Organic Chemistry

FIFTH EDITION

Maitland Jones, Jr.

Steven A. Fleming

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Maitland Jones, Jr.

NEW YORK UNIVERSITY

Steven A. Fleming

TEMPLE UNIVERSITY

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Preface to the Fifth Edition

Most students in our organic chemistry courses are not chemistry majors. We wrote this book for those students and anyone who wants a broad yet modern introduction to the subject. We stress general principles because it is impossible to memorize all the details of this vast subject. We want students to learn to make connections, recognize patterns and trends, and use a set of organizing principles to make the material more manageable and understandable. Students who will be taking standardized exams, like the MCAT, will benefit from using this text and gaining a deep understanding of the material. We also believe that the skill of critical thinking is emphasized in this text. This skill will help in science courses taken in the future and, more important, in future decision-making.

Although we have made substantial changes to the fifth edition that will benefit students using this book, the voice remains the same. It is personal and talks directly to the student not only about the material at hand, but also about the "how and why" of organic chemistry. We believe it is much easier to enjoy, and learn, organic chemistry if a strong focus on "Where are we and why are we here?" and "What is the best way to do this?" is maintained. On occasion, we try to help students through a tough part of the subject by pointing out that it *is* tough and then suggesting ways to deal with it. When we talk to students, we try to use our experience to help them succeed, and the book tries to do the same thing.

Every chapter begins with a **Preview** section in which the coming chapter is outlined. At the end of the Preview, we describe the **Essential Skills and Details** students will need for the chapter. At exam time, students can use these sections as guides for study and review.

Organic chemistry is a highly visual subject. Organic chemists think by constructing mental pictures of molecules and communicate with each other by drawing pictures. To help students develop those same skills, we have added **Visualize, Understand, Draw** sections in each chapter. These sections highlight an important skill or concept and break it down into these three general steps with the goal of training students to use these same steps when they are solving problems.

One factor that can make organic chemistry difficult is that new language must be learned. Organic chemists talk to each other using many different conventions and at least some of that language must be learned, or communication is impossible. In addition to general treatments of nomenclature at the beginning of many chapters, we have incorporated numerous **Convention Alerts** in which aspects of the language that chemists use are highlighted.

Throughout the book, reference is made to the connection between organic chemistry and the world of biology. Almost every chapter has a section devoted to the biological relevance of new reactions discussed. We also have **Applications Boxes** to illustrate the relevance of the subject to students' lives.

It can be a great help to be shown profitable (and unprofitable) approaches to problem solving, and we use the **Problem Solving** sections to provide that kind of direction. Each chapter has at least one of these sections with our advice about approaching a type of problem.

There are many moments in organic chemistry when it is important to take stock of where we are. **Summary** sections have been incorporated into every chapter. Here the narrative is broken and the reader is brought up to date on the important points of the previous topic. These summaries serve as excellent "reminder and review" sections when a student is studying for an exam.

Each chapter ends with a summary of **New Concepts**, **Key Terms**, new **Reactions, Mechanisms, and Tools**, new **Syntheses**, and **Common Errors**. These sections recapitulate and reinforce the material of the chapter and serve as excellent study tools.

We incorporate unsolved problems in two ways. There are many such problems scattered throughout the text, and more problems, of all degrees of difficulty, are found at the end of each chapter. They range from drill exercises and simple examples, designed to emphasize important skills and illustrate techniques, to sophisticated, challenging problems. In those last cases, we are careful to provide hints and references to material useful for the solution. All these problems are solved in the *Study Guide*, which does much more than provide a bare-bones answer. It, along with the Problem Solving sections, tries to show students problem-solving techniques that will help them solve future problems. There are also many solved problems in the text, each designed to reinforce a point just made.

Approximately 20% of the problems in the fifth edition are new, including more drill problems for students to use as practice and to build confidence.

Other changes to the fifth edition include:

- New sections to help students with understanding the basics, including a new arrow-pushing section in Chapter 1, a new section on functional groups in Chapter 2, and more on acid–base chemistry in Chapter 2.
- Integration of equilibrium coverage. The material formerly in Chapter 8 has been broken up and integrated into chapters where that material is used.
- An earlier introduction of spectroscopy (formerly Chapter 15 and now Chapter 9) so students are introduced to modern methods of structure determination as early as possible.
- A new chapter on biomolecules (Chapter 21) to help reinforce what students will need to know for biochemistry, which is a topic that will be more important on the MCAT in 2015.
- The separation of substitution and elimination reactions (formerly Chapter 7) into two chapters (Chapters 7 and 8), making the topics more manageable.

Overall Organization

To understand atoms and molecules, one must first think sensibly about electrons, and for that we need to explore a bit of what quantum mechanics tells us. That does *not* mean we will all have to become mathematicians. Far from it. Our discussion here will be purely qualitative, as we need only grasp qualitatively what the mathematicians have to say to us. Qualitative molecular orbital theory is not too complicated a subject for students and requires no mathematics. Yet, this simple theory is amazingly powerful in its ability to rationalize and, especially, to predict structure and reactivity.

The abbreviated tutorial in Chapter 1 on qualitative applications of molecular orbital theory is likely to be new to students. This material is important, as it enables us to emphasize explanations throughout the rest of the book.

Not only are traditional subjects such as conjugation and aromaticity (Chapters 13 and 14) more accessible with the background of Chapter 1, but also explanations for the essential, building-block reactions of organic chemistry (Chapters 7, 8, 10, and 11, for example) become possible. There is, after all, no essential difference between the classic statement "Lewis acids react with Lewis bases" and the idea that the interaction of an empty orbital (electrophile) and a filled orbital (nucleophile) is stabilizing. The latter formulation allows all sorts of seemingly disparate reactions to be gathered together—unified—in a very useful way. (For example, a hydride shift and the S_N1 reaction become partners in a unified theory rather than two wildly different reactions that must be memorized in all their detail.)

The language that makes both the macroscale and the microscale accessible to us is mathematics. Although we need not do the mathematical operations ourselves, we do need to appreciate some of the things that quantum mechanics has to say to us. Chapter 1 also focuses strongly on Lewis structures—pictorial representations of atoms and ions. The ability to write good Lewis structures easily and to determine the locations of charges in molecules with ease is an essential skill. This skill is part of the language of chemistry and will be as important in Chapter 24 as it is in Chapter 1. Perhaps the most important skill that an organic chemistry student needs is the ability to understand arrow pushing. We have moved coverage of this skill to Chapter 1 because it is an utterly critical skill for all that follows.

After the introductory chapter comes a sequence of four chapters devoted largely to aspects of structure (Chapters 2–5). Here the details of the archetypal structures of organic chemistry are introduced. Hybridization is addressed, and the wonderful three-dimensionality of the subject begins to grow in. Some functional groups are introduced, and stereochemistry is dealt with in depth. A particularly vexing and fundamental question concerns what makes two atoms or molecules the same or different. Section 2.14 is a preview of NMR spectroscopy, and while it is not detailed—it is only an introduction—it allows a real discussion of that elusive question of "difference." It also allows reinforcement through a series of new problems introduced throughout the first half of the book.

In Chapter 3, the addition of HX molecules to alkenes allows an introduction to synthesis, as well as a discussion of selectivity, catalysis, and reaction mechanisms, in general.

After the series of "structure" chapters comes Chapter 6 on alcohols, amines, halides, and the properties of solvents. This chapter functions as a lead-in to a discussion of several building-block reactions, the S_N2, S_N1, E2, and E1 reactions.

Chapter 7 digs deeply into the S_N1 and S_N2 reactions. The generality of the reactions between electrophiles and nucleophiles is emphasized. A discussion of kinetics and thermodynamics is used to reinforce the observed chemistry. The concept of organic synthesis begins to take shape. Instructors who want an early focus on multistep syntheses can use the material from Chapter 3, addition to alkenes, with the material from Chapter 7 to go from alkenes to amines, for example.

In Chapter 8, the elimination reactions (E1, E2, and E1cB) are presented in detail. We believe that students are ready to grapple with the multitude of pathways at this point in their organic chemistry training. The utility of the Hammond postulate and the ability to predict hydride shifts in carbocation chemistry are two important concepts in Chapter 8.

Analytical chemistry (Chapter 9) is an essential component of organic chemistry. In the fifth edition, this topic is covered earlier in the text than in the previous edition because it is a useful tool throughout the yearlong course. There is a brief introduction to NMR spectroscopy in Chapter 2 that is very useful for establishing how we know about chemical structure.

Chapters 10 and 11 introduce other building-block reactions and other functional groups in the context of an expansion of the earlier discussion of addition reactions in Chapter 3. Even at these early stages, we introduce the biological applications of organic chemistry. For example, in the chapters devoted to the structure of alkanes and, especially, alkenes, biorelevant examples appear. These do not obscure the essential information of the chapters, however. They are kept as examples, potential extensions, and applications of what we have learned at this point. Later on in the book their role is expanded, with whole chapters (Chapters 21 and 22) devoted to biological topics.

We have added Chapter 21 to this edition. In it we learn more about bioorganic chemistry. The coverage includes lipids and alkaloids. The chapter also includes a compilation of the chemistry observed in nature that involves neutral, lipophilic molecules and basic molecules such as amines.

The basic reactions of the alkyl halides (Chapters 7 and 8) and alkenes (Chapters 10–13) provide a foundation for the chemistry of aromatic rings (Chapters 14–15) and carbonyl compounds (Chapters 16–20), the subjects of a series of chapters in the second half of the book. The last few chapters constitute a series of Special Topics. We expect that most instructors will choose to emphasize biological aspects of our science, and Chapters 21 and 22 provide an opportunity to do that. Alternatively, a more physical approach would see the exciting chemistry of Chapters 23 and 24 as more appropriate.

Instructor Resources

Test Bank. The fifth edition Test Bank contains more than 1200 questions from which to choose. Questions are organized by chapter section, and each question is ranked by difficulty and one of six distinct levels based on Bloom's Taxonomy: Remembering, Understanding, Applying, Analyzing, Evaluating, and Creating. 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 effortlessly to 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:

- Selected photographs and every piece of line art in JPEG format
- Selected 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 Web site includes:

- Selected photographs and every piece of line art in JPEG format
- Selected 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*
- Test bank in PDF, Word RTF, and ExamView formats

Clickers in Action: Active Learning in Organic Chemistry (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.

Student Resources

Study Guide/Solutions Manual (Maitland Jones, Jr., New York University; Henry L. Gingrich, Princeton University; Steven A. Fleming, Temple University). Written by the textbook authors, this guide provides students with fully worked solutions to all unworked problems that appear in the text. In addition to the solutions presented for each specific problem, the authors present good problem-solving strategies for solving organic chemistry problems in general.

Organic Reaction Animations (ORA) Online (Steven A. Fleming, Paul Savage, and Greg Hart) is a compilation of more than 50 organic reactions whose pathways have been calculated and animated to help students visualize the events that occur in the most important organic reactions. Almost every chapter has a set of ORA problems so that students can use the ORA software to work specific problems and help with their visualization of the material. Students receive access to ORA by using the ebook code that is included with every *new* textbook. A code can also be purchased separately.

Orgo 3D Web. This free and open Web site is available to all students and includes more than 350 interactive, three-dimensional molecules from the text. These structures were made in Chem3D and can be manipulated in space and viewed in several ways (ball-and-stick, space-filling, etc.). In addition, there is a short write-up and usually a few questions (and answers!) for most of the molecules.

SmartWork, created by chemistry educators, is the most intuitive online tutorial and homework system available for organic chemistry. A powerful engine supports and grades a diverse range of questions written for the fifth edition 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 the fifth edition so students have an instant reference and are prompted to read.

Instructors can draw from Norton's bank of more than 3000 high-quality, class-tested questions or use our innovative authoring tools easily to modify existing questions 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 fifth edition 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 pre-set pools or create their own.

Acknowledgments

Books don't get written by setting an author on his or her way and then waiting for the manuscript to appear. There is a great deal more work to be done than that. In general, it is an editor's job to make it possible for the author to do the best of which he is capable. Don Fusting, Joe Wisnovsky, Vanessa Drake-Johnson, and, for the fourth and fifth editions, Erik Fahlgren at W. W. Norton were exemplary in their execution of that role. Our special thanks go to Erik for keeping the big picture in mind and for keeping us more or less on track. Jeannette Stiefel was the copy editor for the first three editions; Philippa Solomon and Connie Parks copyedited the fourth edition. Christopher Curioli copyedited this edition. Kate Barry and Christopher Granville were early project editors at Norton. Carla Talmadge succeeded them for the fourth and fifth editions and was exceptionally helpful and creative in her dealings with too many author-produced problems. Renee Cotton, assistant editor, was a great help in innumerable ways, from helping pick the new chapter openers to improving the layout of Chapter 22. Without the team at W. W. Norton, the fifth edition would not have happened.

This book also profited immensely from the comments and advice of an army of reviewers and colleagues. We are very much in their debt. Their names and affiliations follow this preface. Two special reviewers, Henry L. Gingrich of Princeton and Ronald M. Magid of the University of Tennessee, read the work line by line, word by word, comma by missing comma. Their comments, pungent at times but helpful always, were all too accurate in uncovering both the gross errors and lurking oversimplifications in the early versions of this work. Insight from colleagues at Temple has helped polish our work, as they have answered many questions that have come up during the preparation of the fifth edition.

We have especially enjoyed learning from our many students and hope the students who use this text will appreciate the attention we have given to addressing the "Why" questions in organic chemistry and life. Our effort to go as far as we can to explain the natural phenomena is the distinguishing feature of this text.

Despite all the efforts of editors and reviewers, errors will persist. These are our fault only. When you find them, let us know.

Maitland Jones, Jr.
Cape North, June 2013

Steven A. Fleming
Philadelphia, June 2013

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Introduction

These days, a knowledge of science must be part of the intellectual equipment of any educated person. Of course, that statement may always have been true, but we think there can be no arguing that an ability to confront the problems of concern to scientists is especially important today. Our world is increasingly technological, and many of our problems, and the answers to those problems, have a scientific or technological basis. Anyone who hopes to understand the world we live in, to evaluate many of the pressing questions of the present and the future—and to vote sensibly on them—must be scientifically literate.

The study of chemistry is an ideal way to acquire at least part of that literacy. Chemistry is a central science in the sense that it bridges such disparate areas as physics and biology and connects those long-established sciences to the emerging disciplines of molecular biology and materials science. Similarly, as this book shows, organic chemistry sits at the center of chemistry, where it acts as a kind of intellectual glue, providing connections between all areas of chemistry. One does not have to be a chemist, or even a scientist, to profit from the study of organic chemistry.

The power of organic chemistry comes from its ability to give insight into so many parts of our lives. How does penicillin work? Why is Teflon nonstick? Why does drinking a cup of coffee help me stay awake? How do plants defend themselves against herbivores? Why is ethyl alcohol a depressant? All these questions have answers based in organic chemistry. And the future will be filled with more organic chemistry—and more questions. What's a buckyball or a nanotube, and how might it be important to my life? How might an organic superconductor be constructed? Why is something called the Michael reaction important in a potential cancer therapy? Read on, because this book will help you to deal with questions such as these, and many more we can't even think up yet.

What Is Organic Chemistry?   Organic chemistry is traditionally described as the chemistry of carbon-containing compounds. Until the 19th century, it was thought that *organic* molecules were related in an immutable way to living things, hence the term organic. The idea that organic compounds could be made only from molecules derived from living things was widespread and gave rise to the notion of a vital force being present in carbon-containing molecules. In 1828, Friedrich Wöhler (1800–1882) synthesized urea, a certified organic substance, from heating ammonium cyanate, a compound considered to be inorganic.[1] Wöhler's experiment

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[1]Wöhler's urea is an end product of the metabolism of proteins in mammals and is a major component of human urine. An adult human excretes about 25 g (6–8 level teaspoons) of urea each day. The formation of urea is our way of getting rid of the detritus of protein breakdown through a series of enzymatic reactions. If you are missing one of the enzymes necessary to produce urea, it's very bad news indeed, as coma and rapid death result.

really did not speak to the question of vital force, and he knew this. The problem was that at the time there were no sources of ammonium cyanate that did not involve such savory starting materials as horns and blood—surely "vital" materials. The real coup de grâce for vitalism came some years later when Adolph Wilhelm Hermann Kolbe (1818–1884) synthesized acetic acid from elemental carbon and inorganic materials in 1843–1844 (see structures below).

Acetic Acid   **Urea**
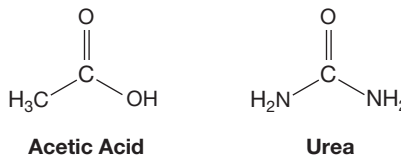
Despite the demise of the vital-force idea, carbon-containing molecules certainly do have a strong connection to living things, including ourselves. Indeed, carbon provides the backbone for all the molecules that make up the soft tissues of our bodies. Our ability to function as living, sentient creatures depends on the properties of carbon-containing organic molecules, and we are about to embark on a study of their structures and transformations.

Organic chemistry has come far from the days when chemists were simply collectors of observations. In the beginning, chemistry was largely empirical, and the questions raised were, more or less, along the lines of "What's going to happen if I mix this stuff with that stuff?" or "I wonder how many different things I can isolate from the sap of this tree?" Later, it became possible to collate knowledge and to begin to rationalize the large numbers of collected observations. Questions now could be expanded to deal with finding similarities in different reactions, and chemists began to have the ability to make predictions. Chemists began the transformation from the hunter-gatherer stage to modern times, in which we routinely seek to use what we know to generate new knowledge.

Many advances have been critical to that transformation; chief among them is our increased analytical ability. Nowadays, the structure of a new compound, be it isolated from tree sap or produced in a laboratory, cannot remain a mystery for long. Today, the former work of years can often be accomplished in hours. This expertise has enabled chemists to peer more closely at the *why* questions, to think more deeply about reactivity of molecules. This point is important because the emergence of unifying principles has allowed us to teach organic chemistry in a different way, to teach in a fashion that largely frees students from the necessity to memorize organic chemistry. That is what this book tries to do: to teach concepts and tools, not vast compendia of facts. The aim of this book is to provide frameworks for generalizations, and the discussions of topics are all designed with this aim in mind.

We will see organic molecules of all types in this book. Organic compounds range in size from hydrogen (H_2)—a kind of honorary organic molecule even though it doesn't contain carbon—to the enormously complex biomolecules, which typically contain thousands of atoms and have molecular weights in the hundreds of thousands. Despite this diversity and the apparent differences between small and big molecules, the study of all molecular properties always begins the same way, with structure. Structure determines reactivity, which provides a vehicle for navigating from the reactions of one kind of molecule to another and back again. So, early on, this book deals extensively with structure.

What Do Organic Chemists Do?   Structure determination has traditionally been one of the things that practicing organic chemists do with their lives. In the early days, such activity took the form of uncovering the gross connectivity of the

atoms in the molecule in question: What was attached to what? Exactly what are those molecules isolated from the Borneo tree or made in a reaction in the lab? Such questions are quickly answered by application of today's powerful spectroscopic techniques or, in the case of solids, by X-ray diffraction crystallography. And small details of structure lead to enormous differences in properties: morphine, a painkilling agent in wide current use, and heroin, a powerfully addictive narcotic, differ only by the presence of two acetyl groups (CH3CO units), a tiny difference in their large and complex structures.

Today, much more subtle questions are being asked about molecular structure. How long can a bond between atoms be stretched before it goes "boing," in its quiet, molecular voice, and the atoms are no longer attached? How much can a bond be squeezed? How much can a bond be twisted? These are structural questions and reveal much about the properties of atoms and molecules—in other words, about the constituents of us and the world around us.

Many chemists are more concerned with how reactions take place, with the study of "reaction mechanisms." Of course, these people depend on those who study structure; one can hardly think about how reactions occur if one doesn't know the detailed structures—connectivity of atoms, three-dimensional shape—of the molecules involved. In a sense, every chemist must be a structural chemist. The study of reaction mechanisms is an enormously broad subject. It includes people who look at the energy changes involved when two atoms form a molecule or, conversely, when a molecule is forced to come apart to its constituent atoms, as well as those who study the reactions of the huge biomolecules of our bodies—proteins and polynucleotides. How much energy is required to make a certain reaction happen? Or, how much energy is given off when it happens? You are familiar with both kinds of processes. For example, burning is clearly a process in which energy is given off as both heat and light.

Chemists also want to know the details of how molecules come together to make other molecules. Must they approach each other in a certain direction? Are there catalysts—molecules not changed by the reaction—that are necessary? There are many such questions. A full analysis of a reaction mechanism requires knowledge of the structures and energies of all molecules involved in the process, including species called intermediates—molecules of fleeting existence that cannot usually be isolated because they go on quickly to other species. One also must have an idea of the structure and energy of the highest energy point in a reaction, called the transition state. Such species cannot be isolated—they are energy maxima, not energy minima—but they can be studied nonetheless. We will see how.

Still other chemists focus on synthesis. The goal in such work is the construction of a target molecule from smaller, available molecules. In earlier times, the reason for such work was sometimes structure determination. One set out to make a molecule one suspected of being the product of some reaction of interest. Now, determination of structure is not usually the goal. And it must be admitted that nature is still a *much* better synthetic chemist than any human. There is simply no contest; evolution has generated systems exquisitely designed to make breathtakingly complicated molecules with spectacular efficiency. We cannot hope to compete. Why, then, even try? The reason is that there is a cost to the evolutionary development of synthesis, and that is specificity. Nature can make a certain molecule in an extraordinarily competent way, but nature can't make changes on request. The much less efficient syntheses devised by humans are far more flexible than the syntheses of nature, and one reason for the chemist's interest in synthesis is the possibility of generating molecules of nature in systematically modified forms. We hope to make small

changes in the structures and to study the influence on biological properties induced by those changes. In that way, it could be possible to find therapeutic agents of greatly increased efficiency, for example, or to stay ahead of microbes that become resistant to certain drugs. Nature can't quickly change the machinery for making an antibiotic molecule to which the microbes have become resistant, but humans can.

What's Happening Now? It's Not All Done. In every age, some people have believed that there is little left to be done. All the really great stuff is behind us, and all we can hope for is to mop up some details; we won't be able to break really new ground. And every age has been dead wrong in this notion. By contrast, the slope of scientific discovery continues to increase. We learn more every year, and not just details. Right now the frontiers of molecular biology—a kind of organic chemistry of giant molecules, we would claim—are the most visibly expanding areas, but there is much more going on.

In structure determination, completely new kinds of molecules are appearing. For example, just a few years ago a new form of carbon, the soccer ball–shaped C_{60}, was synthesized in bulk by the simple method of vaporizing a carbon rod and collecting the products on a cold surface. Even more recently it has been possible to capture atoms of helium and argon inside the soccer ball. These are the first neutral compounds of helium ever made. Molecules connected as linked chains or as knotted structures are now known. No one knows what properties these new kinds of molecules will have. Some will certainly turn out to be mere curiosities, but others will influence our lives in new and unexpected ways.

The field of organic reaction mechanisms continues to expand as we become better able to look at detail. For example, events on a molecular timescale are becoming visible to us as our spectrometers become able to look at ever smaller time periods. Molecules that exist for what seems a spectacularly short time—microseconds or nanoseconds—are quite long-lived if one can examine them on the femtosecond timescale. Indeed, the Nobel Prize in Chemistry in 1999 was given to Ahmed H. Zewail (b. 1946) of Caltech for just such work. Nowadays, we are moving ever further into the strange realm of the attosecond time regime. We are sure to learn much more about the details of the early stages of chemical reactions in the next few years.

At the moment, we are still defining the coarse picture of chemical reactions. Our resolution is increasing, and we will soon see microdetails we cannot even imagine at the moment. It is a very exciting time. What can we do with such knowledge? We can't answer that question yet, but chemists are confident that with more detailed knowledge will come an ability to take finer control of the reactions of molecules. At the other end of the spectrum, we are learning how macromolecules react, how they coil and uncoil, arranging themselves in space so as to bring two reactive molecules to just the proper orientation for reaction. Here we are seeing the bigger picture of how much of nature's architecture is designed to facilitate positioning and transportation of molecules to reactive positions. We are learning how to co-opt nature's methods by modifying the molecular machinery so as to bring about new results.

We can't match nature's ability to be specific and efficient. Over evolutionary time, nature has just had too long to develop methods of doing exactly the right thing. But we are learning how to make changes in nature's machinery—biomolecules—that lead to changes in the compounds synthesized. It is likely that we will be able to co-opt nature's methods, deliberately modified in specific ways, to retain the specificity but change the resulting products. This is one frontier of synthetic chemistry.

The social consequences of this work are surely enormous. We are soon going to be able to tinker in a controlled way with much of nature's machinery. How does humankind control itself? How does it avoid doing bad things with this power? Those questions are not easy, but there is no hiding from them. We are soon going to be faced with the most difficult social questions of human history, and how we deal with them will determine the quality of our lives and those of our children. That's one big reason that education in science is so important today. It is not that we will need more scientists; rather it is that we must have a scientifically educated population in order to deal sensibly with the knowledge and powers that are to come. So, this book is not specifically aimed at the dedicated chemist-to-be. That person can use this book, but so can anyone who will need to have an appreciation of organic chemistry in his or her future—and that's nearly everyone these days.

How to Study Organic Chemistry

Work with a Pencil.   We were taught very early that "Organic chemistry must be read with a pencil." Truer words were never spoken. You can't read this book, or any chemistry book, in the way you can read books in other subjects. You *must* write things as you go along. There is a real connection between the hand and the brain in this business, it seems. When you come to the description of a reaction, especially where the text tells you that it is an important reaction, by all means take the time to draw out the steps yourself. It is not enough to read the text and look at the drawings; it is not sufficient to highlight. Neither of these procedures is reading with a pencil. Highlighting does not reinforce learning in the way that working out the steps of the synthesis or chemical reaction at hand does. You might even make a collection of file cards labeled "Reaction descriptions" on which you force yourself to write out the steps of the reaction. Another set of file cards should be used to keep track of the various ways to make molecules. At first, these cards will be few in number, and sparsely filled, but as we reach the middle of the course, there will be an explosion in the number of synthetic methods available. This subject can sneak up on you, and keeping a catalog will help you to stay on top of this part of the subject. We will try to help you to work in this interactive way by interrupting the text with problems and with solutions that follow immediately when we think it is time to stop, take stock, and reinforce a point before going on. These problems are important. You can read right by them, of course, or read the answer without stopping to do the problem, but to do so will be to cheat yourself and make it harder to learn the subject. Doing these in-chapter problems is a part of reading with a pencil and should be very helpful in getting the material under control. There is no more important point to be made than this one. Ignore it at your peril!

Don't Memorize.   In the old days, courses in organic chemistry rewarded people who could memorize. Indeed, the notorious dependence of medical school admission committees on the grade in organic chemistry may have stemmed from the need to memorize in medical school. If you could show that you could do it in organic, you could be relied on to be able to memorize that the shin bone was connected to the foot bone, or whatever. Nowadays, memorization is the road to disaster; there is just too much material. Those who teach this subject have come to see an all too familiar pattern. There is a group of people who do very well early and then crash sometime around the middle of the first semester. These folks didn't

suddenly become stupid or lazy; they were relying on memorization and simply ran out of memory. Success these days requires generalization, understanding of principles that unify seemingly disparate reactions or collections of data. Medical schools still regard the grade in organic as important, but it is no longer because they look for people who can memorize. Medicine, too, has outgrown the old days. Now medical schools seek people who have shown that they can understand a complex subject, people who can generalize.

Work in Groups.   Many studies have shown that an effective way to learn is to work in small groups. Form a group of your roommates or friends, and solve problems for each other. Assign each person one or two problems to be solved for the group. Afterward, work through the solution found in the chapter or *Study Guide*. You will find that the exercise of explaining the problem to others will be enormously useful. You will learn much more from "your" problems than from the problems solved by others. When Mait teaches organic chemistry at Princeton, and now at NYU, he increasingly replaces lecture with small-group problem solving.

Work the Problems.   As noted above, becoming good at organic chemistry is an interactive process; you can't just read the material and hope to become an expert. Expertise in organic chemistry requires experience, a commodity that by definition you are very low on at the start of your study. Doing the problems is vital to gaining the necessary experience. Resist the temptation to look at the answer before you have tried to do the problem. Disaster awaits you if you succumb to this temptation, for you cannot learn effectively that way, and there will be no answers available on the examinations until it is too late. That is not to say that you must be able to solve all the problems straight away. There are problems of all difficulty levels in each chapter, and some of them are very challenging indeed. Even though the problem is hard or very hard, give it a try. When you are truly stuck, that is the time to gather a group to work on it. Only as a last resort should you take a peek at the *Study Guide*. There you will find not just a bare-bones answer, but, often, advice on how to do the problem as well. Giving hard problems is risky, because there is the potential for discouraging people. Please don't worry if some problems, especially hard ones, do not come easily or do not come at all. Each of us in this business has favorite problems that we still can't solve. Some of these form the basis of our research efforts and may not yield, even to determined efforts, for years. A lot of the pleasure in organic chemistry is working challenging problems, and it would not be fair to deprive you of such fun.

Use All the Resources Available to You.   You are not alone. Moreover, everyone will have difficulty at one time or another. The important thing is to get help when you need it. Of course, the details will differ at each college or university, but there are very likely to be extensive systems set up to help you. Professors have office hours, there are probably teaching assistants with office hours, and there will likely be help, review, or question sessions at various times. Professors are there to help you, and they will not be upset if you show enough interest to ask questions about a subject they love. "Dumb questions" do not exist! You are not expected to be an instant genius in this subject, and many students are too shy to ask perfectly reasonable questions. Don't be one of those people!

If you feel uncertain about a concept or problem in the book—or lecture—get help soon! This subject is highly cumulative, and ignored difficulties will come back to haunt you. We know that many teachers tell you that it is impossible to

skip material and survive, but this time it is true. What happens in December or April depends on September, and you can't wait and wait, only to "turn it on" at the end of the semester or year. Almost no one can cram organic chemistry. Careful, attentive, daily work is the route to success, and getting help with a difficult concept or a vexing problem is best done immediately. Over the life of the early editions of this book, Mait interacted with many of you by e-mail, much to his pleasure. Of course, we can't begin to replace local sources of help, and we can't be relied on in an emergency, as we might be out of touch with e-mail, but we can usually be reached at mj55@nyu.edu or sfleming@temple.edu. We look forward to your comments and questions.

Atoms and Molecules; Orbitals and Bonding

1
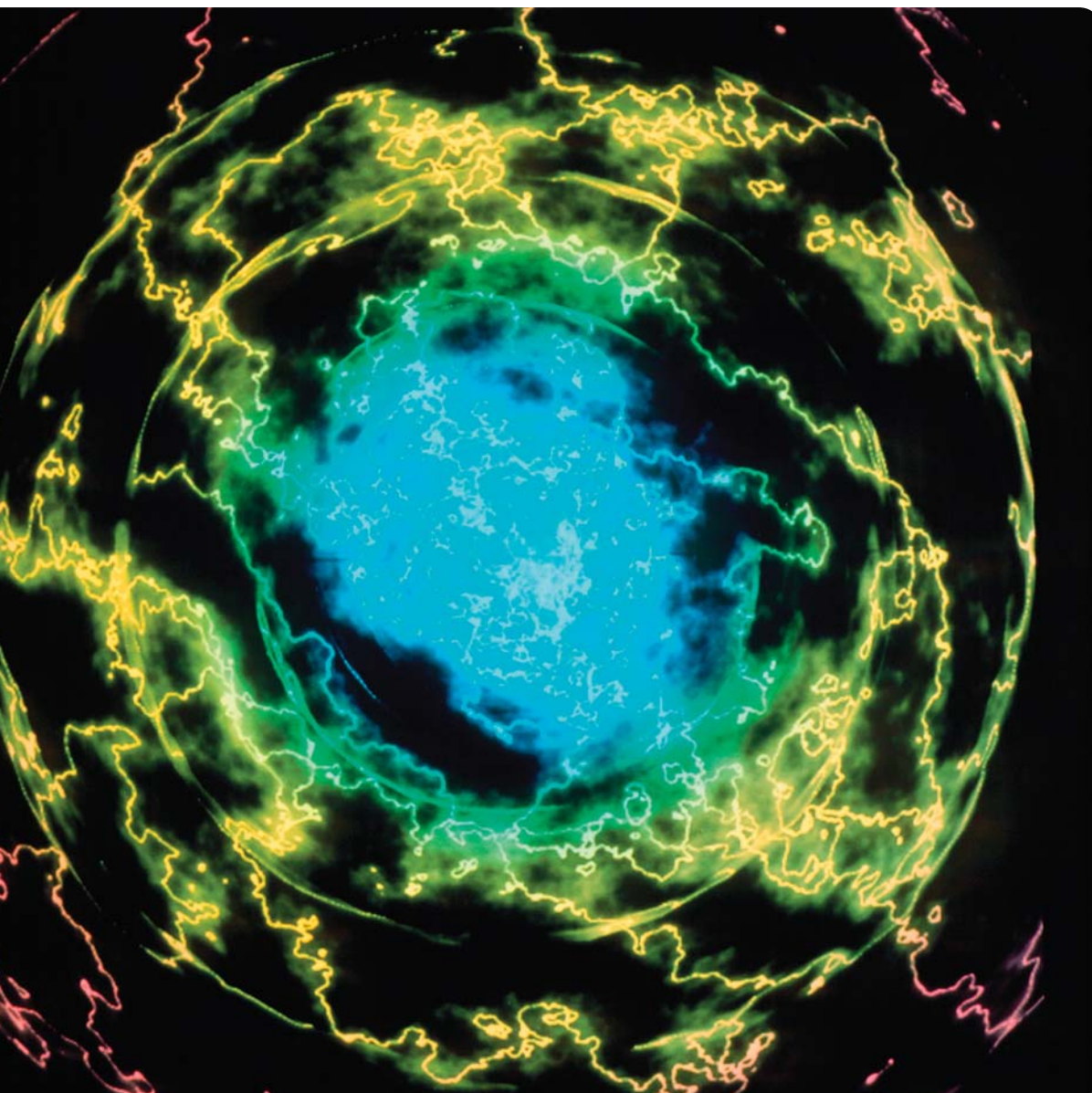
ELECTRON DENSITY OF A HELIUM ATOM   This image represents the quantum cloud of electrons surrounding a helium atom. Colors represent the local electric charge density, essentially the probability that one of the atom's four electrons will be found at a given point. The colors run from blue (highest probability) to red (lowest probability). The chaotic appearance of the image is due to the presence of a nearby charged particle; when in equilibrium, the atom would appear more symmetrical. This is a more appropriate illustration than the older ideas of fixed "orbitals" for electrons, sometimes referred to as the Bohr model, and is due to the principles of modern quantum theory.

> When it comes to atoms, language can be used only as in poetry. The poet too, is not nearly so concerned with describing facts as with creating images.
>
> —NIELS BOHR TO WERNER HEISENBERG[1]

1.1 Preview

The picture of atoms that all scientists had in their collective mind's eye at the beginning of the past century was little different from that of the ancient Greek philosopher Democritus (~460–370 B.C.), who envisioned small, indivisible particles as the constituents of matter. These particles were called **atoms**, from the Greek word for *indivisible*. The English chemist John Dalton (1766–1844) had the idea that different atoms might have different characteristic masses, but he did not abandon the notion of a solid, uniform atom. That picture did not begin to change dramatically until 1897, when another English physicist, J. J. Thomson (1856–1940), discovered the negatively charged elementary particle called the **electron**. Thomson postulated a spongelike atom with the negatively charged electrons embedded within a positively charged material, rather like raisins in a pudding. In 1909, Ernest Rutherford's (1871–1937) discovery that an atom was mostly empty space demolished the pudding picture and led to his celebrated planetary model of the atom, in which electrons were seen as orbiting a compact, positively charged **nucleus**, the core of positively charged protons and neutral neutrons at the center of the atom.

It was Niels Bohr who made perhaps the most important modification of the planetary model. He made the brilliant and largely intuitive[2] suggestion that electrons were required to occupy only certain orbits. Because an electron's energy depends on the distance of its orbit from the positively charged nucleus, Bohr's suggestion amounted to saying that electrons in atoms can have only certain energies. An electron might have energy x or energy $2x$ but nothing in between. Whenever a property is restricted to certain values in this way, we say the property is *quantized*. Although this notion may seem strange, there are similar phenomena in the everyday world. You cannot create just any tone by blowing across the mouth of a bottle, for example. Say you start by blowing gently and creating a given tone. The tone you hear depends on the size and shape of the particular bottle, but if you gradually increase how hard you blow, which gradually increases the energy you are supplying, the tone does not change smoothly. Instead, you hear the first tone unchanged over a certain range of energy input then a *sudden* change in tone when just the right "quantum" of energy has been provided.

In the 1920s and 1930s, several mathematical descriptions emerged from the need to understand Bohr's quantum model of the atom. It became clear that we must take a probabilistic view of the subatomic world. Werner Heisenberg discovered that it is not possible to determine simultaneously both the position and momentum (mass times speed) of an electron.[3] Thus, we can determine where an electron is at any given time only in terms of probability. We *can* say, for example,

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[1] Niels Bohr (1885–1962) and Werner Heisenberg (1901–1976) were pioneers in the development of quantum theory, the foundation of our current understanding of chemical bonding.

[2] Some people's intuitions are better able than others' to cope with the unknown!

[3] This idea is extraordinarily profound—and troubling. The **Heisenberg uncertainty principle** (which states that the product of the uncertainty in position times the uncertainty in momentum is a constant) seems to limit fundamentally our access to knowledge. For an exquisite exposition of the human consequences of the uncertainty principle, see Jacob Bronowski, *The Ascent of Man*, Chapter 11 (Little Brown, New York, 1973).

that there is a 90% probability of finding the electron in a certain volume of space, but we *cannot* say that at a given instant the electron is at a particular point in space.

The further elaboration of this picture of the atom has given us the conceptual basis for all modern chemistry: the idea of the orbital. Loosely speaking, an **orbital** describes the region of space surrounding an atomic nucleus that may be occupied by either an electron or a pair of electrons of a certain energy. Both the combining of atoms to form molecules and the diverse chemical reactions these molecules undergo involve, at a fundamental level, the interactions of electrons in orbitals. This notion will appear throughout this book; it is the most important unifying principle of organic chemistry. In atoms, we deal with **atomic orbitals**, and in molecules, we deal with **molecular orbitals**.

Various graphic conventions are used in this book to represent atoms and molecules (letters for atoms, dots for electrons not involved in bonding, and lines for electrons in bonds), but it is important to keep in mind from the outset that the model that most closely approximates our current understanding of reality at the atomic and molecular level is the cloudy, indeterminate—you might even say poetic—image of the orbital.[4]

There is great conceptual overlap between the concept of an orbital and the notion you probably encountered in general chemistry of shells of electrons surrounding the atomic nucleus. For example, you are accustomed to thinking of the noble gas elements as having filled shells of electrons: two electrons for helium in the first shell, two electrons in the first shell and eight in the second shell for neon, and so on. In the noble gases, the outermost, or valence, shells are filled. We will speak of those valence shells as valence orbitals. We shall say much more about orbitals in a moment, especially about their shapes, but the point to "get" here is the move from the old word *shell* to the new word *orbital*.

ESSENTIAL SKILLS AND DETAILS

The following list of Essential Skills and Details, a version of which will appear in every chapter, is designed to alert you to the important parts of the chapter and, especially, to aid you in reviewing. After you finish the chapter or before an examination, it is a good idea to return to this list and make sure you are clear on all the Essential Skills and Details.

1. Writing correct Lewis dot structures for atoms, ions (charged atoms and molecules), and neutral molecules is an absolutely critical skill that will be essential throughout this book.
2. Take charge! It is necessary to be able to determine the formal charge of an atom, especially an atom in a molecule.
3. You have to be able to write the resonance forms (different electronic structures) that, taken together, give a more accurate picture of molecules than does any single structure.
4. Learn how to use the curved arrow formalism to "push" pairs of electrons in writing resonance forms and in sketching electron flow in chemical reactions.
5. Atoms have their electrons in atomic orbitals. Molecules have their electrons in molecular orbitals. Learning how molecular orbitals derive from atomic orbitals will be an essential skill. The set of "rules" on p. 36 should help.
6. Remember the sign convention for exothermic ($\Delta H°$ is negative) and endothermic ($\Delta H°$ is positive) reactions.
7. You surely do not have to memorize all the bond strengths, but by the end of this chapter you should have a good idea of the trends, such as $C\equiv C > C = C > C-C$.

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[4]In the wonderful quote that opens this chapter, Niels Bohr points out that once we transcend the visible world, all that is possible is modeling or image making. To us, what is even more marvelous about the quote is the simple word *too*: It was obvious to Bohr that scientists speak in images, and he was pointing out to Heisenberg that there was another group of people out there in the world who did the same thing—poets.
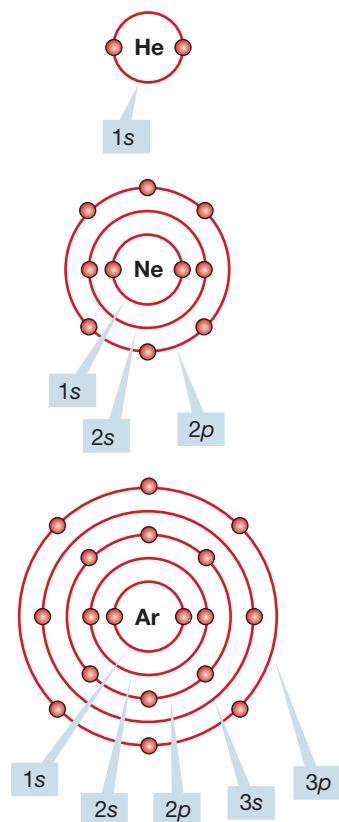
FIGURE 1.1 Schematic representations of He, Ne, and Ar.

1.2 Atoms and Atomic Orbitals

In a neutral atom, the nucleus, or core of positively charged protons and neutral neutrons, is surrounded by a number of negatively charged electrons equal to the number of protons. If the number of electrons and protons is not equal, the atom must be charged and is called an **ion**. A negatively charged atom or molecule is called an **anion**; a positively charged species is a **cation**. (One of the tests of whether or not you know how to "talk organic chemistry" is the pronunciation of the word *cation*. It is *kat*-eye-on, not *kay*-shun.)

The energy required to remove an electron from an atom to form a cation is called the **ionization potential**. In general, the farther away an electron is from the nucleus, the easier it is to remove the electron, and thus the ionization potential is lower.

Much of the chemistry of atoms is dominated by the gaining or losing of electrons to achieve the electronic configuration of one of the noble gases (He, Ne, Ar, Kr, Xe, and Rn). The noble gases have especially stable filled shells of electrons: 2 for He, 10 for Ne (2 + 8), 18 for Ar (2 + 8 + 8), and so on. The idea that filling certain shells creates especially stable configurations is known as the **octet rule**. With the exception of the first shell, called the 1*s* orbital, which can hold only two electrons, all shells fill with eight electrons; thus, this rule specifies an octet. The second shell can hold eight electrons: two in the subshell called the 2*s* orbital and six in the subshell 2*p* orbitals. We will soon explain these numbers and names, but first we need to understand the labels. Figure 1.1 shows schematic illustrations of three noble gases and their orbital designations. These pictures do not give good three-dimensional representations of these species, but they do show subshell occupancy. Better pictures are forthcoming.

The two electrons surrounding the helium (He) nucleus completely fill the first shell, and for this reason it is most difficult to remove an electron from He. Helium has an especially high ionization potential, 24.6 eV/atom = 566 kcal/mol = 2370 kJ/mol.[5] Likewise, the chemical inertness of the other noble gases, which also have high ionization potentials, is the result of the stability of their filled valence shells.

Electrons can be added to atoms as well as removed. The energy that is released by adding an electron to an atom to form an anion is called the atom's **electron affinity**, which is measured in electron volts. The noble gases have very low electron affinities. Conversely, atoms to which addition of an electron would complete a noble gas configuration have high electron affinities. The classic example is fluorine: The addition of a single electron yields a fluoride ion, F^-, which has the electronic configuration of Ne. Both F^- and Ne are 10-electron species, as Figure 1.2 shows.

FIGURE 1.2 Addition of an electron to a fluorine atom gives a fluoride ion.

$_9F$ +   1 electron $\longrightarrow$ $_9F^-$ similar to $_{10}Ne$

Fluorine   **Fluoride**   **Neon**
9 protons   9 protons   10 protons
9 electrons   10 electrons   10 electrons

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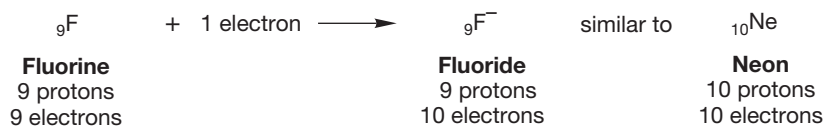
[5]There are several units of energy in use. Organic chemists commonly use kilocalories per mole (kcal/mol); physicists use the electron volt (eV). One electron volt/molecule translates into about 23 kcal/mol. Recently, the International Committee on Weights and Measures suggested that the kilojoule (kJ) be substituted for kilocalorie. So far, organic chemists in some countries, including the United States, seem to have resisted this suggestion. We will provide kcal/mol and parenthetical kJ/mol values throughout the text (1 kcal is equal to 4.184 kJ).

HELIUM

Helium (He) is the only substance that remains liquid under its own pressure at the lowest temperature recorded. Helium is present at only ~5 ppm in Earth's atmosphere, but it reaches substantially higher concentrations in natural gas, from which it is obtained. Helium is formed from the radioactive decay of heavy elements. For example, a kilogram of uranium gives 865 L of helium after complete decay. There's not much helium on Earth, but there is *a lot* in the universe. About 23% of the known mass of the universe is helium, mostly produced by thermonuclear fusion reactions between hydrogen nuclei in stars. So, an outside observer of our universe (whatever that means!) would probably conclude that helium is some of the most important stuff around.

The NASA space shuttle launched on July 8, 2011, used more than 28,000 L of liquid helium. The transition from liquid to gaseous helium provided necessary pressure to the system, and the helium helped push out the combustion products formed during the liftoff.

Single atoms, such as the fluorine atom shown on the left in Figure 1.2, are often written in the form $_Z^W\text{C}$, where W represents the mass number (number of protons and neutrons in the nucleus), Z represents the atomic number (number of protons in the nucleus), and C is the element symbol, here C for carbon. Thus, this notation for fluorine is $_9^{19}\text{F}$. In this book, the superscript W value is omitted, which leads to the $_9\text{F}$ and $_{10}\text{Ne}$ symbols you see in Figure 1.2.

Table 1.1 shows ionization potentials and electron affinities of some elements arranged as in the periodic table. Notice that with the exception of hydrogen, atoms with low ionization potentials, which are atoms that have easily removed electrons, cluster on the left side of the periodic table, and atoms with high electron affinities, which are atoms that accept electrons easily, are on the right side (excluding the noble gases).

CONVENTION ALERT
Atomic Numbers of Elements

TABLE 1.1 Some Ionization Potentials (Black) and Electron Affinities (Red) in Electron Volts

H 13.60 0.75									He 24.59 ~0
Li 5.39 0.62	Be 9.32 ~0			B 8.30 0.24	C 11.26 1.27	N 14.53 ~0	O 13.62 1.47	F 17.42 3.34	Ne 21.56 ~0
Na 5.14 0.55	Mg 7.65 ~0			Al 5.99 0.46	Si 8.15 1.24	P 10.49 0.77	S 10.36 2.08	Cl 12.97 3.61	Ar 15.75 ~0

Atoms having low ionization potentials often transfer an electron to atoms having high electron affinities, forming **ionic bonds**. In an ionically bonded species, such as sodium fluoride (Na^+F^-), the atoms are held together by the electrostatic attraction of the opposite charges. In sodium fluoride, both Na^+ and F^- have filled second shells, and each has achieved the stable electronic configuration of the noble

gas Ne. In potassium chloride (K^+Cl^-), both ions have the electronic configuration of Ar, another noble gas (Fig. 1.3).

FIGURE 1.3 In the ionic compounds NaF and KCl, each atom can achieve a noble gas electronic configuration with a filled octet of electrons.

$_{11}Na^+$ and $_9F^-$ Resemble $_{10}Ne$ $_{19}K^+$ and $_{17}Cl^-$ Resemble $_{18}Ar$

10 Electrons   10 Electrons   18 Electrons   18 Electrons
    each   each

Ionically bonded compounds are traditionally the province of inorganic chemistry. Nearly all of the compounds of organic chemistry are bound not by ionic bonds but rather by **covalent bonds**, which are bonds formed by the sharing of electrons.

1.2a Quantum Numbers   We have just developed pictures of some atoms and ions. Let's elaborate a bit to provide a fuller picture of atomic orbitals. Your reward for bearing with an increase in complexity will be a much-increased ability to think about structure and reactivity. The most useful models for explaining and predicting chemical behavior focus on the qualitative aspects of atomic (and molecular) orbitals, so it is time to learn more about them.

The electrons in atoms do not occupy simple circular orbits. To describe an electron in the vicinity of a nucleus, Erwin Schrödinger (1887–1961) developed a formula called a *wave equation*. Schrödinger recognized that electrons have properties of both particles and waves. The solutions to Schrödinger's wave equation, called **wave functions** and written **ψ** (pronounced "sigh"), have many of the properties of waves. They can be positive in one region, negative in another, or zero in between.

An orbital is mathematically described by a wave function, ψ, and the square of the wave function, ψ^2, is proportional to the probability of finding an electron in a given volume. There are regions or points in space where ψ and ψ^2 are both 0 (zero probability of finding an electron in these regions), and such regions or points are called **nodes**. However, ψ^2 does not vanish at a large distance from the nucleus but rather maintains a finite value, even if inconsequentially small.

Each electron is described by a set of four **quantum numbers**. Quantum numbers are represented by the symbols n, l, m_l, and s. The first two quantum numbers define the orbital of the electron. The first one, called the principal quantum number, is represented by n and may have the integer values $n = 1, 2, 3, 4$, and so on. It is related to the distance of the electron from the nucleus and hence to the energy of the electron. It describes the atomic shell the electron occupies. The higher the value of n, the greater the average distance of the electron from the nucleus and the greater the electron's energy. The principal quantum number of the highest-energy electron of an atom also determines the row occupied by the atom in the periodic table. For example, the electron in H and the two electrons in He are all $n = 1$, as Table 1.2 shows, and so these two atoms are in the first row of the table. The principal quantum number in Li, Be, B, C, N, O, F, and Ne is $n = 2$, which tells us that electrons can be in the second shell for these atoms and places the atoms in the second row. The elements Na, Mg, Al, Si, P, S, Cl, and Ar are in the third row, and orbitals for the electrons in these atoms correspond to $n = 1, 2,$ or 3.

The second quantum number, l, is related to the shape of the orbital and depends on the value of n. It may have only the integer values $l = 0, 1, 2, 3, \ldots,$

TABLE 1.2 Principal Quantum Number (n) of the Highest-Energy Electron

Atom	n
H, He	1
Li, Be, B, C, N, O, F, Ne	2
Na, Mg, Al, Si, P, S, Cl, Ar	3

$(n - 1)$. So, for an orbital for which $n = 1$, l must be 0; for $n = 2$, l can be 0 or 1; and for $n = 3$, the three possible values of l are 0, 1, and 2.

Each value of l signifies a different orbital shape. We shall learn about these shapes in a moment, but for now just remember that each shape is represented by a letter. The orbital for which $l = 0$ is spherical, and the letter s is used to designate all spherical orbitals. For higher values of l, we do not have the convenience of easily remembered letters the way we do with "s for spherical." Instead, you just have to remember that p is used for orbitals for which $l = 1$, d is used for those for which $l = 2$, and f is used for $l = 3$. These letters associated with the various values of l lead to the common orbital designations shown in Table 1.3.

The third quantum number, m_l, depends on l. It may have the integer values $-l, \ldots, 0, \ldots, +l$, and is related to the orientation of the orbital in space. Table 1.4 presents the possible values of n, l, and m_l for $n = 1, 2$, and 3. Orbitals of the same shell (n) and the same shape (l) are at the same energy regardless of the m_l value.

TABLE 1.3 Relationship between n and l

n	l	Orbital Designation
1	0	$1s$
2	0	$2s$
2	1	$2p$
3	0	$3s$
3	1	$3p$
3	2	$3d$

TABLE 1.4 Relationship between n, l, and m_l

n	l	m_l	Orbital Designation
1	0	0	$1s$
2	0	0	$2s$
2	1	-1	$2p$
2	1	0	$2p$
2	1	$+1$	$2p$
3	0	0	$3s$
3	1	-1	$3p$
3	1	0	$3p$
3	1	$+1$	$3p$
3	2	-2	$3d$
3	2	-1	$3d$
3	2	0	$3d$
3	2	$+1$	$3d$
3	2	$+2$	$3d$

Finally, there is s, the spin quantum number, which may have only the two values $\pm 1/2$.

Table 1.5 lists all the possible combinations of quantum numbers through $n = 3$.

TABLE 1.5 Possible Combinations of Quantum Numbers for $n = 1, 2$, and 3

n	l	m_l	s	Orbital Designation
1	0	0	$\pm\frac{1}{2}$	$1s$
2	0	0	$\pm\frac{1}{2}$	$2s$
2	1	$-1, 0, +1$	$\pm\frac{1}{2}$ each value of m_l	$2p$
3	0	0	$\pm\frac{1}{2}$	$3s$
3	1	$-1, 0, +1$	$\pm\frac{1}{2}$ each value of m_l	$3p$
3	2	$-2, -1, 0, +1, +2$	$\pm\frac{1}{2}$ each value of m_l	$3d$

Be careful. The s that designates the spin quantum number is not the same as the s in a $1s$ or $2s$ orbital. What is electron spin anyway? The word *spin* tries to make an analogy with the macroscopic world—in some ways, the electron behaves like a spinning top that can spin either clockwise or counterclockwise.

CONVENTION ALERT
Electron Spin

As shown in Tables 1.3–1.5, orbitals are designated with a number and a letter—1s, 2s, 2p, and so on. The number in the designation tells us the n value for a given orbital, and the letter tells us the l value. Thus, the notation 1s means the orbital for which $n = 1$ and $l = 0$. Because l values can be only 0 to $n - 1$, 1s is the only orbital possible for $n = 1$. The 2s orbital has $n = 2$ and $l = 0$, but now l can also be 1 ($n - 1 = 2 - 1 = 1$), and so we also have 2p orbitals, for which $n = 2, l = 1$. For the 2p orbitals, m_l, which runs from 0 to $\pm l$, may take the values $-1, 0, +1$. Thus there are three 2p orbitals, one for each value of m_l. These equi-energetic orbitals are differentiated by arbitrarily designating them as 2p_x, 2p_y, or 2p_z. A little later we will see that the x, y, z notation indicates the relative orientation of the 2p orbitals in space.

For $n = 3$, we have orbitals 3s ($n = 3, l = 0$) and 3p ($n = 3, l = 1$). Just as for the 2p orbitals, m_l may now take the values $-1, 0, +1$. The three 3p orbitals are designated as 3p_x, 3p_y, and 3p_z. With $n = 3$, l can also be 2 ($n - 1 = 2$), so we have the 3d ($n = 3, l = 2$) orbitals, and m_l may now take the values $-2, -1, 0, +1$, and $+2$. Thus there are five 3d orbitals. These turn out to have the complicated designations 3$d_{x^2-y^2}$, 3d_{z^2}, 3d_{xy}, 3d_{yz}, and 3d_{xz}. Mercifully, in organic chemistry we very rarely have to deal with 3d orbitals and need not consider the f orbitals, for which $n = 4$ and are even more complicated.

For all of the orbitals in Tables 1.4 and 1.5, the spin quantum number s may be either $+1/2$ or $-1/2$. We may now designate an electron occupying the lowest-energy orbital, 1s, as either 1s with $s = +1/2$ or 1s with $s = -1/2$ *but nothing else*. Similarly, there are only two possibilities for electrons in the 2p_x orbital: 2p_x with $s = +1/2$ or 2p_x with $s = -1/2$. The same is true for all orbitals—3p_z, 4d_{xy}, or whatever. Only two values are possible for the spin quantum number. That is why it is impossible for more than two electrons to occupy any orbital!

The convention used to designate electron spin shows the electrons as up-pointing ($\uparrow$) and down-pointing ($\downarrow$) arrows. Two electrons having opposite spins are denoted $\uparrow\downarrow$ and are said to have **paired spins**. Two electrons having the same spin are denoted $\uparrow\uparrow$ and are said to have **parallel spins**, or **unpaired spins**.

How many electrons occupy a given orbital in an atom is indicated with a superscript. When we write 1s^2 we mean that the 1s orbital is occupied by two electrons, and these electrons must have opposite (paired, with $s = +1/2$ and $s = -1/2$) spin quantum numbers. The designation 1s^3 is meaningless because there is no way to put a *different* third electron in any orbital. No two electrons may have the same values of the four quantum numbers. This rule is called the **Pauli principle** after Wolfgang Pauli (1900–1958), who first articulated it in 1925. These ideas are summarized in Figure 1.4.

1s^2 means the 1s orbital
contains two electrons:

Electron No. 1   Electron No. 2

$n = 1, l = 0, m_l = 0, s = +\frac{1}{2}$ $n = 1, l = 0, m_l = 0, s = -\frac{1}{2}$

FIGURE 1.4 Two electrons in the same orbital must have opposite (paired) spins.

In Table 1.6, we see the entry 1s^2, which means there are two electrons in the 1s orbital. It would seem that 1s^1 would be the appropriate notation for a 1s orbital occupied by one electron. That notation is rarely used, however, and the superscript "1" is almost always understood.

1.2b Electronic Configurations

We can now use the quantum numbers n, l, m_l, and s to write electronic descriptions, called configurations, for atoms using

what is known as the **aufbau principle** (*aufbau* is German for "building up" or "construction"). This principle simply makes the reasonable assumption that we should fill the available orbitals in order of their energies, starting with the lowest-energy orbital. To form these descriptions of neutral atoms, we add electrons until they are equal to the number of protons in the nucleus. Table 1.6 gives the electronic configurations of H, He, Li, Be, and B.

For carbon, the atom after boron in the periodic table, we have a choice to make in adding the last electron. The first five electrons are placed as in boron, but where does the sixth electron go? One possibility would be to put it in the same orbital as the fifth electron to produce the electronic configuration $_6C = 1s^2 2s^2 2p_x^2$ (Fig. 1.5a). In such an atom, the spins of the two electrons in the $2p_x$ orbital must be paired (opposite spins).
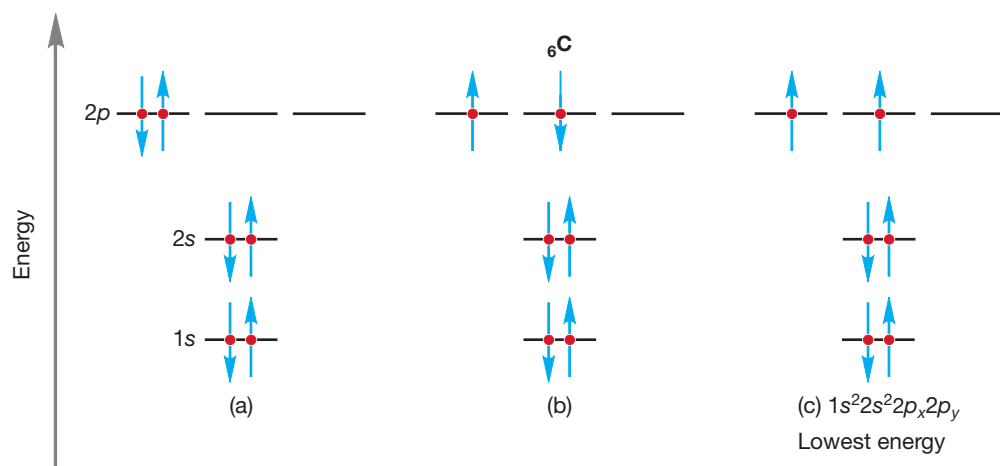
TABLE 1.6 Electronic Descriptions of Some Atoms

Atom	Electronic Configuration
$_1$H	$1s$
$_2$He	$1s^2$
$_3$Li	$1s^2 2s$
$_4$Be	$1s^2 2s^2$
$_5$B	$1s^2 2s^2 2p_x$

FIGURE 1.5   An application of Hund's rule. The electronic configuration with the largest number of parallel (same direction) spins is lowest in energy. Note use of the arrow convention to show electron spin.

WORKED PROBLEM 1.1 Explain why the two electrons in the $2p_x$ orbital of carbon ($_6C = 1s^2 2s^2 2p_x^2$) must have paired spins ($+1/2$ and $-1/2$).

ANSWER[6]   Because they are in the same orbital ($2p_x$), both electrons have the same values for the three quantum numbers n, l, and m_l ($n = 2$, $l = 1$, $m_l = +1, 0,$ or -1). If the spin quantum numbers were not opposite, one $+1/2$, the other $-1/2$, the two electrons would not be different from each other! The Pauli principle (no two electrons may have the same values of the four quantum numbers) ensures that two electrons in the same orbital must have different spin quantum numbers.

Alternatively, the sixth electron in the carbon atom could be placed in another $2p$ orbital to produce $_6C = 1s^2 2s^2 2p_x 2p_y$ (Fig. 1.5b). The only difference is the presence of two electrons in a *single* $2p$ orbital ($_6C = 1s^2 2s^2 2p_x^2$) in Figure 1.5a versus one electron in each of two *different* $2p$ orbitals ($_6C = 1s^2 2s^2 2p_x 2p_y$) in Figure 1.5b. The three $2p$ orbitals are of equal energy (because each has $n = 2$, $l = 1$), so how should we make this choice? Electron–electron repulsion would seem to make the second arrangement the better one, but there is still another consideration. When two electrons occupy different but equi-energetic orbitals, their spins can either be paired ($\uparrow\downarrow$) or unpaired ($\uparrow\uparrow$). **Hund's rule** (Friedrich Hund, 1896–1997) holds that for a given electron configuration, the state with the greatest number of unpaired

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[6]Worked Problems are answered in whole or in part in the text. When only part of a problem is worked, that part will have an asterisk. Complete answers can be found in the *Study Guide*.