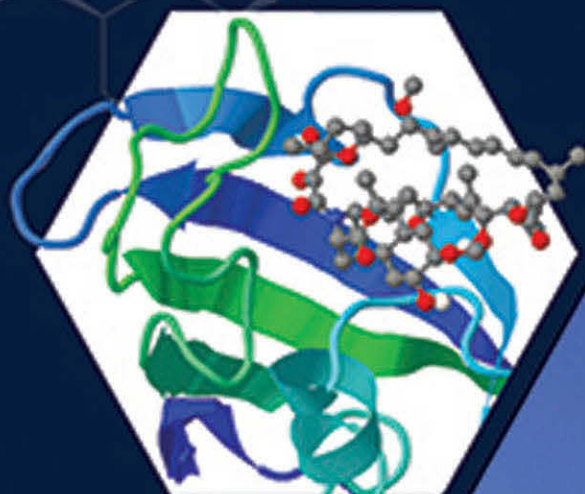


T. W. GRAHAM SOLOMONS

CRAIG B. FRYHLE

SCOTT A. SNYDER



ORGANIC CHEMISTRY

TWELFTH EDITION

WILEY

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PERIODIC TABLE OF THE ELEMENTS

1 IA		2 IIA												13 IIIA		14 IVA		15 VA		16 VIA		17 VIIA		18 VIIIA																																																										
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1 H Hydrogen 1.0079	2 He Helium 4.0026	3 Li Lithium 6.941	4 Be Beryllium 9.0122	11 Na Sodium 22.990	12 Mg Magnesium 24.305	19 K Potassium 39.098	20 Ca Calcium 40.078	37 Rb Rubidium 85.468	55 Cs Cesium 132.91	87 Fr Francium (223)	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.409	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.91	46 Pd Palladium 106.42	47 Ag Silver 107.87	48 Cd Cadmium 112.41	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.60	53 I Iodine 126.90	54 Xe Xenon 131.29	57 *La Lanthanum 138.91	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 173.04	71 *Lu Lutetium 174.97	88 Ra Radium (226)	89 #Ac Actinium (227)	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)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (266)	107 Bh Bohrium (264)	108 Hs Hassium (277)	109 Mt Meitnerium (268)	110 Ds Darmstadtium (281)	111 Rg Roentgenium (272)	112 Cn Copernicium (285)	113 Uut Uut (284)	114 Flerovium (289)	115 Uup Uup (288)	116 Lv Livermorium (293)	117 Uus Uus (294)	118 Uuo Uuo (294)

*Lanthanide Series

Actinide Series

TABLE 3.1 RELATIVE STRENGTH OF SELECTED ACIDS AND THEIR CONJUGATE BASES

	Acid	Approximate pK_a	Conjugate Base	
 Increasing acid strength	Strongest acid			Weakest base
	HSbF_6	< -12	SbF_6^-	
	HI	-10	I^-	
	H_2SO_4	-9	HSO_4^-	
	HBr	-9	Br^-	
	HCl	-7	Cl^-	
	$\text{C}_6\text{H}_5\text{SO}_3\text{H}$	-6.5	$\text{C}_6\text{H}_5\text{SO}_3^-$	
	$(\text{CH}_3)_2\text{OH}^+$	-3.8	$(\text{CH}_3)_2\text{O}$	
	$(\text{CH}_3)_2\text{C}=\text{OH}^+$	-2.9	$(\text{CH}_3)_2\text{C}=\text{O}$	
	$(\text{CH}_3)\text{OH}_2^+$	-2.5	CH_3OH	
	H_3O^+	-1.74	H_2O	
	HNO_3	-1.4	NO_3^-	
	$\text{CF}_3\text{CO}_2\text{H}$	0.18	CF_3CO_2^-	
	HF	3.2	F^-	
	$\text{C}_6\text{H}_5\text{CO}_2\text{H}$	4.21	$\text{C}_6\text{H}_5\text{CO}_2^-$	
	$\text{C}_6\text{H}_5\text{NH}_3^+$	4.63	$\text{C}_6\text{H}_5\text{NH}_2$	
	$\text{CH}_3\text{CO}_2\text{H}$	4.75	CH_3CO_2^-	
	H_2CO_3	6.35	HCO_3^-	
	$\text{CH}_3\text{COCH}_2\text{COCH}_3$	9.0	$\text{CH}_3\text{COCHCOCH}_3^-$	
	NH_4^+	9.2	NH_3	
	$\text{C}_6\text{H}_5\text{OH}$	9.9	$\text{C}_6\text{H}_5\text{O}^-$	
	HCO_3^-	10.2	CO_3^{2-}	
	CH_3NH_3^+	10.6	CH_3NH_2	
	H_2O	15.7	HO^-	
	$\text{CH}_3\text{CH}_2\text{OH}$	16	$\text{CH}_3\text{CH}_2\text{O}^-$	
	$(\text{CH}_3)_3\text{COH}$	18	$(\text{CH}_3)_3\text{CO}^-$	
	CH_3COCH_3	19.2	$^-\text{CH}_2\text{COCH}_3$	
	$\text{HC}\equiv\text{CH}$	25	$\text{HC}\equiv\text{C}^-$	
	$\text{C}_6\text{H}_5\text{NH}_2$	31	$\text{C}_6\text{H}_5\text{NH}^-$	
	H_2	35	H^-	
	$(i\text{-Pr})_2\text{NH}$	36	$(i\text{-Pr})_2\text{N}^-$	
	NH_3	38	$^-\text{NH}_2$	
$\text{CH}_2=\text{CH}_2$	44	$\text{CH}_2=\text{CH}^-$		
Weakest acid	CH_3CH_3	50	CH_3CH_2^-	Strongest base



 Increasing base strength

Organic Chemistry



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12e

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For Annabel and Ella. TWGS

For my mother and in memory of my father. CBF

For Cathy and Sebastian. SAS

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Library of Congress Cataloging-in-Publication Data

Names: Solomons, T. W. Graham, author. | Fryhle, Craig B. | Snyder, S. A. (Scott A.)

Title: Organic chemistry.

Description: 12th edition / T.W. Graham Solomons, Craig B. Fryhle, Scott A.

Snyder. | Hoboken, NJ : John Wiley & Sons, Inc., 2016. | Includes index.

Identifiers: LCCN 2015042208 | ISBN 9781118875766 (cloth)

Subjects: LCSH: Chemistry, Organic—Textbooks.

Classification: LCC QD253.2 .S65 2016 | DDC 547—dc23 LC record available at <http://lccn.loc.gov/2015042208>

ISBN 978-1-118-87576-6

Binder-ready version ISBN 978-1-119-07725-1

The inside back cover will contain printing identification and country of origin if omitted from this page. In addition, if the ISBN on the back cover differs from the ISBN on this page, the one on the back cover is correct.

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1



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ANSWERS TO SELECTED PROBLEMS can be found at www.wiley.com/college/solomons

EULA



Preface

“IT’S ORGANIC CHEMISTRY!”

That’s what we want students to exclaim after they become acquainted with our subject. Our lives revolve around organic chemistry, whether we all realize it or not. When we understand organic chemistry, we see how life itself would be impossible without it, how the quality of our lives depends upon it, and how examples of organic chemistry leap out at us from every direction. That’s why we can envision students enthusiastically exclaiming “It’s organic chemistry!” when, perhaps, they explain to a friend or family member how one central theme—organic chemistry—permeates our existence. We want to help students experience the excitement of seeing the world through an organic lens, and how the unifying and simplifying nature of organic chemistry helps make many things in nature comprehensible.

Our book makes it possible for students to learn organic chemistry well and to see the marvelous ways that organic chemistry touches our lives on a daily basis. Our book helps students develop their skills in **critical thinking**, **problem solving**, and **analysis**—skills that are so important in today’s world, no matter what career paths they choose. The richness of organic chemistry lends itself to solutions for our time, from the fields of health care, to energy, sustainability, and the environment. After all, it’s organic chemistry!

Energized by the power of organic chemistry and the goals of making our book an even more **efficient** and **relevant** tool for learning, we have made a number of important changes in this edition.

NEW TO THIS EDITION....

We share the same goals and motivations as our colleagues in wanting to give students the best experience that they can have in organic chemistry. We also share the challenges of deciding what students need to know and how the material should be organized. In that spirit, our reviewers and adopters have helped guide a number of the changes that we have made in this edition.

Simultaneously achieving efficiency and adding breadth We have redistributed and streamlined material from our old Chapter 21 about phenols, aryl halides, aryl ethers, benzyne, and nucleophilic aromatic substitution in a way that eliminates redundancy and places it in the context of other relevant material earlier in the book. At the same time, we wanted to update and add breadth to our book by creating a new *Chapter 21, Transition Metal Complexes* about transition metal organometallic compounds and their uses in organic synthesis. Previously, transformations like the Heck-Mizoroki, Suzuki-Miyaura, Stille, Sonogashira, and olefin metathesis reactions had only been part of a special topic in our book, but as the exposure of undergraduates to these processes has become more widespread, we felt it essential to offer instructors a chapter that they could incorporate into their course if they wished. Streamlining and redistributing the content in our old Chapter 21 allowed us to do this, and we thank our reviewers for helping to prompt this change.

Transition metal organometallic complexes: Promoters of key bond-forming reactions Our new Chapter 21 brings students a well-rounded and manageable introduction to transition metal organometallic complexes and their use in organic synthesis. We begin the chapter with an introduction to the structure and common mechanistic steps of reactions involving transition metal organometallic compounds. We then introduce the essentials of important cross-coupling reactions such as the Heck-Mizoroki, Suzuki-Miyaura, Stille, Sonogashira, dialkylcuprate (Gilman), and olefin metathesis reactions at a level that is practical and useful for undergraduates. We intentionally organized the chapter so that instructors could move directly to the practical applications of these important reactions if they desire, skipping general background information on transition metal complexes if they wished.

Aromatic efficiency Our coverage of aromatic substitution reactions (*Chapter 15*) has been refocused by making our presentation of electrophilic aromatic substitution more efficient at the same time as we included topics of nucleophilic aromatic substitution and benzyne that had

previously been in Chapter 21. Now all types of aromatic substitution reactions are combined in one chapter, with an enhanced flow that is exactly the same length as the old chapter solely on electrophilic aromatic reactions.

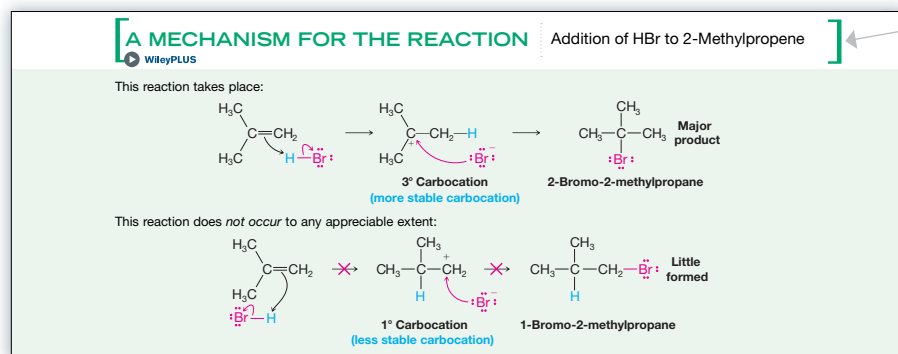
A focus on the practicalities of spectroscopy Students in an introductory organic chemistry course need to know how to use spectroscopic data to explore structure more than they need to understand the theoretical underpinnings of spectroscopy. To that end, we have shortened *Chapter 9, Nuclear Magnetic Resonance* by placing aspects of NMR instrumentation and theory in a new special topic that is a standalone option for instructors and students. At the same time, we maintain our emphasis on using spectroscopy to probe structure by continuing to introduce IR in *Chapter 2, Families of Carbon Compounds: Functional Groups, Intermolecular Forces, and Infrared (IR) Spectroscopy*, where students can learn to easily correlate functional groups with their respective infrared signatures and use IR data for problems in subsequent chapters.

Organizing nucleophilic substitution and elimination topics Some instructors find it pedagogically advantageous to present and assess their students' knowledge of nucleophilic substitution reactions before they discuss elimination reactions. Following the advice of some reviewers, we have adjusted the transition between *Chapters 6, Nucleophilic Reactions: Properties and Substitution Reactions of Alkyl Halides* and *7, Alkenes and Alkynes I: Properties and Synthesis; Elimination Reactions of Alkyl Halides* so that an instructor can pause cleanly after Chapter 6 to give an assessment on substitution, or flow directly into Chapter 7 on elimination reactions if they wish.

Synthesizing the Material The double entendre in the name of our new Synthesizing the Material problems is not lost in the ether. In this new group of problems, found at the end of Chapters 6-21, students are presented with either multistep synthetic transformations and unknown products, or target molecules whose precursors they must deduce by retrosynthetic analysis. Problems in our Synthesizing the Material groups often call upon reagents and transformations covered in prior chapters. Thus, while students work on synthesizing a chemical material, they are also synthesizing knowledge.

ONGOING PEDAGOGICAL STRENGTHS

Mechanisms: Showing How Reactions Work Student success in organic chemistry hinges on understanding mechanisms. We do all that we can to insure that our mechanism boxes contain every detail needed to help students learn and understand how reactions work. Over the years reviewers have said that our book excels in depicting clear and accurate mechanisms. This continues to be true in our 12th edition, and it is now augmented by animated mechanism videos found in WileyPLUS with ORION. We also use a **mechanistic approach** when introducing new reaction types so that students can understand the generalities and appreciate common themes. For example, our chapters on carbonyl chemistry are organized according to the mechanistic themes of nucleophilic addition, acyl substitution, and reactivity at the α -carbon. Mechanistic themes are also emphasized regarding alkene addition reactions, oxidation and reduction, and electrophilic aromatic substitution.



A MECHANISM FOR THE REACTION Stepped out reactions with just the right amount of detail provide the tools for students to understand rather than memorize reaction mechanisms.

Cementing knowledge by working problems: As athletes and musicians know, practice makes perfect. The same is true with organic chemistry. Students need to work all kinds of problems to learn chemistry. Our book has over 1400 in-text problems that students can use to cement their knowledge. **Solved Problems** help students learn where to begin. **Practice Problems** help them hone their skills and commit knowledge to memory. Many more problems at the end of each chapter help students reinforce their learning, focus on specific areas of content, and assess their overall skill level with that chapter's material. Learning Group Problems engage students in synthesizing information and concepts from throughout a chapter and can be used to facilitate collaborative learning in small groups, or serve as a culminating activity that demonstrates student mastery over an integrated set of principles. Supplementary material provided to instructors includes suggestions about how to orchestrate the use of learning groups. Hundreds more online problems are available through WileyPLUS with ORION, to help students target their learning and achieve mastery. Instructors can flip their classroom by doing in-class problem solving using Learning Group Problems, clicker questions, and other problems, while allowing our textbook and tutorial resources in WileyPlus to provide out of class learning.

SOLVED PROBLEMS

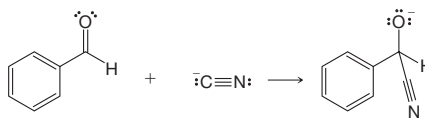
model problem solving strategies.

PRACTICE PROBLEMS

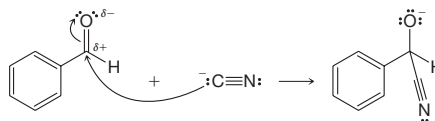
provides opportunities to check progress.

SOLVED PROBLEM 3.3

Identify the electrophile and the nucleophile in the following reaction, and add curved arrows to indicate the flow of electrons for the bond-forming and bond-breaking steps.



STRATEGY AND ANSWER: The aldehyde carbon is electrophilic due to the electronegativity of the carbonyl oxygen. The cyanide anion acts as a Lewis base and is the nucleophile, donating an electron pair to the carbonyl carbon, and causing an electron pair to shift to the oxygen so that no atom has more than an octet of electrons.



Use the curved-arrow notation to write the reaction that would take place between $(\text{CH}_3)_2\text{NH}$ and boron trifluoride. Identify the Lewis acid, Lewis base, nucleophile, and electrophile and assign appropriate formal charges.

PRACTICE PROBLEM 3.4

Laying the foundation earlier, getting to the heart of the matter quickly: Certain tools are absolutely key to success in organic chemistry. Among them is the ability to draw structural formulas quickly and correctly. In this edition, we help students learn these skills even sooner than ever before by moving coverage of structural formulas and the use of curved arrows earlier in the text (Section 3.2). We have woven together instruction about Lewis structures, covalent bonds, and dash structural formulas, so that students build their skills in these areas as a coherent unit, using organic examples that include alkanes, alkenes, alkynes, and alkyl halides. Similarly, Lewis and Brønsted-Lowry acid-base chemistry is fundamental to student success. We present a streamlined and highly efficient route to student mastery of these concepts in Chapter 3.

Increased emphasis on multistep synthesis: Critical thinking and analysis skills are key to problem solving and life. Multistep organic synthesis problems are perfectly suited to honing these skills. In this edition we introduce new *Synthesizing the Material* problems at the end of Chapters 6-21. These problems sharpen students' analytical skills in synthesis and retrosynthesis, and help them synthesize their knowledge by integrating chemical reactions that they have learned throughout the course.



A strong balance of synthetic methods Students need to learn methods of organic synthesis that are useful, as environmentally friendly as possible, and that are placed in the best overall contextual framework. As mentioned earlier, our new Chapter 21 gives mainstream coverage to reactions that are now essential to practicing organic chemists – transitional metal organometallic reactions. Other modern methods that we cover include the Jacobsen and Sharpless epoxidations (in *The Chemistry of...* boxes). In the 11th edition we incorporated the Swern oxidation (Section 12.4), long held as a useful oxidation method and one that provides a less toxic alternative to chromate oxidations in some cases. We also restored coverage of the Wolff-Kishner reduction (Section 16.8C) and the Baeyer-Villiger oxidation (Section 16.12), two methods whose importance has been proven by the test of time. The chemistry of radical reactions was also refocused and streamlined by reducing thermochemistry content and by centralizing the coverage of allylic and benzylic radical substitutions (including NBS reactions) in Chapter 10.

“Why do these topics matter?” is a feature that bookends each chapter with a teaser in the opener and a captivating example of organic chemistry in the closer. The chapter opener seeks to whet the student’s appetite both for the core chemistry in that chapter as well as hint at a prize that comes at the end of the chapter in the form of a *“Why do these topics matter?”* vignette. These closers consist of fascinating nuggets of organic chemistry that stem from research relating to medical, environmental, and other aspects of organic chemistry in the world around us, as well as the history of the science. They show the rich relevance of what students have learned to applications that have direct bearing on our lives and wellbeing. For example, in Chapter 6, the opener talks about some of the benefits and drawbacks of making substitutions in a recipe, and then compares such changes to the nucleophilic displacement reactions that similarly allow chemists to change molecules and their properties. The closer then shows how exactly such reactivity has enabled scientists to convert simple table sugar into the artificial sweetener Splenda which is 600 times as sweet, but has no calories!


Key Ideas as Bullet Points The amount of content covered in organic chemistry can be overwhelming to students. To help students focus on the most essential topics, key ideas are emphasized as bullet points in every section. In preparing bullet points, we have distilled appropriate concepts into simple declarative statements that convey core ideas accurately and clearly. No topic is ever presented as a bullet point if its integrity would be diminished by oversimplification, however.

“How to” Sections Students need to master important skills to support their conceptual learning. “How to” Sections throughout the text give step-by-step instructions to guide students in performing important tasks, such as using curved arrows, drawing chair conformations, planning a Grignard synthesis, determining formal charges, writing Lewis structures, and using ^{13}C and ^1H NMR spectra to determine structure.

The Chemistry of . . . Virtually every instructor has the goal of showing students how organic chemistry relates to their field of study and to their everyday life experience. The authors assist their colleagues in this goal by providing boxes titled *“The Chemistry of . . .”* that provide interesting and targeted examples that engage the student with chapter content.

Summary and Review Tools: At the end of each chapter, Summary and Review Tools provide visually oriented roadmaps and frameworks that students can use to help organize and assimilate concepts as they study and review chapter content. Intended to accommodate diverse learning styles, these include Synthetic Connections, Concept Maps, thematic Mechanism Review Summaries, and the detailed Mechanism for the Reaction boxes already mentioned. We also provide Helpful Hints and richly annotated illustrations throughout the text.

Special Topics: Instructors and students can use our Special Topics to augment their coverage in a number of areas. ^{13}C NMR can be introduced early in the course using the special topic that comes after Chapter 4 on the structure of alkanes and cycloalkanes. Polymer chemistry, now a required topic by the American Chemistry Society for certified bachelor degrees, can be covered in more depth than already presented in Chapters 10 and 17 by using the special topics that follow these chapters. Our special topic on electrocyclic and cycloaddition reactions can be used to augment students’ understanding of these reactions after their introduction to conjugated alkenes,



the Diels-Alder reaction, and aromatic compounds in Chapters 13-15. In-depth coverage of some topics in biosynthesis and natural products chemistry can be invoked using our special topics on biosynthesis and alkaloids.

ORGANIZATION—An Emphasis on the Fundamentals

So much of organic chemistry makes sense and can be generalized if students master and apply a few fundamental concepts. Therein lays the beauty of organic chemistry. If students learn the essential principles, they will see that memorization is not needed to succeed.

Most important is for students to have a solid understanding of structure—of hybridization and geometry, steric hindrance, electronegativity, polarity, formal charges, and resonance—so that they can make intuitive sense of mechanisms. It is with these topics that we begin in Chapter 1. In Chapter 2 we introduce the families of functional groups—so that students have a platform on which to apply these concepts. We also introduce intermolecular forces, and infrared (IR) spectroscopy—a key tool for identifying functional groups. Throughout the book we include calculated models of molecular orbitals, electron density surfaces, and maps of electrostatic potential. These models enhance students' appreciation for the role of structure in properties and reactivity.

We begin our study of mechanisms in the context of acid-base chemistry in Chapter 3. Acid-base reactions are fundamental to organic reactions, and they lend themselves to introducing several important topics that students need early in the course: (1) curved arrow notation for illustrating mechanisms, (2) the relationship between free-energy changes and equilibrium constants, and (3) the importance of inductive and resonance effects and of solvent effects.

In Chapter 3 we present the first of many “A Mechanism for the Reaction” boxes, using an example that embodies both Brønsted-Lowry and Lewis acid-base principles. All throughout the book, we use boxes like these to show the details of key reaction mechanisms. All of the Mechanism for the Reaction boxes are listed in the Table of Contents so that students can easily refer to them when desired.

A central theme of our approach is to emphasize the relationship between structure and reactivity. This is why we choose an organization that combines the most useful features of a functional group approach with one based on reaction mechanisms. Our philosophy is to emphasize mechanisms and fundamental principles, while giving students the anchor points of functional groups to apply their mechanistic knowledge and intuition. The structural aspects of our approach show students what organic chemistry is. Mechanistic aspects of our approach show students how it works. And wherever an opportunity arises, we show them what it does in living systems and the physical world around us.

In summary, our writing reflects the commitment we have as teachers to do the best we can to help students learn organic chemistry and to see how they can apply their knowledge to improve our world. The enduring features of our book have proven over the years to help students learn organic chemistry. The changes in our 12th edition make organic chemistry even more accessible and relevant. Students who use the in-text learning aids, work the problems, and take advantage of the resources and practice available in WileyPLUS with ORION (our online teaching and learning solution) will be assured of success in organic chemistry.

FOR ORGANIC CHEMISTRY

WileyPLUS with ORION

A Powerful Teaching and Learning Solution

WileyPLUS with ORION provides students with a personal, adaptive learning experience so they can build their proficiency on topics and use their study time most effectively. WileyPLUS with ORION helps students learn by working with them as their knowledge grows, by learning about them.

New To WileyPLUS with ORION for Organic Chemistry, 12e

Hallmark review tools in the print version of *Organic Chemistry* such as Concept Maps and Summaries of Reactions are also now interactive exercises that help students develop core skills and competencies

- New interactive Concept Map exercises
- New interactive Summary of Reactions exercises
- New interactive Mechanism Review exercises
- New video walkthroughs of key mechanisms

Summary of Alkene Addition Reactions

Reaction	Reaction Conditions	Electrophile	Nucleophile	Key Intermediates or Transition State	Regioselectivity	Stereochemistry of Addition	Product*
Hydrohalogenation Hydration (acid cat.)	$H-X$ Cat. H^+ , H_2O	H^+	X^-	Carbocation	Markovnikov	Not controlled	$R_1R_2C=CX + H_2O \rightarrow R_1R_2C(OH)X$ $Nu = X \text{ or } OH$
Halogenation Halohydrin Formation	X_2 (nonnucleophilic solvent) $E_2RCH_2E + H_2O$ (nucleophilic solvent)	X_2	H_2O	Cyclic Halonium Ion	Markovnikov	Anti	$R_1R_2C=CX_2 + H_2O \rightarrow R_1R_2C(OH)X_2$ $Nu = X \text{ or } OH$
Oxymercuration-Demercuration	(1) $Hg(OAc)_2, H_2O$ D.E. (E = H or C) (2) $NaBH_4, HO^-$	$Hg(OAc)_2$	H_2O	Mercurinium Ion	Markovnikov	Not controlled	$R_1R_2C=CX_2 + H_2O \rightarrow R_1R_2C(OH)X_2$ $Nu = X \text{ or } OH$
Hydroboration-Oxidation	(1) BH_3, THF (2) H_2O_2, HO^-	BH_3	H_2O_2	Organoborane	Anti-Markovnikov	Syn	$R_1R_2C=CX_2 + H_2O_2 \rightarrow R_1R_2C(OH)X_2$ $Nu = OH$
1,2-Dihydroxylation	(1) OsO_4 (2) $NaHSO_4$	OsO_4	$NaHSO_4$	Oscetone	Not applicable	Syn	$R_1R_2C=CX_2 + H_2O_2 \rightarrow R_1R_2C(OH)X_2$ $Nu = OH$

*The generic alkene shown has a substitution pattern that allows both regioselectivity and stereochemistry of the products to be discussed.

*The products are formed as a mixture of enantiomers in each case.

Summary of Alkene Addition Reactions

Reaction	Reaction Conditions	Electrophile	Nucleophile	Key Intermediates or Transition State	Regioselectivity	Stereochemistry of Addition	Product*
Hydrohalogenation	$H-X$	H^+	X^-	Carbocation	Markovnikov	Not controlled	$R_1R_2C=CX + H-X \rightarrow R_1R_2C(OH)X$ $Nu = X \text{ or } OH$
Hydration (acid cat.)	Cat. H^+ , H_2O	H^+	H_2O	Carbocation	Markovnikov	Not controlled	$R_1R_2C=CX + H_2O \rightarrow R_1R_2C(OH)X$ $Nu = X \text{ or } OH$
Halogenation (nonnucleophilic solvent)	X_2	X_2	H_2O	Cyclic Halonium Ion	Markovnikov	Anti	$R_1R_2C=CX_2 + H_2O \rightarrow R_1R_2C(OH)X_2$ $Nu = X \text{ or } OH$
Halohydrin Formation (nucleophilic solvent)	$E_2RCH_2E + H_2O$	X_2	H_2O	Cyclic Halonium Ion	Markovnikov	Anti	$R_1R_2C=CX_2 + H_2O \rightarrow R_1R_2C(OH)X_2$ $Nu = X \text{ or } OH$
Oxymercuration-Demercuration	(1) $Hg(OAc)_2, H_2O$ D.E. (E = H or C) (2) $NaBH_4, HO^-$	$Hg(OAc)_2$	H_2O	Mercurinium Ion	Markovnikov	Not controlled	$R_1R_2C=CX_2 + H_2O \rightarrow R_1R_2C(OH)X_2$ $Nu = X \text{ or } OH$
Hydroboration-Oxidation	(1) BH_3, THF (2) H_2O_2, HO^-	BH_3	H_2O_2	Organoborane	Anti-Markovnikov	Syn	$R_1R_2C=CX_2 + H_2O_2 \rightarrow R_1R_2C(OH)X_2$ $Nu = OH$
1,2-Dihydroxylation	(1) OsO_4 (2) $NaHSO_4$	OsO_4	$NaHSO_4$	Oscetone	Not applicable	Syn	$R_1R_2C=CX_2 + H_2O_2 \rightarrow R_1R_2C(OH)X_2$ $Nu = OH$

*The generic alkene shown has a substitution pattern that allows both regioselectivity and stereochemistry of the products to be discussed.

*The products are formed as a mixture of enantiomers in each case.

NEW INTERACTIVES: Interactive versions of Concept Maps, Synthetic Connections, and other review tools help students test their knowledge and develop core competencies.



Unique to ORION, students **begin** by taking a quick **diagnostic** for any chapter. This will determine each student's baseline proficiency on each topic in the chapter. Students see their individual diagnostic report to help them decide what to do next with the help of ORION's recommendations.



For each topic, students can either Study, or Practice. **Study** directs the students to the specific topic they choose in WileyPLUS, where they can read from the e-textbook, or use the variety of relevant resources available there. Students can also **practice**, using questions and feedback powered by ORION's adaptive learning engine. Based on the results of their diagnostic and ongoing practice, ORION will present students with questions appropriate for their current level of understanding, and will continuously adapt to each student, helping them build their proficiency.



ORION includes a number of reports and ongoing recommendations for students to help them maintain their proficiency over time for each topic. Students can easily access ORION from multiple places within WileyPLUS. It does not require any additional registration, and there will not be any additional charge for students using this adaptive learning system.

Breadth and Depth in Available Assessments: Four unique vehicles for assessment are available to instructors for creating online homework and quizzes and are designed to enable and support problem-solving skill development and conceptual understanding

WILEYPLUS ASSESSMENT FOR ORGANIC CHEMISTRY

REACTION EXPLORER

MEANINGFUL PRACTICE WITH MECHANISMS AND SYNTHESIS
(A DATABASE OF OVER 100,000 ALGORITHM-GENERATED PROBLEMS)

IN CHAPTER/EOC ASSESSMENT

90-100% OF REVIEW PROBLEMS AND END OF CHAPTER
QUESTIONS ARE CODED FOR ONLINE ASSESSMENT

CONCEPT MASTERY

PRE-BUILT CONCEPT MASTERY ASSIGNMENTS
(FROM A DATABASE OF OVER 25,000 QUESTIONS)

TEST BANK

RICH TESTBANK CONSISTING OF OVER 3,000 QUESTIONS

Reaction Explorer A student's ability to understand mechanisms and predict synthesis reactions greatly impacts her/his level of success in the course. Reaction Explorer is an interactive system for **learning and practicing reactions, syntheses and mechanisms** in organic chemistry with advanced support for the automatic generation of random problems and curved arrow mechanism diagrams.

MECHANISM EXPLORER:

valuable practice with reactions and mechanisms

SYNTHESIS EXPLORER:

meaningful practice doing single and multi-step synthesis

End of Chapter Problems. Approximately 90% of the end of chapter problems are included in WileyPLUS with ORION. Many of the problems are algorithmic and feature structure drawing/assessment functionality using MarvinSketch, with immediate answer feedback and video question assistance. A subset of these end of chapter problems is linked to **Guided Online tutorials** which are stepped-out problem-solving tutorials that walk the student through the problem, offering individualized feedback at each step.

Prebuilt concept mastery assignments Students must continuously practice and work organic chemistry in order to master the concepts and skills presented in the course. Prebuilt concept mastery assignments offer students ample opportunities for practice, covering all the major topics and concepts within an organic chemistry course. Each assignment is organized by topic and features **feedback for incorrect answers**. These assignments are drawn from a unique database of over 25,000 questions, over half of which require students to draw a structure using MarvinSketch.



What do students receive with WileyPLUS with ORION?

- The complete digital textbook, saving students up to 60% off the cost of a printed text.
- Question assistance, including links to relevant sections in the online digital textbook.
- Immediate feedback and proof of progress, 24/7.
- Integrated, multi-media resources that address your students' unique learning styles, levels of proficiency, and levels of preparation by providing multiple study paths and encourage more active learning.

WileyPLUS with ORION Student resources

Chapter 0 General Chemistry Refresher. To ensure students have mastered the necessary prerequisite content from general chemistry, and to eliminate the burden on instructors to review this material in lecture, WileyPLUS with ORION now includes a complete chapter of core general chemistry topics with corresponding assignments. Chapter 0 is available to students and can be assigned in WileyPLUS to ensure and gauge understanding of the core topics required to succeed in organic chemistry.

Prelecture Assignments. Preloaded and ready to use, these assignments have been carefully designed to assess students prior to their coming to class. Instructors can assign these pre-created quizzes to gauge student preparedness prior to lecture and tailor class time based on the scores and participation of their students.

Video Mini-Lectures, Office Hour Videos, and Solved Problem Videos In each chapter, several types of video assistance are included to help students with conceptual understanding and problem solving strategies. The video mini-lectures focus on challenging concepts; the office hours videos take these concepts and apply them to example problems, emulating the experience that a student would get if she or he were to attend office hours and ask for assistance in working a problem. The Solved Problem videos demonstrate good problems solving strategies for the student by walking through in text solved problems using audio and a whiteboard. The goal is to illustrate good problem solving strategies.

Skill Building Exercises are animated exercises with instant feedback to reinforce the key skills required to succeed in organic chemistry.


3D Molecular Visualizations use the latest visualization technologies to help students visualize concepts with audio. Instructors can assign quizzes based on these visualizations in WileyPLUS.

What do instructors receive with WileyPLUS with ORION?

- Reliable resources that reinforce course goals inside and outside of the classroom.
- The ability to easily identify students who are falling behind by tracking their progress and offering assistance easily, even before they come to office hours. Using WileyPLUS with ORION simplifies and automates such tasks as student performance assessment, creating assignments, scoring student work, keeping grades, and more.
- Media-rich course materials and assessment content that allow you to customize your classroom presentation with a wealth of resources and functionality from PowerPoint slides to a database of rich visuals. You can even add your own materials to your WileyPLUS with ORION course.

Additional Instructor Resources

All Instructor Resources are available within WileyPLUS with ORION or they can be accessed by contacting your local Wiley Sales Representative. Many of the assets are located on the book companion site, www.wiley.com/college/solomons



Test Bank Authored by Robert Rossi, of Gloucester County College, Jeffrey Allison, of Austin Community College, and Gloria Silva, of Carnegie Melon University.

PowerPoint Lecture slides PowerPoint Lecture Slides have been prepared by Professor William Tam, of the University of Guelph and his wife, Dr. Phillis Chang, and Gary Porter, of Bergen Community College.

Personal Response System (“Clicker”) Questions

Digital Image Library Images from the text are available online in JPEG format. Instructors may use these images to customize their presentations and to provide additional visual support for quizzes and exams.

ADDITIONAL STUDENT RESOURCES

Study Guide and Solutions Manual (Paperback: 978-1-119-07732-9; Binder-Ready: 978-1-119-07733-6)

The Study Guide and Solutions Manual for *Organic Chemistry, Twelfth Edition*, authored by Graham Solomons, Craig Fryhle, and Scott Snyder with prior contributions from Robert Johnson (Xavier University) and Jon Antilla (University of South Florida), **contains explained solutions to all of the problems in the text.** The Study Guide also contains:

- An introductory essay “Solving the Puzzle—or—Structure is Everything” that serves as a bridge from general to organic chemistry
- Summary tables of reactions by mechanistic type and functional group
- A review quiz for each chapter
- A set of hands-on molecular model exercises
- Solutions to problems in the Special Topics that are found with the text in WileyPLUS.

MOLECULAR VISIONS™ MODEL KITS

We believe that the tactile and visual experience of manipulating physical models is key to students’ understanding that organic molecules have shape and occupy space. To support our pedagogy, we have arranged with the Darling Company to bundle a special ensemble of Molecular Visions™ model kits with our book (for those who choose that option). We use Helpful Hint icons and margin notes to frequently encourage students to use hand-held models to investigate the three-dimensional shape of molecules we are discussing in the book.

CUSTOMIZATION AND FLEXIBLE OPTIONS TO MEET YOUR NEEDS

Wiley Custom Select allows you to create a textbook with precisely the content you want, in a simple, three-step online process that brings your students a cost-efficient alternative to a traditional textbook. Select from an extensive collection of content at <http://customselect.wiley.com>, upload your own materials as well, and select from multiple delivery formats—full color or black and white print with a variety of binding options, or eBook. Preview the full text online, get an instant price quote, and submit your order; we’ll take it from there.

WileyFlex offers content in flexible and cost-saving options to students. Our goal is to deliver our learning materials to our customers in the formats that work best for them, whether it’s a traditional text, eTextbook, WileyPLUS, loose-leaf binder editions, or customized content through Wiley Custom Select.

Acknowledgments

We are especially grateful to the following people who provided detailed reviews and participated in focus groups that helped us prepare this new edition of Organic Chemistry.

ARIZONA

Cindy Browder, *Northern Arizona University*
Tony Hascall, *Northern Arizona University*

ARKANSAS

Kenneth Carter, *University of Central Arkansas*
Sean Curtis, *University of Arkansas-Fort Smith*

CALIFORNIA

Thomas Bertolini, *University of Southern California*
Rebecca Broyer, *University of Southern California*
Paul Buonora, *California State University-Long Beach*
Steven Farmer, *Sonoma State University*
Andreas Franz, *University of the Pacific*
John Spence, *California State University Sacramento*
Daniel Wellman, *Chapman University*
Pavan Kadandale, *University of California Irvine*
Jianhua Ren, *University of the Pacific*
Harold (Hal) Rogers, *California State University Fullerton*
Liang Xue, *University of the Pacific*

CONNECTICUT

Andrew Karatjas, *Southern Connecticut State University*

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France-Isabelle Auzanneau, *University of Guelph*



Many people have helped with this edition, and we owe a great deal of thanks to each one of them. We thank Sean Hickey (*University of New Orleans*) for his reviews and assistance with aspects of WileyPlus. We are grateful to Alan Shusterman (*Reed College*) and Warren Hehre (Wavefunction, Inc.) for assistance in prior editions regarding explanations of electrostatic potential maps and other calculated molecular models. We would also like to thank those scientists who allowed us to use or adapt figures from their research as illustrations for a number of the topics in our book.

A book of this scope could not be produced without the excellent support we have had from many people at John Wiley and Sons, Inc. Joan Kalkut, Sponsoring Editor, led the project from the outset and provided careful oversight and encouragement through all stages of work on the 12th edition. We thank Nick Ferrari, Editor, for his guidance and support as well. Elizabeth Swain brought the book to print through her incredible skill in orchestrating the production process and converting manuscript to final pages. Photo Editor MaryAnn Price obtained photographs that so aptly illustrate examples in our book. Maureen Eide led development of the striking new design of the 12th edition. Alyson Rentrop coordinated work on the Study Guide and Solutions Manual as well as WileyPlus components. Mallory Fryc ensured coordination and cohesion among many aspects of this project, especially regarding reviews and supplements. Kristine Ruff enthusiastically and effectively helped tell the 'story' of our book to the many people we hope will consider using it. Without the support of Petra Recter, Vice President and Publisher, this book would not have been possible. We are thankful to all of these people and others behind the scenes at Wiley for the skills and dedication that they provided to bring this book to fruition.

TWGS with gratitude to my wife Judith for her continuing support. She joins me in dedicating this edition to our granddaughter, Ella, and her mother, Annabel.

CBF would like to thank Deanna, who has been a steadfast life partner since first studying chemistry together decades ago. He also thanks his daughter Heather for help with some chemical formulas. His mother, whose model of scholarly endeavors continues, and father, who shared many science-related tidbits, have always been inspirational.

SAS would like to thank his parents, his mentors, his colleagues, and his students for all that they have done to inspire him. Most of all, he would like to thank his wife Cathy for all that she does and her unwavering support.

T. W. GRAHAM SOLOMONS
CRAIG B. FRYHLE
SCOTT A. SNYDER



About the Authors

T. W. GRAHAM SOLOMONS did his undergraduate work at The Citadel and received his doctorate in organic chemistry in 1959 from Duke University where he worked with C. K. Bradsher. Following this he was a Sloan Foundation Postdoctoral Fellow at the University of Rochester where he worked with V. Boekelheide. In 1960 he became a charter member of the faculty of the University of South Florida and became Professor of Chemistry in 1973. In 1992 he was made Professor Emeritus. In 1994 he was a visiting professor with the Faculté des Sciences Pharmaceutiques et Biologiques, Université René Descartes (Paris V). He is a member of Sigma Xi, Phi Lambda Upsilon, and Sigma Pi Sigma. He has received research grants from the Research Corporation and the American Chemical Society Petroleum Research Fund. For several years he was director of an NSF-sponsored Undergraduate Research Participation Program at USF. His research interests have been in the areas of heterocyclic chemistry and unusual aromatic compounds. He has published papers in the *Journal of the American Chemical Society*, the *Journal of Organic Chemistry*, and the *Journal of Heterocyclic Chemistry*. He has received several awards for distinguished teaching. His organic chemistry textbooks have been widely used for 30 years and have been translated into French, Japanese, Chinese, Korean, Malaysian, Arabic, Portuguese, Spanish, Turkish, and Italian. He and his wife Judith have a daughter who is a building conservator and a son who is a research biochemist.

CRAIG BARTON FRYHLE is a Professor of Chemistry at Pacific Lutheran University where he served as Department Chair for roughly 15 years. He earned his B.A. degree from Gettysburg College and Ph.D. from Brown University. His experiences at these institutions shaped his dedication to mentoring undergraduate students in chemistry and the liberal arts, which is a passion that burns strongly for him. His research interests have been in areas relating to the shikimic acid pathway, including molecular modeling and NMR spectrometry of substrates and analogues, as well as structure and reactivity studies of shikimate pathway enzymes using isotopic labeling and mass spectrometry. He has mentored many students in undergraduate research, a number of who have later earned their Ph.D. degrees and gone on to academic or industrial positions. He has participated in workshops on fostering undergraduate participation in research, and has been an invited participant in efforts by the National Science Foundation to enhance undergraduate research in chemistry. He has received research and instrumentation grants from the National Science Foundation, the M J. Murdock Charitable Trust, and other private foundations. His work in chemical education, in addition to textbook coauthorship, involves incorporation of student-led teaching in the classroom and technology-based strategies in organic chemistry. He has also developed experiments for undergraduate students in organic laboratory and instrumental analysis courses. He has been a volunteer with the hands-on science program in Seattle public schools, and Chair of the Puget Sound Section of the American Chemical Society. His passion for climbing has led to ascents of high peaks in several parts of the world. He resides in Seattle with his wife, where both enjoy following the lives of their two daughters as they unfold in new ways and places.

SCOTT A. SNYDER grew up in the suburbs of Buffalo NY and was an undergraduate at Williams College, where he graduated summa cum laude in 1999. He pursued his doctoral studies at The Scripps Research Institute in La Jolla CA under the tutelage of K. C. Nicolaou as an NSF, Pfizer, and Bristol-Myers Squibb predoctoral fellow. While there, he co-authored the graduate textbook *Classics in Total Synthesis II* with his doctoral mentor. Scott was then an NIH postdoctoral fellow with E. J. Corey at Harvard University. In 2006, Scott began his independent career at Columbia University, moved to The Scripps Research Institute on their Jupiter FL campus in 2013, and in 2015 assumed his current position as Professor of Chemistry at the University of Chicago. His research interests lie in the arena of natural products total synthesis, particularly in the realm of unique polyphenols, alkaloids, and halogenated materials. To date, he has trained more than 60 students at the high school, undergraduate, graduate, and postdoctoral levels and co-authored more than 50 research and review articles. Scott has received a number of awards and honors, including a Camille and Henry Dreyfus New Faculty Award, an Amgen Young Investigator Award, an Eli Lilly Grantee Award, a Bristol-Myers Squibb Unrestricted Grant Award, an Alfred P. Sloan Foundation Fellowship, a DuPont Young Professor Award, and an Arthur C. Cope Scholar Award from the American Chemical Society. He has also received awards recognizing his teaching, including a Cottrell Scholar Award from the Research Corporation for Science Advancement. He lives in Chicago with his wife Cathy and son Sebastian where he enjoys gardening, cooking, cycling, and watching movies.

To the Student

Contrary to what you may have heard, organic chemistry does not have to be a difficult course. It will be a rigorous course, and it will offer a challenge. But you will learn more in it than in almost any course you will take—and what you learn will have a special relevance to life and the world around you. However, because organic chemistry can be approached in a logical and systematic way, you will find that with the right study habits, mastering organic chemistry can be a deeply satisfying experience. Here, then, are some suggestions about how to study:

1. Keep up with your work from day to day—never let yourself get behind.

Organic chemistry is a course in which one idea almost always builds on another that has gone before. It is essential, therefore, that you keep up with, or better yet, be a little ahead of your instructor. Ideally, you should try to stay one day ahead of your instructor's lectures in your own class preparations. Your class time, then, will be much more helpful because you will already have some understanding of the assigned material. Use WileyPlus study tools (Including ORION) to help with your pre-class learning.

2. Study material in small units, and be sure that you understand each new section before you go on to the next.

Again, because of the cumulative nature of organic chemistry, your studying will be much more effective if you take each new idea as it comes and try to understand it completely before you move on to the next concept.

3. Work all of the in-chapter and assigned problems.

One way to check your progress is to work each of the in-chapter problems when you come to it. These problems have been written just for this purpose and are designed to help you decide whether or not you understand the material that has just been explained. You should also carefully study the Solved Problems. If you understand a Solved Problem and can work the related in-chapter problem, then you should go on; if you cannot, then you should go back and study the preceding material again. Work all of the problems assigned by your instructor from the text and WileyPlus. A notebook for homework is helpful. When you go to your instructor for help, show her/him your attempted homework, either in written form or in WileyPlus online format.

4. Write when you study. Write the reactions, mechanisms, structures, and so on, over and over again. Organic chemistry is best assimilated through the fingertips by writing, and not through the eyes by simply looking, or by highlighting mate-

rial in the text, or by referring to flash cards. There is a good reason for this. Organic structures, mechanisms, and reactions are complex. If you simply examine them, you may think you understand them thoroughly, but that will be a misperception. The reaction mechanism may make sense to you in a certain way, but you need a deeper understanding than this. You need to know the material so thoroughly that you can explain it to someone else. This level of understanding comes to most of us (those of us without photographic memories) through writing. Only by writing the reaction mechanisms do we pay sufficient attention to their details, such as which atoms are connected to which atoms, which bonds break in a reaction and which bonds form, and the three-dimensional aspects of the structures. When we write reactions and mechanisms, connections are made in our brains that provide the long-term memory needed for success in organic chemistry. We virtually guarantee that your grade in the course will be directly proportional to the number of pages of paper that you fill with your own writing in studying during the term.

5. Learn by teaching and explaining. Study with your student peers and practice explaining concepts and mechanisms to each other. Use the Learning Group Problems and other exercises your instructor may assign as vehicles for teaching and learning interactively with your peers.

6. Use the answers to the problems in the Study Guide in the proper way.

Refer to the answers only in two circumstances: (1) When you have finished a problem, use the Study Guide to check your answer. (2) When, after making a real effort to solve the problem, you find that you are completely stuck, then look at the answer for a clue and go back to work out the problem on your own. The value of a problem is in solving it. If you simply read the problem and look up the answer, you will deprive yourself of an important way to learn.

7. Use molecular models when you study.

Because of the three-dimensional nature of most organic molecules, molecular models can be an invaluable aid to your understanding of them. When you need to see the three-dimensional aspect of a particular topic, use the Molecular Visions™ model set that may have been packaged with your textbook, or buy a set of models separately. An appendix to the *Study Guide* that accompanies this text provides a set of highly useful molecular model exercises.

8. Make use of the rich online teaching resources in WileyPLUS including ORION's adaptive learning system.

CHAPTER

1

The Basics

BONDING AND MOLECULAR STRUCTURE



Organic chemistry plays a role in all aspects of our lives, from the clothing we wear, to the pixels of our television and computer screens, to preservatives in food, to the inks that color the pages of this book. If you take the time to understand organic chemistry, to learn its overall logic, then you will truly have the power to change society. Indeed, organic chemistry provides the power to synthesize new drugs, to engineer molecules that can make computer processors run more quickly, to understand why grilled meat can cause cancer and how its effects can be combated, and to design ways to knock the calories out of sugar while still making food taste deliciously sweet. It can explain biochemical processes like aging, neural functioning, and cardiac arrest, and show how we can prolong and improve life. It can do almost anything.

IN THIS CHAPTER WE WILL CONSIDER:

- what kinds of atoms make up organic molecules
- the principles that determine how the atoms in organic molecules are bound together
- how best to depict organic molecules

[WHY DO THESE TOPICS MATTER?] At the end of the chapter, we will see how some of the unique organic structures that nature has woven together possess amazing properties that we can harness to aid human health. See

▶ **WileyPLUS** for additional examples, videos, and practice.

1.1 LIFE AND THE CHEMISTRY OF CARBON COMPOUNDS—WE ARE STARDUST



NASA/Photo Researchers, Inc.

Supernovae were the crucibles in which the heavy elements were formed.

Organic chemistry is the chemistry of compounds that contain the element carbon.

If a compound does not contain the element carbon, it is said to be *inorganic*.

Look for a moment at the periodic table inside the front cover of this book. More than a hundred elements are listed there. The question that comes to mind is this: why should an entire field of chemistry be based on the chemistry of compounds that contain this one element, carbon? There are several reasons, the primary one being this: **carbon compounds are central to the structure of living organisms and therefore to the existence of life on Earth. We exist because of carbon compounds.**

What is it about carbon that makes it the element that nature has chosen for living organisms? There are two important reasons: carbon atoms can form strong bonds to other carbon atoms to form rings and chains of carbon atoms, and carbon atoms can also form strong bonds to elements such as hydrogen, nitrogen, oxygen, and sulfur. Because of these bond-forming properties, carbon can be the basis for the huge diversity of compounds necessary for the emergence of living organisms.

From time to time, writers of science fiction have speculated about the possibility of life on other planets being based on the compounds of another element—for example, silicon, the element most like carbon. However, the bonds that silicon atoms form to each other are not nearly as strong as those formed by carbon, and therefore it is very unlikely that silicon could be the basis for anything equivalent to life as we know it.

1.1A What Is the Origin of the Element Carbon?

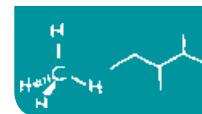
Through the efforts of physicists and cosmologists, we now understand much of how the elements came into being. The light elements hydrogen and helium were formed at the beginning, in the Big Bang. Lithium, beryllium, and boron, the next three elements, were formed shortly thereafter when the universe had cooled somewhat. All of the heavier elements were formed millions of years later in the interiors of stars through reactions in which the nuclei of lighter elements fuse to form heavier elements.

The energy of stars comes primarily from the fusion of hydrogen nuclei to produce helium nuclei. This nuclear reaction explains why stars shine. Eventually some stars begin to run out of hydrogen, collapse, and explode—they become supernovae. Supernovae explosions scatter heavy elements throughout space. Eventually, some of these heavy elements drawn by the force of gravity became part of the mass of planets like the Earth.

1.1B How Did Living Organisms Arise?

This question is one for which an adequate answer cannot be given now because there are many things about the emergence of life that we do not understand. However, we do know this. Organic compounds, some of considerable complexity, are detected in outer space, and meteorites containing organic compounds have rained down on Earth since it was formed. A meteorite that fell near Murchison, Victoria, Australia, in 1969 was found to contain over 90 different amino acids, 19 of which are found in living organisms on Earth. While this does not mean that life arose in outer space, it does suggest that events in outer space may have contributed to the emergence of life on Earth.

In 1924 Alexander Oparin, a biochemist at the Moscow State University, postulated that life on Earth may have developed through the gradual evolution of carbon-based molecules in a “primordial soup” of the compounds that were thought to exist on a prebiotic Earth: methane, hydrogen, water, and ammonia. This idea was tested by experiments carried out at the University of Chicago in 1952 by Stanley Miller and Harold Urey. They showed that amino acids and other complex organic compounds are synthesized when an electric spark (think of lightning) passes through a flask containing a mixture of these four compounds (think of the early atmosphere). Miller and Urey reported in their 1953 publication that five amino acids (essential constituents of proteins) were formed. In 2008, examination of archived solutions from Miller and Urey’s original experiments revealed that 22 amino acids, rather than the 5 amino acids originally reported, were actually formed.

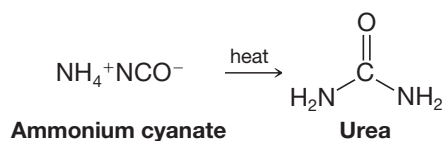


Similar experiments have shown that other precursors of biomolecules can also arise in this way—compounds such as ribose and adenine, two components of RNA. Some RNA molecules can not only store genetic information as DNA does, they can also act as catalysts, as enzymes do.

There is much to be discovered to explain exactly how the compounds in this soup became living organisms, but one thing seems certain. The carbon atoms that make up our bodies were formed in stars, so, in a sense, we are stardust.

1.1C Development of the Science of Organic Chemistry

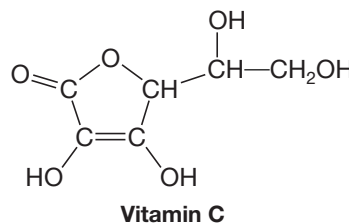
The science of organic chemistry began to flower with the demise of a nineteenth century theory called vitalism. According to vitalism, organic compounds were only those that came from living organisms, and only living things could synthesize organic compounds through intervention of a vital force. Inorganic compounds were considered those compounds that came from nonliving sources. Friedrich Wöhler, however, discovered in 1828 that an organic compound called urea (a constituent of urine) could be made by evaporating an aqueous solution of the inorganic compound ammonium cyanate. With this discovery, the synthesis of an organic compound, began the evolution of organic chemistry as a scientific discipline.



An RNA molecule

THE CHEMISTRY OF... Natural Products

Despite the demise of vitalism in science, the word “organic” is still used today by some people to mean “coming from living organisms” as in the terms “organic vitamins” and “organic fertilizers.” The commonly used term “organic food” means that the food was grown without the use of synthetic fertilizers and pesticides. An “organic vitamin” means to these people that the vitamin was isolated from a natural source and not synthesized by a chemist. While there are sound arguments to be made against using food contaminated with certain pesticides, while there may be environmental benefits to be obtained from organic farming, and while “natural” vitamins may contain beneficial substances not present in synthetic vitamins, it is impossible to argue that pure “natural” vitamin C, for example, is healthier than pure “synthetic” vitamin C, since the two substances are identical in all respects. In science today, the study of compounds from living organisms is called natural products chemistry. In the closer to this chapter we will consider more about why natural products chemistry is important.



Vitamin C is found in various citrus fruits.



FOODCOLLECTION/image Source

1.2 ATOMIC STRUCTURE

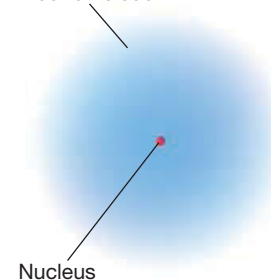
Before we begin our study of the compounds of carbon we need to review some basic but familiar ideas about the chemical elements and their structure.

- The **compounds** we encounter in chemistry are made up of **elements** combined in different proportions.
- **Elements** are made up of **atoms**. An atom (Fig. 1.1) consists of a dense, positively charged *nucleus* containing **protons** and **neutrons** and a surrounding cloud of **electrons**.

Each proton of the nucleus bears one positive charge; electrons bear one negative charge. Neutrons are electrically neutral; they bear no charge. Protons and neutrons have

FIGURE 1.1 An atom is composed of a tiny nucleus containing protons and neutrons and a large surrounding volume containing electrons. The diameter of a typical atom is about 10,000 times the diameter of its nucleus.

Electron cloud



Nucleus

nearly equal masses (approximately 1 atomic mass unit each) and are about 1800 times as heavy as electrons. Most of the **mass** of an atom, therefore, comes from the mass of the nucleus; the atomic mass contributed by the electrons is negligible. Most of the **volume** of an atom, however, comes from the electrons; the volume of an atom occupied by the electrons is about 10,000 times larger than that of the nucleus.

The elements commonly found in organic molecules are carbon, hydrogen, nitrogen, oxygen, phosphorus, and sulfur, as well as the halogens (fluorine, chlorine, bromine, and iodine).

Each **element** is distinguished by its **atomic number (Z)**, a **number equal to the number of protons in its nucleus**. Because an atom is electrically neutral, **the atomic number also equals the number of electrons surrounding the nucleus**.

1.2A Isotopes

Before we leave the subject of atomic structure and the periodic table, we need to examine one other observation: **the existence of atoms of the same element that have different masses**.

For example, the element carbon has six protons in its nucleus giving it an atomic number of 6. Most carbon atoms also have six neutrons in their nuclei, and because each proton and each neutron contributes one atomic mass unit (1 amu) to the mass of the atom, carbon atoms of this kind have a mass number of 12 and are written as ^{12}C .

- **Although all the nuclei of all atoms of the same element will have the same number of protons**, some atoms of the same element **may have different masses** because they have **different numbers of neutrons**. Such atoms are called **isotopes**.

For example, about 1% of the atoms of elemental carbon have nuclei containing 7 neutrons, and thus have a mass number of 13. Such atoms are written ^{13}C . A tiny fraction of carbon atoms have 8 neutrons in their nucleus and a mass number of 14. Unlike atoms of carbon-12 and carbon-13, atoms of carbon-14 are radioactive. The ^{14}C isotope is used in *carbon dating*. The three forms of carbon, ^{12}C , ^{13}C , and ^{14}C , are isotopes of one another.

Most atoms of the element hydrogen have one proton in their nucleus and have no neutron. They have a mass number of 1 and are written ^1H . A very small percentage (0.015%) of the hydrogen atoms that occur naturally, however, have one neutron in their nucleus. These atoms, called *deuterium* atoms, have a mass number of 2 and are written ^2H . An unstable (and radioactive) isotope of hydrogen, called *tritium* (^3H), has two neutrons in its nucleus.

● PRACTICE PROBLEM 1.1

There are two stable isotopes of nitrogen, ^{14}N and ^{15}N . How many protons and neutrons does each isotope have?

1.2B Valence Electrons

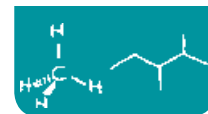
We discuss the electron configurations of atoms in more detail in Section 1.10. For the moment we need only to point out that the electrons that surround the nucleus exist in **shells** of increasing energy and at increasing distances from the nucleus. The most important shell, called the **valence shell**, is the outermost shell because the electrons of this shell are the ones that an atom uses in making chemical bonds with other atoms to form compounds.

- How do we know how many electrons an atom has in its valence shell? We look at the periodic table. The number of electrons in the valence shell (called **valence electrons**) is equal to the group number of the atom. For example, carbon is in group **IVA** and carbon has *four* valence electrons; oxygen is in group **VIA** and oxygen has *six* valence electrons. The halogens of group **VIIA** all have *seven* electrons.

● PRACTICE PROBLEM 1.2

How many valence electrons does each of the following atoms have?

(a) Na (b) Cl (c) Si (d) B (e) Ne (f) N



1.3 CHEMICAL BONDS: THE OCTET RULE

The first explanations of the nature of chemical bonds were advanced by G. N. Lewis (of the University of California, Berkeley) and W. Kössel (of the University of Munich) in 1916. Two major types of chemical bonds were proposed:

- 1. Ionic** (or electrovalent) bonds are formed by the transfer of one or more electrons from one atom to another to create ions.
- 2. Covalent** bonds result when atoms share electrons.

The central idea in their work on bonding is that atoms without the electronic configuration of a noble gas generally react to produce such a configuration because these configurations are known to be highly stable. For all of the noble gases except helium, this means achieving an octet of electrons in the valence shell.

- The **valence shell** is the outermost shell of electrons in an atom.
- The tendency for an atom to achieve a configuration where its valence shell contains eight electrons is called the **octet rule**.

The concepts and explanations that arise from the original propositions of Lewis and Kössel are satisfactory for explanations of many of the problems we deal with in organic chemistry today. For this reason we shall review these two types of bonds in more modern terms.

1.3A Ionic Bonds

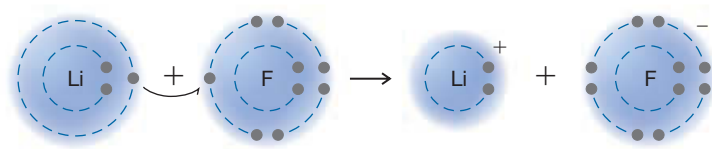
Atoms may gain or lose electrons and form charged particles called **ions**.

- An **ionic bond** is an attractive force between oppositely charged ions.

One source of such ions is a reaction between atoms of widely differing electronegativities (Table 1.1).

- **Electronegativity** is a measure of the ability of an atom to attract electrons.
- Electronegativity increases as we go across a horizontal row of the periodic table from left to right and it increases as we go up a vertical column (Table 1.1).

An example of the formation of an ionic bond is the reaction of lithium and fluorine atoms:



Lithium, a typical metal, has a very low electronegativity; fluorine, a nonmetal, is the most electronegative element of all. The loss of an electron (a negatively charged species)

[HELPFUL HINT]

Terms and concepts that are fundamentally important to your learning organic chemistry are set in bold blue type. You should learn them as they are introduced. These terms are also defined in the glossary.

[HELPFUL HINT]

We will use electronegativity frequently as a tool for understanding the properties and reactivity of organic molecules.

TABLE 1.1 ELECTRONEGATIVITIES OF SOME OF THE ELEMENTS

Increasing electronegativity →						
		H 2.1				
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8						Br 2.8

↑ Increasing electronegativity

by the lithium atom leaves a lithium cation (Li^+); the gain of an electron by the fluorine atom gives a fluoride anion (F^-).

- Ions form because atoms can achieve the electronic configuration of a noble gas by gaining or losing electrons.

The lithium cation with two electrons in its valence shell is like an atom of the noble gas helium, and the fluoride anion with eight electrons in its valence shell is like an atom of the noble gas neon. Moreover, crystalline lithium fluoride forms from the individual lithium and fluoride ions. In this process, negative fluoride ions become surrounded by positive lithium ions, and positive lithium ions by negative fluoride ions. In this crystalline state, the ions have substantially lower energies than the atoms from which they have been formed. Lithium and fluorine are thus “stabilized” when they react to form crystalline lithium fluoride. We represent the formula for lithium fluoride as LiF , because that is the simplest formula for this ionic compound.

Ionic substances, because of their strong internal electrostatic forces, are usually very high melting solids, often having melting points above 1000°C . In polar solvents, such as water, the ions are solvated (see Section 2.13D), and such solutions usually conduct an electric current.

- Ionic compounds, often called **salts**, form only when atoms of very different electronegativities transfer electrons to become ions.

● PRACTICE PROBLEM 1.3

Using the periodic table, which element in each pair is more electronegative?

- (a) Si, O (b) N, C (c) Cl, Br (d) S, P

1.3B Covalent Bonds and Lewis Structures

When two or more atoms of the same or similar electronegativities react, a complete transfer of electrons does not occur. In these instances the atoms achieve noble gas configurations by *sharing electrons*.

- **Covalent bonds** form by sharing of electrons between atoms of similar electronegativities to achieve the configuration of a noble gas.
- **Molecules** are composed of atoms joined exclusively or predominantly by covalent bonds.

Molecules may be represented by electron-dot formulas or, more conveniently, by formulas where each pair of electrons shared by two atoms is represented by a line.

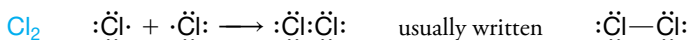
- A **dash structural formula** has lines that show bonding electron pairs and includes elemental symbols for the atoms in a molecule.

Some examples are shown here:

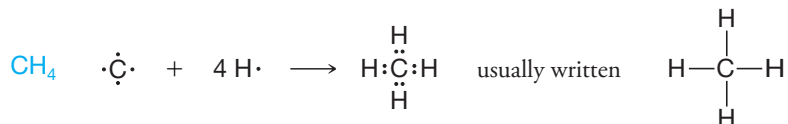
1. Hydrogen, being in group IA of the periodic table, has one valence electron. Two hydrogen atoms share electrons to form a hydrogen molecule, H_2 .

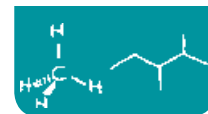


2. Because chlorine is in group VIIA, its atoms have seven valence electrons. Two chlorine atoms can share electrons (one electron from each) to form a molecule of Cl_2 .

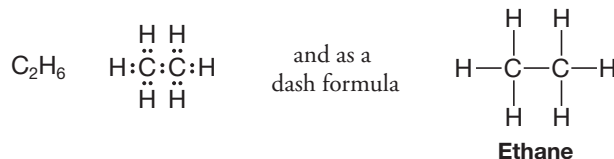


3. A carbon atom (group IVA) with four valence electrons can share each of these electrons with four hydrogen atoms to form a molecule of methane, CH_4 .



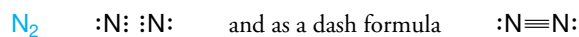


Two carbon atoms can use one electron pair between them to form a **carbon-carbon single bond** while also bonding hydrogen atoms or other groups to achieve an octet of valence electrons. Consider the example of ethane below.

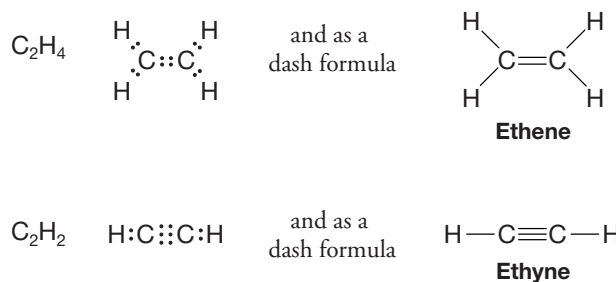


These formulas are often called **Lewis structures**; in writing them we show all of the valence electrons. Unshared electron pairs are shown as dots, and in dash structural formulas, bonding electron pairs are shown as lines.

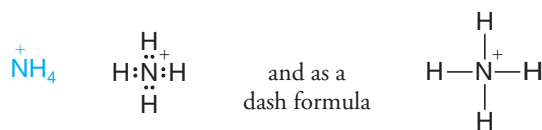
4. Atoms can share *two or more pairs of electrons* to form **multiple covalent bonds**. For example, two nitrogen atoms possessing five valence electrons each (because nitrogen is in group VA) can share electrons to form a **triple bond** between them.



Carbon atoms can also share more than one electron pair with another atom to form a multiple covalent bond. Consider the examples of a **carbon-carbon double bond** in ethene (ethylene) and a **carbon-carbon triple bond** in ethyne (acetylene).



5. Ions, themselves, may contain covalent bonds. Consider, as an example, the ammonium ion.



Consider the following compounds and decide whether the bond in them would be ionic or covalent.

- (a) KCl (b) F₂ (c) PH₃ (d) CBr₄

PRACTICE PROBLEM 1.4

1.4 HOW TO WRITE LEWIS STRUCTURES

Several simple rules allow us to draw proper Lewis structures:

- 1. Lewis structures show the connections between atoms in a molecule or ion using only the valence electrons of the atoms involved.** Valence electrons are those of an atom's outermost shell.
- 2. For main group elements, the number of valence electrons a neutral atom brings to a Lewis structure is the same as its group number in the periodic table.**

[HELPFUL HINT]

The ability to write proper **Lewis structures** is one of the most important tools for learning organic chemistry.

[HELPFUL HINT]

“HONC if you love organic chemistry,” as shown below, is a useful mnemonic to remember the typical number of electrons that hydrogen, oxygen, nitrogen, and carbon share with other atoms to reach a full octet; it also reflects the number of bonds that these atoms like to make in most organic molecules.

Hydrogen = 1 electron (or bond)

Oxygen = 2 electrons (or bonds)

Nitrogen = 3 electrons (or bonds)

Carbon = 4 electrons (or bonds)

Carbon, for example, is in group IVA and has four valence electrons; the halogens (e.g., fluorine) are in group VIIA and each has seven valence electrons; hydrogen is in group IA and has one valence electron.

3. If the structure we are drawing is a negative ion (an anion), we add one electron for each negative charge to the original count of valence electrons. If the structure is a positive ion (a cation), we subtract one electron for each positive charge.

4. In drawing Lewis structures we try to give each atom the electron configuration of a noble gas. To do so, we draw structures where atoms share electrons to form covalent bonds or transfer electrons to form ions.

a. Hydrogen forms one covalent bond by sharing its electron with an electron of another atom so that it can have two valence electrons, the same number as in the noble gas helium.

b. Carbon forms four covalent bonds by sharing its four valence electrons with four valence electrons from other atoms, so that it can have eight electrons (the same as the electron configuration of neon, satisfying the octet rule).

c. To achieve an octet of valence electrons, elements such as nitrogen, oxygen, and the halogens typically share only some of their valence electrons through covalent bonding, leaving others as unshared electron pairs. Nitrogen typically shares three electrons, oxygen two, and the halogens one.

The following problems illustrate the rules above.

SOLVED PROBLEM 1.1

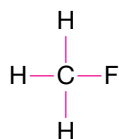
Write the Lewis structure of CH_3F .

STRATEGY AND ANSWER:

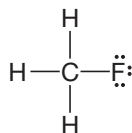
- 1.** We find the total number of valence electrons of all the atoms:

$$\begin{array}{cccc} 4 & + & 3(1) & + & 7 & = & 14 \\ \uparrow & & \uparrow & & \uparrow & & \\ \text{C} & & 3\text{H} & & \text{F} & & \end{array}$$

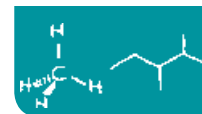
- 2.** We use pairs of electrons to form bonds between all atoms that are bonded to each other. We represent these bonding pairs with lines. In our example this requires four pairs of electrons (8 of the 14 valence electrons).



- 3.** We then add the remaining electrons in pairs so as to give each hydrogen 2 electrons (a duet) and every other atom 8 electrons (an octet). In our example, we assign the remaining 6 valence electrons to the fluorine atom in three non-bonding pairs.

**PRACTICE PROBLEM 1.5**

Write the Lewis structure of (a) CH_2F_2 (difluoromethane) and (b) CHCl_3 (chloroform).

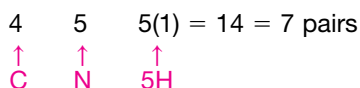


SOLVED PROBLEM 1.2

Write a Lewis structure for methylamine (CH_3NH_2).

STRATEGY AND ANSWER:

1. We find the total number of valence electrons for all the atoms.



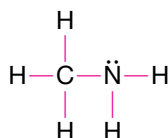
2. We use one electron pair to join the carbon and nitrogen.



3. We use three pairs to form single bonds between the carbon and three hydrogen atoms.

4. We use two pairs to form single bonds between the nitrogen atom and two hydrogen atoms.

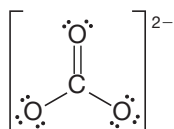
5. This leaves one electron pair, which we use as a lone pair on the nitrogen atom.



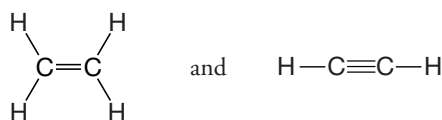
Write the Lewis structure of CH_3OH .

PRACTICE PROBLEM 1.6

5. If necessary, we use multiple bonds to satisfy the octet rule (i.e., give atoms the noble gas configuration). The carbonate ion (CO_3^{2-}) illustrates this:



The organic molecules ethene (C_2H_4) and ethyne (C_2H_2), as mentioned earlier, have a double and triple bond, respectively:

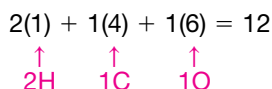


SOLVED PROBLEM 1.3

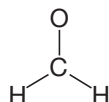
Write the Lewis structure of CH_2O (formaldehyde).

STRATEGY AND ANSWER:

1. Find the total number of valence electrons of all the atoms:



2. (a) Use pairs of electrons to form single bonds.



(continues on next page)