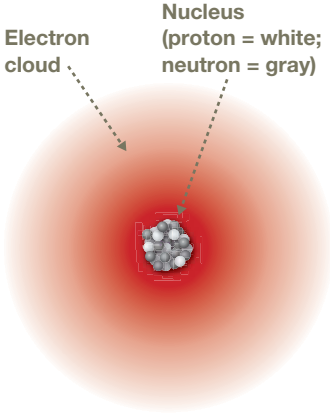


FIGURE 1-4 Basic structure of the atom Atoms are composed of a nucleus surrounded by a cloud of electrons. Protons (white) and neutrons (gray) make up the nucleus. (This figure is not to scale. If it were, the size of the electron cloud is so much larger than the size of the nucleus that its radius would be on the order of 500 meters!)

TABLE 1-1 Charges and Masses of Subatomic Particles

Particle	Charge (a.u.)	Mass (a.u.)
Proton	+1	~1
Neutron	0	~1
Electron	−1	~0.0005

a.u. = atomic units

However, the space that electrons occupy (i.e., the *electron cloud*) is much larger than the nucleus. In other words,

- The size of an atom is essentially defined by the size of its electron cloud.
- The vast majority of an electron cloud (and thus the vast majority of an atom) is empty space.

Table 1-1 lists the mass and charge of each of these elementary particles. Notice that the masses of the proton and neutron are significantly greater than that of the electron, so the mass of an atom is essentially the mass of just the nucleus.

An atom, by definition, has no net charge. Consequently, the number of electrons in an atom must equal the number of protons. The number of protons in the nucleus, called the **atomic number** (Z), defines the element. For example, a nucleus that has six protons has an atomic number of 6, and can only be a carbon nucleus.

If the number of protons and the number of electrons are not equal, then the entire **species** (that particular combination of protons, neutrons, and electrons) bears a net charge, and is called an **ion**. A negatively charged ion, an **anion** (pronounced AN-ion), results from an excess of electrons. A positively charged ion, a **cation** (pronounced CAT-ion), results from a deficiency of electrons.

SOLVED problem 1.1 How many protons and electrons does a cation of the carbon atom have if its net charge is +1?

Think How many protons are there in the nucleus of a carbon atom? Does a cation have more protons than electrons, or vice versa? How many more, given the net charge of the species?

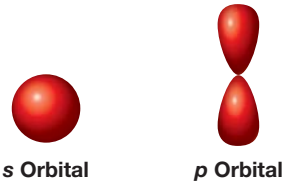
Solve A carbon atom's nucleus has six protons. A cation with a +1 charge should have one more proton than it has electrons, so this species must have five electrons.

problem 1.2 **(a)** How many protons and electrons does an anion of the carbon atom have if its net charge is −1? **(b)** How many protons and electrons does a cation of the oxygen atom have if its net charge is +1? **(c)** How many protons and electrons does an anion of the oxygen atom have if its net charge is −1?

1.3b Atomic Orbitals and Shells

Electrons in an isolated atom reside in **atomic orbitals**. As we shall see, the exact location of an electron can never be pinpointed. An orbital, however, specifies the region of space where the probability of finding a given electron is high. More simplistically, we can view orbitals as "rooms" that house electrons. Atomic orbitals are examined in greater detail in Chapter 3; for now, it will suffice to review some of their more basic concepts.

1. Atomic orbitals have different shapes. An *s* orbital, for example, is a sphere, whereas a *p* orbital has a "dumbbell" shape with two lobes (Fig. 1-5). Each orbital is centered on the nucleus of its atom or ion.
2. Atomic orbitals are organized in *shells* (also known as *energy levels*). A **shell** is defined by the **principal quantum number**, ***n***. There are an infinite number of shells in an atom, given that n can assume any integer value from 1 to infinity.
   a. The first shell ($n = 1$) contains only an *s* orbital, called "1*s*."
   b. The second shell ($n = 2$) contains one *s* orbital and three *p* orbitals, called "2*s*," "$2p_x$," "$2p_y$," and "$2p_z$."
   c. The third shell ($n = 3$) contains one *s* orbital, three *p* orbitals, and five *d* orbitals.



***s* Orbital** ***p* Orbital**

FIGURE 1-5 Orbitals Orbitals represent regions in space where an electron is likely to be. An *s* orbital is spherical, and a *p* orbital is a dumbbell.

3. Up to two electrons are allowed in any orbital.
   a. Therefore, the first shell can contain up to two electrons (a **duet**).
   b. The second shell can contain up to eight electrons (an **octet**).
   c. The third shell can contain up to 18 electrons.
4. With increasing shell number, the *size* and *energy* of the atomic orbital increases. For example, comparing *s* orbitals in the first three shells, the size and energy increase in the order $1s < 2s < 3s$, as shown in Figure 1-6. Similarly, a $2p$ orbital is smaller in size and lower in energy than a $3p$ orbital.
5. Within a given shell, an atomic orbital's energy increases in the following order: $s < p < d$, etc. In the second shell, for example, the $2s$ orbital is lower in energy than the $2p$.

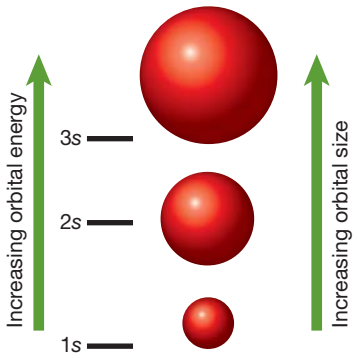


FIGURE 1-6 Relationship between principal quantum number, orbital size, and orbital energy As the shell number of an orbital increases, its size and energy increase, too. The horizontal black lines indicate each orbital's energy.

1.3c Ground State Electron Configurations: Valence Electrons and Core Electrons

The way in which electrons are arranged in atomic orbitals is called the atom's **electron configuration**. The *most stable* (i.e., the lowest energy) electron configuration is called the **ground state** configuration. Knowing an atom's ground state configuration provides insight into the atom's chemical behavior, as we will see.

With the relative energies of atomic orbitals established, an atom's ground state electron configuration can be obtained by applying the following three rules:

1. **Pauli's exclusion principle:** No more than two electrons (i.e., zero, one, or two electrons) can occupy a single orbital; two electrons in the same orbital must have opposite spins.
2. **Aufbau principle:** Each successive electron must fill the lowest energy orbital available.
3. **Hund's rule:** All orbitals *at the same energy* must contain a single electron before a second electron can be paired in the same orbital.

According to these three rules, the first 18 electrons fill orbitals as indicated in Figure 1-7.

1.1 YOUR TURN

In Figure 1-7, place a box around all of the orbitals in the second shell and label them.

Answers to Your Turns are in the back of the book.

In the ground state, the six electrons found in a carbon atom would fill the orbitals as shown in Figure 1-8, with two electrons in the $1s$ orbital, two electrons in the $2s$ orbital, and one electron in each of two different $2p$ orbitals (it doesn't matter which two). The shorthand notation for this electron configuration is $1s^2 2s^2 2p^2$.

Knowing the ground state electron configuration of an atom, we can distinguish *valence* electrons from *core* electrons.

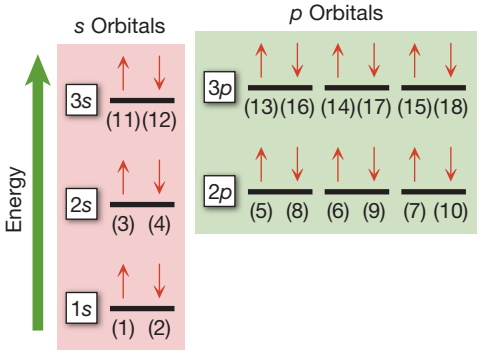


FIGURE 1-7 Energy diagram of atomic orbitals for the first 18 electrons The order of electron filling is indicated in parentheses. Each horizontal black line represents a single orbital. Each successive electron fills the lowest energy orbital available. Notice in the $2p$ and $3p$ sets of orbitals that no electrons are paired up until after the addition of the fourth electron.

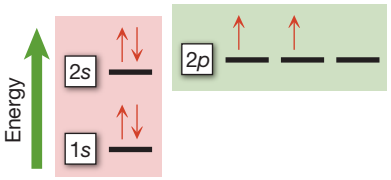


FIGURE 1-8 Energy diagram for the ground state electron configuration of the carbon atom This configuration is abbreviated $1s^2 2s^2 2p^2$.

- **Valence electrons** are those occupying the highest energy (i.e., valence) shell. For the carbon atom, the valence shell is the $n = 2$ shell.
- **Core electrons** occupy the remaining lower energy shells of the atom. For the carbon atom, the core electrons occupy the $n = 1$ shell.

The notion of valence electrons is important because, as we discuss in Section 1.5, *bonding is governed primarily by the valence electrons*. As we can see in Figure 1-8, for example, carbon has four valence electrons and two core electrons, so bonding involving carbon is governed by those four valence electrons.

YOUR TURN 1.2

In Figure 1-8, place a circle around the valence electrons and label them. Place a box around all of the core electrons and label them.

The periodic table is organized in such a way that *the number of valence shell electrons of an atom can be read from the element's group number* (a copy of the periodic table appears inside the book's front cover). Carbon is located in group 4A, consistent with its four valence electrons. Similarly, chlorine is found in group 7A, so it has seven valence electrons. Its ground state electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^5$; that is, seven electrons occupy the third shell (the valence shell).

Atoms are especially stable when they have completely filled valence shells. This is exemplified by the **noble gases** (group 8A), such as helium and neon, because they have completely filled valence shells and they do *not* form bonds to make compounds. Although the specific origin of this "extra" stability is beyond the scope of this book, the consequences are the basis for the "octet rule" and the "duet" rule we routinely use when drawing Lewis structures (Section 1.5).

SOLVED problem 1.3 Write the ground state electron configuration of the nitrogen atom. How many valence electrons does it have? How many core electrons does it have?

Think How many total electrons are there in a nitrogen atom? What is the order in which the atomic orbitals should be filled (see Fig. 1-7)? What is the valence shell and where do the core electrons reside?

Solve There are seven total electrons ($Z = 7$ for N). The first two are placed in the 1s orbital and the next two in the 2s orbital, leaving one electron for each of the three 2p orbitals. The electron configuration is $1s^2 2s^2 2p^3$. The valence shell is the second shell, so there are five valence electrons and two core electrons.

problem 1.4 Write the ground state electron configuration of the oxygen atom. How many valence electrons are there? How many core electrons are there?

1.4 The Covalent Bond: Bond Energy and Bond Length

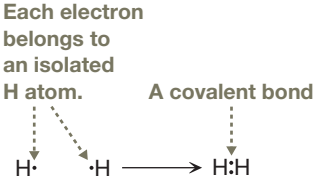


FIGURE 1-9 A covalent bond A covalent bond is the sharing of two electrons between nuclei.

A *covalent bond* is one of two types of fundamental bonds in chemistry; the other, an ionic bond, is discussed in Section 1.8. A **covalent bond** is characterized by the *sharing of valence electrons* between two or more atoms, as shown for two H atoms in Figure 1-9.

In Section 1.5, we will explore how various molecules can be constructed from atoms through the formation of such bonds, but first we must examine more closely the nature of covalent bonds. In particular, why do they form at all?

We can begin to answer these questions by examining Figure 1-10a, which illustrates how the energy of two H atoms changes as a function of the distance between their

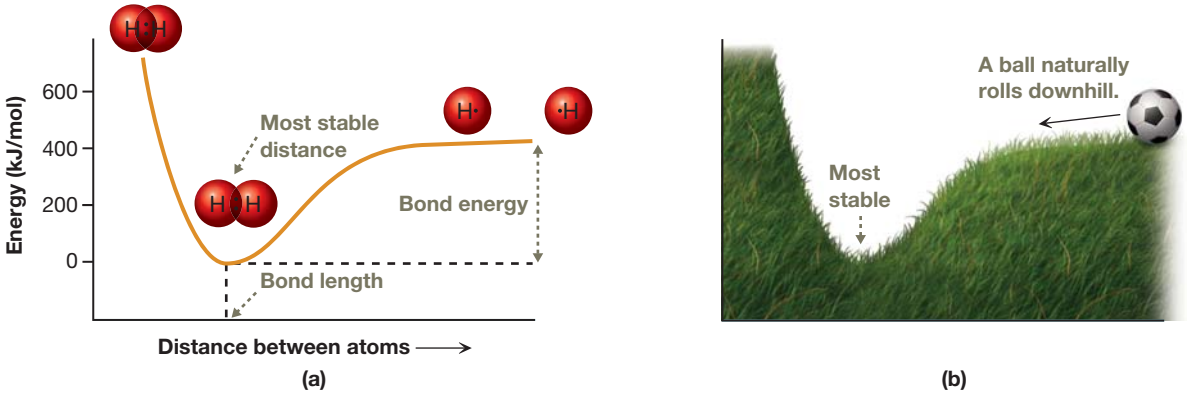


FIGURE 1-10 Formation of a chemical bond (a) Plot of energy as a function of internuclear distance for two H atoms. The H atoms are most stable at the distance at which energy is a minimum. (b) A ball at the top of a hill becomes more stable at the bottom of the hill, and therefore tends to roll downhill.

nuclei. Namely, when two H atoms separated by a large distance are brought together, their total energy begins to decrease. At one particular internuclear distance, the energy of the molecule is at a minimum, while at shorter distances the energy rises dramatically.

The two H atoms are most stable at the internuclear distance that corresponds to that energy minimum, a distance called the **bond length** of the H—H bond. The energy that would be required to remove the H atoms from that internuclear distance to infinity is the **bond strength**, or **bond energy**, of the H—H bond.

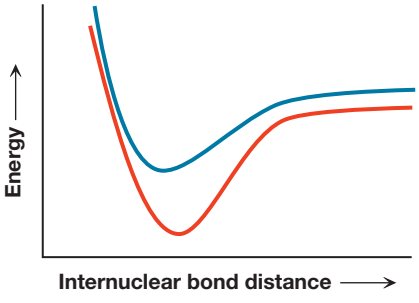
We can relate this process to a more familiar one of a ball rolling down a hill (Fig. 1-10b). A ball at the top of a hill has more potential energy than the ball at the bottom of the hill. This is why the ball at the top of the hill will tend to roll downhill, coming to rest at the bottom. By the same token, it requires energy to roll the ball from the bottom of the hill back to the top.

1.3 YOUR TURN

Estimate the bond energy of the bond represented by Figure 1-10a.

The shape of the energy curve in Figure 1-10a is similar to that which describes the stretching and compressing of a spring connecting two masses (Fig. 1-11). The minimum in energy corresponds to the spring's rest position—that is, when it is neither stretched nor compressed. Both stretching and compressing the spring from its rest position require energy. Thus, it is often convenient to *think of a covalent bond as a spring that connects two atoms.* (This view of the chemical bond is extended further in the discussion of infrared spectroscopy in Chapter 15.)

SOLVED problem 1.5 In the diagram below, which curve represents a stronger covalent bond?



Think How can bond breaking be represented for each curve? Which of those processes requires more energy?

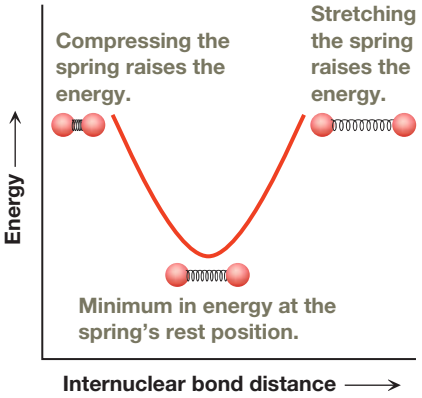


FIGURE 1-11 The spring model of a covalent bond The energy curve of a spring connecting two masses resembles that of the covalent bond shown in Figure 1-10a. Both stretching and compressing the spring from its rest position cause a rise in energy.