

NINTH EDITION

ORGANIC CHEMISTRY

BROWN | IVERSON | ANSLYN | FOOTE



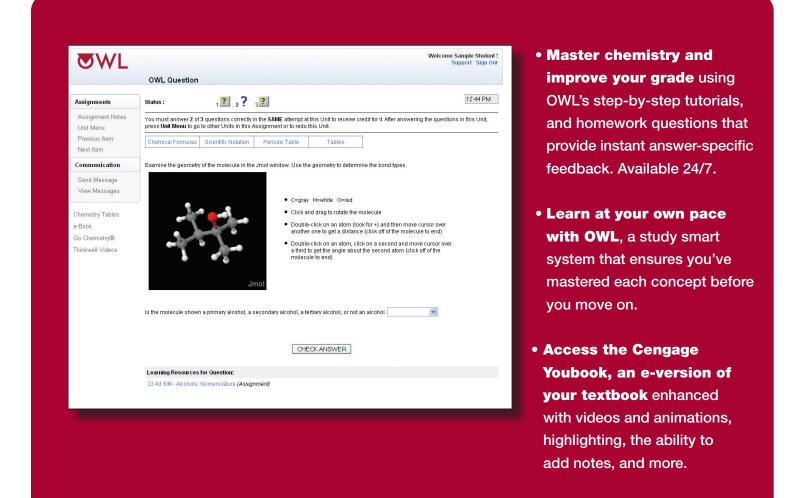
Some Important O	Some Important Organic Functional Groups	roups					
	Functional Group*	Example	IUPAC Name		Functional Group*	Example	IUPAC Name
Acid anhydride		O O CH ₃ COCCH ₃	Ethanoic anhydride (Acetic anhydride)	Carboxylic acid	H-Ö-2-	O CH ₃ COH	Ethanoic acid (Acetic acid)
	: Ö=		Ethanoyl chloride	Disulfide		$\mathrm{CH_3SSCH_3}$	Dimethyl disulfide
Acid chloride		CH ₃ CCI	(Acetyl chloride) Ethanol	Epoxide		H_2 C \longrightarrow C H_2	Oxirane (Ethylene oxide)
Alcohol	HO: O:	СН ₃ СН ₂ ОН О	(Ethyl alcohol)	7	—(· :(· Ö=(0=0	Methyl ethanoate
Aldehyde	—C—H	\mathbb{C}_{H_3} CH	Ethanal (Acetaldehyde)	Ester		CH3COCH3	(Meuly acetate)
Alkane		$\mathrm{CH_3CH_3}$	Ethane	Ettlet Haloalkane	 ::: <u>:</u>	CH_3CH_2CI	Chloroethane
					X = F, Cl, Br, I	ı	(Ethyl chloride)
Alkene	C = C	CH_2 = CH_2	Ethene (Ethylene)	Ketone	:	O CH.CCH.	Propanone (Acetone)
Alkyne	—D≡D—	НС≡СН	Ethyne (Acetylene)	Nitrile	—C≡N:	CH ₃ —C≡N	Ethanenitrile (Acetonitrile)
Amide	;Z- ;=: 	$\overset{\text{O}}{\underset{\text{CH}_3}{\parallel}}\text{CH}_2$	Ethanamide (Acetamide)	Nitro	Ö + 	$\mathrm{CH_3NO_2}$	Nitromethane
Amine, primary	$-\overset{\boldsymbol{\cdot}}{\overset{\boldsymbol{\cdot}}{\overset{\cdot}{\overset{\cdot}{\overset{\cdot}{\overset{\cdot}{\overset{\cdot}$	$\mathrm{CH_{3}CH_{2}NH_{2}}$	Ethylamine	Phenol	HO	но—	Phenol
Amine, secondary	NH-	$(\mathrm{CH_3CH_2})_2\mathrm{NH}$	Diethylamine	Sulfide		$\mathrm{CH_3SCH_3}$	Dimethyl sulfide
Amine, tertiary	 Z 	$(\mathrm{CH_3CH_2})_3\mathrm{N}$	Triethylamine	Thiol	H—————————————————————————————————————	$\mathrm{CH_{3}CH_{2}SH}$	Ethanethiol (Ethyl mercaptan)

^{*} Where bonds to an atom are not specified, the atom is assumed to be bonded to one or more carbon or hydrogen atoms in the rest of the molecule.



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Organic Chemistry

Ninth Edition

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Dedication

This Ninth Edition is dedicated to the memory of our dear friend and colleague, Christopher Foote. Chris's insights, encouragement, and dedication to this project can never be replaced. His kind and nurturing spirit lives on in all who are lucky enough to have known him.

About the Authors

William H. Brown taught chemistry at Beloit College, where he was twice named Teacher of the Year. His teaching responsibilities included organic chemistry, advanced organic chemistry, and special topics in pharmacology and drug synthesis. He received his PhD from Columbia University under the direction of Gilbert Stork and did postdoctoral work at the California Institute of Technology and the University of Arizona

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Christopher S. Foote received his PhD from Harvard University. His scholarly credits include Sloan Fellow; Guggenheim Fellow; ACS Baekland Award; ACS Cope Scholar; Southern California Section ACS Tolman Medal; President, American Society for Photobiology; and Senior Editor, *Accounts of Chemical Research*. He was a Professor of Chemistry at the University of California, Los Angeles.

Sheila A. Iverson received BA degrees in both Mathematics and Chemistry from the University of Oregon and a PhD in Chemistry from the California Institute of Technology. Her early work helped build the foundation for the protein engineering revolution, especially in the area of antibody therapeutics. Sheila shifted to patent law after moving to Austin, writing patents primarily in the biotechnology arena. Sheila and Brent have four grown daughters and one granddaughter.

Contents in Brief

Preface / xxix

Acknowledgments / xxxv

- 1. Covalent Bonding and Shapes of Molecules / 1
- 2. Alkanes and Cycloalkanes / 73
- 3. Stereoisomerism and Chirality / 130
- 4. Acids and Bases / 174
- 5. Alkenes: Bonding, Nomenclature, and Properties / 213
- **6.** Reactions of Alkenes / 237
- **7.** Alkynes / 298
- 8. Haloalkanes, Halogenation, and Radical Reactions / 338
- **9.** Nucleophilic Substitution and β -Elimination / 378
- **10.** Alcohols / 443
- 11. Ethers, Epoxides, and Sulfides / 498
- 12. Infrared Spectroscopy / 544
- 13. Nuclear Magnetic Resonance Spectroscopy / 567
- **14.** Mass Spectrometry / 615
- 15. An Introduction to Organometallic Compounds / 639
- **16.** Aldehydes and Ketones / 663
- 17. Carboxylic Acids / 739
- **18.** Functional Derivatives of Carboxylic Acids / 777
- 19. Enolate Anions and Enamines / 846
- 20. Dienes, Conjugated Systems, and Pericyclic Reactions / 921
- 21. Benzene and the Concept of Aromaticity / 968
- 22. Reactions of Benzene and Its Derivatives / 1027
- **23.** Amines / 1072
- 24. Catalytic Carbon-Carbon Bond Formation / 1131

- **25.** Carbohydrates / 1174
- **26.** Organic Polymer Chemistry / 1211





- **27.** Lipids / OL-1
- 28. Amino Acids and Proteins / OL-31
- 29. Nucleic Acids / OL-71

Appendices

- 1. Thermodynamics and the Equilibrium Constant / A-1
- 2. Major Classes of Organic Acids / A-2
- **3.** Bond Dissociation Enthalpies / A-3
- 4. Characteristic ¹H-NMR Chemical Shifts / A-4
- 5. Characteristic ¹³C-NMR Chemical Shifts / A-5
- **6.** Characteristic Infrared Absorption Frequencies / A-6
- 7. Electrostatic Potential Maps / A-7
- 8. Summary of Stereochemical Terms / A-8
- 9. Summary of the Rules of Nomenclature / A-11
- 10. Organic Chemistry Reaction Roadmaps / Insert

Glossary / G-1

Index / -1

Contents

Preface xxix

1

1.4

1.5

1.6

Ackr	nowledgments xxxv
Covo	lent Bonding and Shapes of Molecules 1
1.1	Electronic Structure of Atoms 2
1.2	Lewis Model of Bonding 7
	CAREERS IN CHEMISTRY Dahlia Haynes , Innovation Portfolio Manager and RDE Technical Leader, SC Johnson 12
	HOW TO: Quickly Figure Out Formal Charge 16
	HOW TO: Draw Lewis Structures from Condensed Structural Formulas 18
1.3	Functional Groups 20

Bond Angles and Shapes of Molecules 27

MCAT PRACTICE: PASSAGE AND QUESTIONS Fullerenes 30

Polar and Nonpolar Molecules 30

Quantum or Wave Mechanics 32

1.7	A Combined Valence Bond and Molecular Orbital Theory Approach to Covalent Bonding 36
	CONNECTIONS TO BIOLOGICAL CHEMISTRY Phosphoesters 44
	HOW TO: Quickly Recognize the Hybridization and Geometry of Atoms 49
1.8	Resonance 50
	HOW TO: Draw Curved Arrows and Push Electrons in Creating Contributing Structures 51
1.9	Molecular Orbitals for Delocalized Systems 56
	MCAT PRACTICE: PASSAGE AND QUESTIONS VSEPR and Resonance 60
1.10	Bond Lengths and Bond Strengths in Alkanes, Alkenes, and Alkynes 62
	PROBLEMS 63
Alkaı	nes and Cycloalkanes 73
2.1	The Structure of Alkanes 74
2.2	Constitutional Isomerism in Alkanes 76
	CAREERS IN CHEMISTRY Amy Rhoden Smith, Program Development Leader, Precision BioSciences 77
2.3	Nomenclature of Alkanes and the IUPAC System 78
2.4	Cycloalkanes 84
2.5	Conformations of Alkanes and Cycloalkanes 88
	HOW TO: Draw Alternative Chair Conformations of Cyclohexane 99
2.6	Cis, Trans Isomerism in Cycloalkanes and Bicycloalkanes 102
	HOW TO: Convert Planar Cyclohexanes to Chair Cyclohexanes 104
	MCAT PRACTICE: PASSAGE AND QUESTIONS Tetrodotoxin 110
2.7	Physical Properties of Alkanes and Cycloalkanes 111
2.8	Reactions of Alkanes 115
2.9	Sources and Importance of Alkanes 117
	CHEMICAL CONNECTIONS Octane Rating: What Those Numbers at the Pump Mean 119
	PROBLEMS 120
Stere	oisomerism and Chirality 130
3.1	Chirality—The Handedness of Molecules 131
3.2	Stereoisomerism 132
	HOW TO: Draw Chiral Molecules 134
0.0	CAREERS IN CHEMISTRY Tricia Johnson , Chemist, U.S. Food and Drug Administration 137
3.3	Naming Chiral Centers—The R,S System 138 CAREERS IN CHEMISTRY Eric Breitung, Research Scientist, New York Metropolitan Museum of Art 140
	HOW TO: Assign R or \$ Configuration to a Chiral Center 141
3.4	Acyclic Molecules with Two or More Stereocenters 142
	HOW TO: Quickly Draw and Recognize Enantiomers and Diastereomers 149

	3.5	Cyclic Molecules with Two or More Chiral Centers 149
	3.6	Tying All the Terminology Together 153
	3.7	Optical Activity—How Chirality Is Detected in the Laboratory 155
	3.8	The Significance of Chirality in the Biological World 159
		CONNECTIONS TO BIOLOGICAL CHEMISTRY Chiral Drugs 161
		MCAT PRACTICE: PASSAGE AND QUESTIONS Amino Acid Stereochemistry 161
	3.9	Separation of Enantiomers—Resolution 163
		PROBLEMS 166
4	Acids	and Bases 174
	4.1	Arrhenius Acids and Bases 175
	4.2	Brønsted-Lowry Acids and Bases 175
		CAREERS IN CHEMISTRY Baskar Nammalwar , Senior Scientist, Forge Therapeutics & Blacksmith Medicines 175
	4.3	Acid Dissociation Constants, pK_a , and the Relative Strengths of Acids and Bases 184
	4.4	The Position of Equilibrium in Acid-Base Reactions 186
		HOW TO: Calculate the Equilibrium Constants for Acid-Base Reactions 188
		CONNECTIONS TO BIOLOGICAL CHEMISTRY The Ionization of Functional Groups at Physiological pH 189
	4.5	Thermochemistry and Mechanisms of Acid-Base Reactions 191
	4.6	Molecular Structure and Acidity 196
		MCAT PRACTICE: PASSAGE AND QUESTIONS Acid-Base Equilibria 201
	4.7	Lewis Acids and Bases 201
		PROBLEMS 204
5	Alker	nes: Bonding, Nomenclature, and Properties 213
	5.1	Structure of Alkenes 215
		HOW TO: Calculate the Index of Hydrogen Deficiency 215
	5.2	Nomenclature of Alkenes 218
		CAREERS IN CHEMISTRY Ingrid Montes, Professor of Organic Chemistry, University of Puerto Rico 219
	5.3	Physical Properties of Alkenes 226
		CHEMICAL CONNECTIONS The Case of the Iowa and New York Strains of the European Corn Borer 226
	5.4	Naturally Occurring Alkenes—Terpene Hydrocarbons 227
		CONNECTIONS TO BIOLOGICAL CHEMISTRY The Importance of Cis Double Bonds in Fats Versus Oils 229
		PROBLEMS 230
6	Reac	tions of Alkenes 237
		14114 41 4 MINALINA AV

Reactions of Alkenes—An Overview 238

7

	6.2	Organic Reactions Involving Reactive Intermediates 239
		CAREERS IN CHEMISTRY Ryann Kress , Registered Nurse, Carilion Roanoke Memorial Hospital 242
	6.3	Terminology 242
	6.4	Electrophilic Additions 245
	6.5	Hydroboration-Oxidation 267
	6.6	Oxidation 271
		HOW TO: Write a Balanced Half-Reaction 274
	6.7	Reduction 277
		CONNECTIONS TO BIOLOGICAL CHEMISTRY Trans Fatty Acids: What They Are and How to Avoid Them 280
	6.8	Molecules Containing Chiral Centers as Reactants or Products 281
		PROBLEMS 286
7	Alkyn	nes 298
	7.1	Structure of Alkynes 299
	7.2	Nomenclature of Alkynes 300
	7.3	Physical Properties of Alkynes 302
	7.4	Acidity of 1-Alkynes 302
		CAREERS IN CHEMISTRY Ivy Tran, Technical Sales Representative, Arclin USA 302
	7.5	Preparation of Alkynes 303
	7.6	Reaction Mechanisms 307
	7.7	Electrophilic Addition to Alkynes 314
	7.8	Hydration of Alkynes to Aldehydes and Ketones 317
	7.9	Reduction of Alkynes 323
	7.10	Organic Synthesis 326
		PROBLEMS 330
8		ulkanes, Halogenation, and Radical Reactions 338
	8.1	Structure 339
	8.2	Nomenclature 339
	8.3	Physical Properties of Haloalkanes 341
	8.4	Preparation of Haloalkanes by Halogenation of Alkanes 345
		CAREERS IN CHEMISTRY Jonathan C. Trent, Associate Director for Clinical Research and the Director of the Bone and Soft-Tissue Sarcoma Group, Sylvester Comprehensive Cancer Center 345
	8.5	Mechanism of Halogenation of Alkanes 350
		CHEMICAL CONNECTIONS Freens 353
	8.6	Allylic Halogenation 358
	8.7	Radical Autoxidation 363

MCAT PRACTICE: PASSAGE AND QUESTIONS Antioxidants 365

8.8	Radical	Addition	of HBr to	o Alkenes	367
	PROBLE	ms 371			

9 Nucleoph	ilic Substitution	and β -Elimination	378
------------	-------------------	--------------------------	-----

- Nucleophilic Substitution in Haloalkanes 379 9.1
 - CAREERS IN CHEMISTRY Halimatu S. Mohammed, Technical Transfer Specialist, WuXi Advanced Therapies 380
- Mechanisms of Nucleophilic Aliphatic Substitution 381 9.2
- Experimental Evidence for S_N1 and S_N2 Mechanisms 386 9.3
- Analysis of Several Nucleophilic Substitution Reactions 403 9.4
- β -Elimination 406 9.5
- Mechanisms of β -Elimination 409 9.6
- Experimental Evidence for E1 and E2 Mechanisms 412 9.7
- Substitution Versus Elimination 419 9.8
- Analysis of Several Competitions Between Substitutions 9.9 and Eliminations 424
 - MCAT PRACTICE: PASSAGE AND QUESTIONS Solvents and Solvation 426
- Neighboring Group Participation 427 9.10

CONNECTIONS TO BIOLOGICAL CHEMISTRY Mustard Gases and the Treatment of Neoplastic Diseases 430

PROBLEMS 432

10 Alcohols 443

- Structure and Nomenclature of Alcohols 444
 - CAREERS IN CHEMISTRY Dana L. Broughton, Patent Attorney, GlaxoSmithKline 445
- 10.2 Physical Properties of Alcohols 447
 - CONNECTIONS TO BIOLOGICAL CHEMISTRY The Importance of Hydrogen Bonding in Drug-Receptor Interactions 449
- Acidity and Basicity of Alcohols 451 10.3
- Reaction of Alcohols with Active Metals 453 10.4
- Conversion of Alcohols to Haloalkanes and Sulfonates 454 10.5
- 10.6 Acid-Catalyzed Dehydration of Alcohols 462
- The Pinacol Rearrangement 468 10.7
 - MCAT PRACTICE: PASSAGE AND QUESTIONS Pinacol Rearrangement 471
- Oxidation of Alcohols 472 10.8
 - CHEMICAL CONNECTIONS Blood Alcohol Screening 476
 - CONNECTIONS TO BIOLOGICAL CHEMISTRY The Oxidation of Alcohols by NAD+
 - MCAT PRACTICE: PASSAGE AND QUESTIONS Alcohol Oxidations 482
- Thiols 483 10.9

PROBLEMS 488

11 Ethers, Epoxides, and Sulfides	498
-----------------------------------	-----

- 11.1 Structure of Ethers 499
- **11.2** Nomenclature of Ethers 499
- 11.3 Physical Properties of Ethers 501
 CAREERS IN CHEMISTRY Miriam Quintal, Managing Principal, Lewis-Burke Associates LLC 502
- **11.4** Preparation of Ethers 503
- 11.5 Reactions of Ethers 508
- 11.6 Silyl Ethers as Protecting Groups 511
- 11.7 Epoxides: Structure and Nomenclature 514
- **11.8** Synthesis of Epoxides 515
- 11.9 Reactions of Epoxides 521

MCAT PRACTICE: PASSAGE AND QUESTIONS Benzo[a]pyrene 525

- **11.10** Ethylene Oxide and Epichlorohydrin: Building Blocks in Organic Synthesis 527
- 11.11 Crown Ethers 529
- **11.12** Sulfides 530

PROBLEMS 533

12 Infrared Spectroscopy 544

- **12.1** Electromagnetic Radiation 545
- **12.2** Molecular Spectroscopy 546
- **12.3** Infrared Spectroscopy 547

CAREERS IN CHEMISTRY LaShonda T. Cureton, Lead Chemist, U.S. Food and Drug Administration 547

- **12.4** Interpreting Infrared Spectra 554
- **12.5** Solving Infrared Spectral Problems 563

PROBLEMS 564

13 Nuclear Magnetic Resonance Spectroscopy 567

13.1 Nuclear Spin States 568

CAREERS IN CHEMISTRY Sathish Kumar Lageshetty, Senior Scientist, CHASM Advanced Materials, Inc. 568

- **13.2** Orientation of Nuclear Spins in an Applied Magnetic Field 569
- **13.3** Nuclear Magnetic "Resonance" 571
- **13.4** An NMR Spectrometer 573
- **13.5** Equivalent Hydrogens 575
- **13.6** Signal Areas *578*
- **13.7** Chemical Shift 579

- **13.8** Signal Splitting and the (n + 1) Rule 584
- **13.9** The Origins of Signal Splitting 586
- **13.10** Stereochemistry and Topicity 594

CHEMICAL CONNECTIONS Magnetic Resonance Imaging 597

- 13.11 13C-NMR 598
- 13.12 Interpretation of NMR Spectra 600

HOW TO: Solve NMR Spectral Problems 603

PROBLEMS 606

14 Mass Spectrometry 615

- **14.1** A Mass Spectrometer 616
- **14.2** Features of a Mass Spectrum 619

CAREERS IN CHEMISTRY RaiAnna Arscott Hopson, Scientist, AMVAC Chemical Corp 620

14.3 Interpreting Mass Spectra 623

CONNECTIONS TO BIOLOGICAL CHEMISTRY Mass Spectrometry of Biological Macromolecules 631

14.4 Mass Spectrometry in the Organic Synthesis Laboratory and Other Applications 633

PROBLEMS 634

15 An Introduction to Organometallic Compounds 639

- **15.1** Organomagnesium and Organolithium Compounds 640 CAREERS IN CHEMISTRY **Kevin Meraz**, Senior Scientist, PDD Inc. 643
- 15.2 Lithium Diorganocopper (Gilman) Reagents 646
- **15.3** Carbenes and Carbenoids 650

MCAT PRACTICE: PASSAGE AND QUESTIONS Inorganic Coordination Compounds 655

PROBLEMS 656

16 Aldehydes and Ketones 663

16.1 Structure and Bonding 664

CAREERS IN CHEMISTRY Weijun Niu, Research Associate, Corning 664

- **16.2** Nomenclature 664
- **16.3** Physical Properties 669
- **16.4** Reactions 670
- **16.5** Addition of Carbon Nucleophiles 672
- **16.6** The Wittig Reaction 679
- **16.7** Addition of Oxygen Nucleophiles 684

	16.8	Addition of Nitrogen Nucleophiles 694
		MCAT PRACTICE: PASSAGE AND QUESTIONS Pyridoxine (Vitamin B ₆): A Carrier of Amino Groups 698
	16.9	Keto-Enol Tautomerism 700
	16.10	Oxidation 705
	16.11	Reduction 708
		CONNECTIONS TO BIOLOGICAL CHEMISTRY NADH: The Biological Equivalent of a Hydride Reducing Agent 713
		HOW TO: Retrosynthetically Dissect an Amine into the Proper Starting Materials for a Reductive Amination 714
	16.12	Reactions at an α -Carbon 718
		PROBLEMS 721
17	Carbo	oxylic Acids 739
	1 7. 1	Structure 740
	17.2	Nomenclature 740
		CAREERS IN CHEMISTRY James Mack, Professor of Chemistry, University of Cincinnati 741
	17.3	Physical Properties 744
		CHEMICAL CONNECTIONS From Willow Bark to Aspirin and Beyond 745
	17.4	Acidity 747
	17.5	Preparation of Carboxylic Acids 752
	17.6	Reduction 752
		CHEMICAL CONNECTIONS Industrial Synthesis of Acetic Acid—Transition Metal Catalysis 753
	17.7	Esterification 755
		CHEMICAL CONNECTIONS Esters as Flavoring Agents 757
	17.8	Conversion to Acid Chlorides 758
		MCAT PRACTICE: PASSAGE AND QUESTIONS Permethrin and Bifenthrin 760
	17.9	Decarboxylation 761
		CONNECTIONS TO BIOLOGICAL CHEMISTRY Ketone Bodies and Diabetes Mellitus 763
		PROBLEMS 765
10	E	ional Devicestives of Carbonalis Asido 777
10		ional Derivatives of Carboxylic Acids 777 Structure and Nomenclature 778
	18.1	
		CHEMICAL CONNECTIONS From Cocaine to Procaine and Beyond 781 CHEMICAL CONNECTIONS From Moldy Clover to a Blood Thinner 782
	18.2	Acidity of Amides, Imides, and Sulfonamides 784
	10.4	CONNECTIONS TO BIOLOGICAL CHEMISTRY The Unique Structure of Amide Bonds 786
	18.3	Characteristic Reactions 787
	18.4	Carboxylic Acid Derivative Reaction Mechanisms 791
	10.7	Carboxyne / Cla Delivative Reaction / Mechanisms / / I

		CAREERS IN CHEMISTRY Shelbie Shelder , Family Medicine Doctor and Resident Physician, Seattle Indian Health Board and Swedish First Hill Hospital 791				
	18.5	Reaction with Water: Hydrolysis 795				
		CHEMICAL CONNECTIONS Mechanistic Alternatives for Ester Hydrolysis: S _N 2 and S _N 1 Possibilities 803				
	18.6	Reaction with Alcohols 809				
	18.7	Reactions with Ammonia and Amines 813				
	18.8 Reaction of Acid Chlorides with Salts of Carboxylic Acids 816					
	18.9	Interconversion of Functional Derivatives 816				
		MCAT PRACTICE: PASSAGE AND QUESTIONS β-Lactam Antibiotics 817				
	18.10	Reactions with Organometallic Compounds 819				
	18.11	Reduction 823				
		PROBLEMS 829				
19	Enola	te Anions and Enamines 846				
	19.1 Formation and Reactions of Enolate Anions: An Overview 847					
	19.2	Aldol Reaction 849				
		CAREERS IN CHEMISTRY Rami Abu-Aita, Chief Medical Physicist, SSM Health for the South Central Wisconsin region 849				
19.3 Claisen and Dieckmann Condensations 858						
19.4 Claisen and Aldol Condensations in the Biological World 865						
		CHEMICAL CONNECTIONS Drugs That Lower Plasma Levels of Cholesterol 866				
	19.5	Enamines 868				
	19.6	Acetoacetic Ester Synthesis 873				
	19.7	Malonic Ester Synthesis 878				
	19.8 Conjugate Addition to α, β -Unsaturated Carbonyl Compounds 882					
	19.9	Crossed Enolate Reactions Using LDA 892				
		MCAT PRACTICE: PASSAGE AND QUESTIONS Ibuprofen: The Evolution of an Industrial Synthesis 897				
		PROBLEMS 899				
20	Diene	es, Conjugated Systems, and Pericyclic Reactions 921				
	20.1	Stability of Conjugated Dienes 922				
		CAREERS IN CHEMISTRY Paul Cunningham , Small Animal Emergency Veterinarian Animal Emergency Centre Pty Ltd. 923				
	20.2	Electrophilic Addition to Conjugated Dienes 926				
	20.3	UV-Visible Spectroscopy 933				
		CHEMICAL CONNECTIONS Curry and Cancer 939				
	20.4	Pericyclic Reaction Theory 939				
	20.5	The Diels-Alder Reaction 942				
	20.6	Sigmatropic Shifts 952				

PROBLEMS 958

21	Benzene and	the	Concept of	Aromaticity	968
----	-------------	-----	------------	-------------	-----

- **21.1** The Structure of Benzene 969
 - CAREERS IN CHEMISTRY Chinenyeze Nwankwoala, Senior Chemist, Ascend Performance Materials 969
- **21.2** The Concept of Aromaticity 974
 - HOW TO: Recognize Aromatic Compounds: Criteria and Caveats 986
- 21.3 Nomenclature 986
- **21.4** Phenols 990
 - MCAT PRACTICE: PASSAGE AND QUESTIONS Capsaicin, "Some Like It Hot" 996
- **21.5** Reactions at a Benzylic Position 1001
 - PROBLEMS 1006

22 Reactions of Benzene and Its Derivatives 1027

- **22.1** Electrophilic Aromatic Substitution 1028
 - CAREERS IN CHEMISTRY Goupu Touthang, Research Chemist, MECS Sulfuric Acid and Environmental Technologies 1028
- 22.2 Disubstitution and Polysubstitution 1041
- **22.3** Nucleophilic Aromatic Substitution 1050
 - PROBLEMS 1055

23 Amines 1072

- 23.1 Structure and Classification 1073
- **23.2** Nomenclature 1074
 - CAREERS IN CHEMISTRY **Brent Dial**, Research Scientist: Organic Chemist, Oak Ridge National Laboratory 1075
- 23.3 Chirality of Amines and Quaternary Ammonium Ions 1078
- **23.4** Physical Properties 1079
 - CHEMICAL CONNECTIONS The Poison Dart Frogs of South America 1080
- **23.5** Basicity 1081
 - MCAT PRACTICE: PASSAGE AND QUESTIONS The Planarity of —NH₂ Groups on Heterocyclic Rings 1086
- 23.6 Reactions with Acids 1090
- **23.7** Preparation 1094
- 23.8 Reaction with Nitrous Acid 1097
- **23.9** Hofmann Elimination 1108
- **23.10** Cope Elimination 1111
 - PROBLEMS 1113

24 Catalytic Carbon-Carbon Bond Formation 1131

24.1 Carbon-Carbon Bond-Forming Reactions from Earlier Chapters 1132

CAREERS IN CHEMISTRY **Arnie R. de Leon**, Senior Process Development Group Leader, Nitto Denko Avecia Inc. 1132

	24.2	Organometallic Compounds and Catalysis 1133							
	24.3	The Heck Reaction 1134							
	24.4	Catalytic Allylic Alkylation 1141							
	24.5	Palladium-Catalyzed Cross-Coupling Reactions 1145							
	24.6								
	24.7	Click Chemistry 1155							
		PROBLEMS 1157							
25	25 Carbohydrates 1174								
	25.1								
		CAREERS IN CHEMISTRY Luis Ernesto Miramontes Cárdenas, Chemist 1180							
	25.2	The Cyclic Structure of Monosaccharides 1181							
		CHEMICAL CONNECTIONS L-Ascorbic Acid (Vitamin C) 1184							
	25.3	5.3 Reactions of Monosaccharides 1186							
		CHEMICAL CONNECTIONS Testing for Glucose 1193							
	MCAT PRACTICE: PASSAGE AND QUESTIONS Fucose 1194								
	25.4 Disaccharides and Oligosaccharides 1195								
	CHEMICAL CONNECTIONS A, B, AB, and O Blood Group Substances 1198								
25.5 Polysaccharides 1199									
		CHEMICAL CONNECTIONS High-Fructose Corn Syrup 1201							
	25.6	3 /							
		PROBLEMS 1203							
26	Orga	nic Polymer Chemistry 1211							
	26.1	The Architecture of Polymers 1212							
	26.2	Polymer Notation and Nomenclature 1213							
		CAREERS IN CHEMISTRY Percy Lavon Julian, Director, Julian Laboratories 1214							
	26.3 Molecular Weights of Polymers 1215								
	26.4	Polymer Morphology—Crystalline Versus Amorphous Materials 1215							
	26.5	Step-Growth Polymerizations 1217							
		CHEMICAL CONNECTIONS Stitches That Dissolve 1224							
	26.6	Chain-Growth Polymerizations 1225							
		CHEMICAL CONNECTIONS Organic Polymers That Conduct Electricity 1229							
		MCAT PRACTICE: PASSAGE AND QUESTIONS The Chemistry of Superglue 1237							
		CHEMICAL CONNECTIONS Recycling of Plastics 1242							
		PROBLEMS 1244							



27 Lipids OL-1

- Find these chapters online.
- **27.1** Triglycerides OL-2
- **27.2** Soaps and Detergents OL-5

CONNECTIONS TO BIOLOGICAL CHEMISTRY FAD/FADH₂: Agents for Electron Transfer in Biological Oxidation-Reductions: Fatty Acid Oxidation OL-7

- 27.3 Prostaglandins OL-9
- **27.4** Steroids OL-11
- 27.5 Phospholipids OL-16

CHEMICAL CONNECTIONS Snake Venom Phospholipases OL-17

27.6 Fat-Soluble Vitamins OL-18

MCAT PRACTICE: PASSAGE AND QUESTIONS Vitamin K, Blood Clotting, and Basicity OL-21

PROBLEMS OL-25

28 Amino Acids and Proteins OL-31

- 28.1 Amino Acids OL-31
- 28.2 Acid-Base Properties of Amino Acids OL-35
- 28.3 Polypeptides and Proteins OL-40
- **28.4** Primary Structure of Polypeptides and Proteins OL-41
- **28.5** Synthesis of Polypeptides OL-48
- **28.6** Three-Dimensional Shapes of Polypeptides and Proteins OL-53

CHEMICAL CONNECTIONS Spider Silk OL-57

PROBLEMS OL-64

29 Nucleic Acids OL-71

- 29.1 Nucleosides and Nucleotides OL-72
- 29.2 The Structure of DNA OL-74

CHEMICAL CONNECTIONS The Search for Antiviral Drugs OL-77

29.3 Ribonucleic Acids OL-81

CHEMICAL CONNECTIONS The Fountain of Youth OL-82

- 29.4 The Genetic Code OL-84
- 29.5 Sequencing Nucleic Acids OL-86

CHEMICAL CONNECTIONS DNA Fingerprinting OL-90

PROBLEMS OL-94

Appendices:

- 1. Thermodynamics and the Equilibrium Constant A-1
- 2. Major Classes of Organic Acids A-2
- 3. Bond Dissociation Enthalpies A-3
- 4. Characteristic ¹H-NMR Chemical Shifts A-4
- 5. Characteristic ¹³C-NMR Chemical Shifts A-5
- 6. Characteristic Infrared Absorption Frequencies A-6
- 7. Electrostatic Potential Maps A-7
- 8. Summary of Stereochemical Terms A-8
- 9. Summary of the Rules of Nomenclature A-11
- 10. Organic Chemistry Reaction Roadmaps Insert

Glossary G-1

Index I-1

List of Mechanisms

Chapter 6 Reactions of Alkenes

- 6.1 Electrophilic Addition of HBr to 2-Butene (Section 6.4A)
- 6.2 Acid-Catalyzed Hydration of Propene (Section 6.4B)
- 6.3 Carbocation Rearrangement in the Addition of HCl to an Alkene (Section 6.4C)
- 6.4 Addition of Bromine with Anti Stereoselectivity (Section 6.4D)
- 6.5 Halohydrin Formation and Its Anti Stereoselectivity (Section 6.4E)
- 6.6 Oxymercuration-Reduction of an Alkene (Section 6.4F)
- 6.7 Hydroboration (Section 6.5)
- 6.8 Oxidation of a Trialkylborane by Alkaline Hydrogen Peroxide (Section 6.5)
- 6.9 Formation of an Ozonide (Section 6.6B)

Chapter 7 Alkynes

- 7.1 Addition of HBr to an Alkyne (Section 7.7B)
- 7.2 $HgSO_4/H_2SO_4$ Catalyzed Hydration of an Alkyne (Section 7.8B)
- 7.3 Reduction of an Alkyne by Sodium in Liquid Ammonia (Section 7.9C)

Chapter 8 Haloalkanes, Halogenation, and Radical Reactions

- 8.1 Radical Chlorination of Ethane (Section 8.5B)
- 8.2 Allylic Bromination of Propene Using NBS (Section 8.6A)
- 8.3 Radical Initiated Non-Markovnikov Addition of HBr to Alkenes (Section 8.8)

Chapter 9 Nucleophilic Substitution and β -Elimination

- 9.1 An S_N2 Reaction (Section 9.2A)
- 9.2 An S_{NI} 1 Reaction (Section 9.2B)
- 9.3 Rearrangement During Solvolysis of 2-Chloro-3-phenylbutane (Section 9.3F)
- 9.4 E1 Reaction of 2-Bromo-2-methylpropane (Section 9.6A)
- 9.5 E2 Reaction of 2-Bromobutane (Section 9.6B)

- 9.6 E2 Reaction of meso-1,2-Dibromo-1,2-diphenylethane (Section 9.7C)
- 9.7 E2 Reaction of the Enantiomers of 1,2-Dibromo-1,2-diphenylethane (Section 9.7C)
- 9.8 E2 Reaction of cis-1-Chloro-2-isopropylcyclohexane (Section 9.7C)
- 9.9 Hydrolysis of a Sulfur Mustard—Participation by a Neighboring Group (Section 9.10)

Chapter 10 Alcohols

- 10.1 Reaction of a 3° Alcohol with HBr—An S_N 1 Reaction (Section 10.5A)
- 10.2 Reaction of a 1° Alcohol with HBr—An $S_N 2$ Reaction (Section 10.5A)
- 10.3 Rearrangement upon Treatment of Neopentyl Alcohol with HCl (Section 10.5A)
- 10.4 Reaction of a Primary Alcohol with PBr₃ (Section 10.5B)
- 10.5 Acid-Catalyzed Dehydration of 2-Butanol—An E1 Reaction (Section 10.6)
- 10.6 Acid-Catalyzed Dehydration of an Unbranched Primary Alcohol (Section 10.6)
- 10.7 The Pinacol Rearrangement of 2,3-Dimethyl-2,3-butanediol (Pinacol) (Section 10.7)
- 10.8 Chromic Acid Oxidation of an Alcohol (Section 10.8A)
- 10.9 Swern Oxidation, Starting at the Point of the Chlorosulfonium Ion (Section 10.8C)
- 10.10 Dess-Martin Oxidation (Section 10.8D)
- 10.11 Oxidation of a Glycol by Periodic Acid (Section 10.8E)
- 10.12 Oxidation of an Alcohol by NAD+ (Section 10.8E)

Chapter 11 Ethers, Epoxides, and Sulfides

- 11.1 Acid-Catalyzed Intermolecular Dehydration of a Primary Alcohol (Section 11.4B)
- 11.2 Acid-Catalyzed Addition of an Alcohol to an Alkene (Section 11.4C)
- 11.3 Acid-Catalyzed Cleavage of a Dialkyl Ether (Section 11.5A)
- 11.4 Epoxidation of an Alkene by RCO₂H (Section 11.8C)
- 11.5 Acid-Catalyzed Hydrolysis of an Epoxide (Section 11.9A)
- 11.6 Nucleophilic Opening of an Epoxide Ring (Section 11.98)

Chapter 14 Mass Spectrometry

- 14.1 McLafferty Rearrangement of a Ketone (Section 14.3E)
- 14.2 McLafferty Rearrangement of a Carboxylic Acid (Section 14.3F)

Chapter 15 An Introduction to Organometallic Compounds

- 15.1 Formation of Dichlorocarbene and Its Reaction with Cyclohexene (Section 15.3B)
- 15.2 The Simmons-Smith Reaction with an Alkene (Section 15.3C)

Chapter 16 Aldehydes and Ketones

- 16.1 Grignard Reagent Reacting with Formaldehyde (Section 16.5A)
- 16.2 Organolithium Reagent Reacting with a Ketone (Section 16.5B)
- 16.3 Alkyne Anion Reacting with a Ketone (Section 16.5C)
- 16.4 Formation of a Cyanohydrin (Section 16.5D)
- 16.5 The Wittig Reaction (Section 16.6)

- 16.6 Base-Catalyzed Formation of a Hemiacetal (Section 16.7B)
- 16.7 Acid-Catalyzed Formation of a Hemiacetal (Section 16.7B)
- 16.8 Acid-Catalyzed Formation of an Acetal (Section 16.7B)
- 16.9 Formation of an Imine from an Aldehyde or a Ketone (Section 16.8A)
- 16.10 Base-Catalyzed Equilibration of Keto and Enol Tautomers (Section 16.9A)
- 16.11 Acid-Catalyzed Equilibration of Keto and Enol Tautomers (Section 16.9A)
- 16.12 Pinnick Oxidation (Section 16.10A)
- 16.13 Sodium Borohydride Reduction of an Aldehyde or a Ketone (Section 16.11A)
- 16.14 Wolff-Kishner Reduction (Section 16.11E)
- 16.15 Acid-Catalyzed α -Halogenation of a Ketone (Section 16.12C)
- 16.16 Base-Promoted α -Halogenation of a Ketone (Section 16.12C)

Chapter 17 Carboxylic Acids

- 17.1 Formation of a Methyl Ester Using Diazomethane (Section 17.7B)
- 17.2 Decarboxylation of a β -Ketocarboxylic Acid (Section 17.9A)
- 17.3 Decarboxylation of a β -Dicarboxylic Acid (Section 17.9B)

Chapter 18 Functional Derivatives of Carboxylic Acids

- 18.1 Hydrolysis of an Acid Chloride (Section 18.5A)
- 18.2 Acid-Catalyzed Ester Hydrolysis (Section 18.5C)
- 18.3 Hydrolysis of an Ester in Aqueous Base (Saponification) (Section 18.5C)
- 18.4 Hydrolysis of an Amide in Aqueous Acid (Section 18.5D)
- 18.5 Hydrolysis of an Amide in Aqueous Base (Section 18.5D)
- 18.6 Hydrolysis of a Cyano Group to an Amide in Aqueous Base (Section 18.5E)
- 18.7 Reaction of an Acid Chloride and Ammonia (Section 18.7A)
- 18.8 Reaction of an Ester with a Grignard Reagent (Section 18.10A)
- 18.9 Reduction of an Ester by Lithium Aluminum Hydride (Section 18.11A)
- 18.10 Reduction of an Amide by Lithium Aluminum Hydride (Section 18.11B)

Chapter 19 Enolate Anions and Enamines

- 19.1 Base-Catalyzed Aldol Reaction (Section 19.2A)
- 19.2 Acid-Catalyzed Aldol Reaction (Section 19.2A)
- 19.3 Acid-Catalyzed Dehydration of an Aldol Product (Section 19.2A)
- 19.4 Claisen Condensation (Section 19.3A)
- 19.5 Alkylation of an Enamine (Section 19.5A)
- 19.6 Michael Reaction—Conjugate Addition of Enolate Anions (Section 19.8A)

Chapter 20 Dienes, Conjugated Systems, and Pericyclic Reactions

- 20.1 1,2- and 1,4-Addition to a Conjugated Diene (Section 20.2A)
- 20.2 The Claisen Rearrangement (Section 20.6A)
- 20.3 The Cope Rearrangement (Section 20.6B)

Chapter 21 Benzene and the Concept of Aromaticity

21.1 Kolbe Carboxylation of Phenol (Section 21.4E)

Chapter 22 Reactions of Benzene and Its Derivatives

- 22.1 Electrophilic Aromatic Substitution—Chlorination (Section 22.1A)
- 22.2 Formation of the Nitronium Ion (Section 22.1B)
- 22.3 Friedel-Crafts Alkylation (Section 22.1C)
- 22.4 Friedel-Crafts Acylation—Generation of an Acylium Ion (Section 22.1C)
- 22.5 Nucleophilic Aromatic Substitution via a Benzyne Intermediate (Section 22.3A)
- 22.6 Nucleophilic Aromatic Substitution by Addition-Elimination (Section 22.3B)

Chapter 23 Amines

- 23.1 Formation of the Nitrosyl Cation (Section 23.8)
- 23.2 Reaction of a 2° Amine with the Nitrosyl Cation to Give an N-Nitrosamine (Section 23.8C)
- 23.3 Reaction of a 1° Amine with Nitrous Acid (Section 23.8D)
- 23.4 The Tiffeneau-Demjanov Reaction (Section 23.8D)
- 23.5 The Hofmann Elimination (Section 23.9)
- 23.6 The Cope Elimination (Section 23.10)

Chapter 24 Catalytic Carbon-Carbon Bond Formation

- 24.1 The Heck Reaction (Section 24.3B)
- 24.2 The Catalytic Cycle for Allylic Alkylation (Section 24.4A)
- 24.3 The Catalytic Cycle of Cross-Coupling (Section 24.5A)

Chapter 26 Organic Polymer Chemistry

- 26.1 Radical Polymerization of a Substituted Ethylene (Section 26.6A)
- 26.2 Ziegler-Natta Catalysis of Ethylene Polymerization (Section 26.6B)
- 26.3 Homogeneous Catalysis for Ziegler-Natta Coordination Polymerization (Section 26.6B)
- 26.4 Initiation of Anionic Polymerization of Alkenes (Section 26.6D)
- 26.5 Initiation of Anionic Polymerization of Butadiene (Section 26.6D)
- 26.6 Initiation of Cationic Polymerization of an Alkene by HF·BF₂ (Section 26.6D)
- 26.7 Initiation of Cationic Polymerization of an Alkene by a Lewis Acid (Section 26.6D)



Chapter 27 Lipids

27.1 Oxidation of a Fatty Acid $-CH_2-CH_2$ to -CH=CH by FAD (Section 27.2C)

Chapter 28 Amino Acids and Proteins

- 28.1 Cleavage of a Peptide Bond at Methionine by Cyanogen Bromide (Section 28.4B)
- 28.2 Edman Degradation—Cleavage of an N-Terminal Amino Acid (Section 28.4B)

Careers in Chemistry

- Dahlia Haynes, Innovation Portfolio Manager and RDE Technical Leader, SC Johnson 12
- 2 Amy Rhoden Smith, Program Development Leader, Precision BioSciences 77
- **3 Tricia Johnson,** Chemist, U.S. Food and Drug Administration 137
- 3 Eric Breitung, Research Scientist, New York Metropolitan Museum of Art 140
- 4 Baskar Nammalwar, Senior Scientist, Forge Therapeutics & Blacksmith Medicines 175
- 5 Ingrid Montes, Professor of Organic Chemistry, University of Puerto Rico 219
- 6 Ryann Kress, Registered Nurse, Carilion Roanoke Memorial Hospital 242
- **7 Ivy Tran,** Technical Sales Representative, Arclin USA 302
- **8 Jonathan C. Trent,** Associate Director for Clinical Research and the Director of the Bone and Soft-Tissue Sarcoma Group, Sylvester Comprehensive Cancer Center 345
- 9 Halimatu S. Mohammed, Technical Transfer Specialist, WuXi Advanced Therapies 380
- **10 Dana L. Broughton,** Patent Attorney, GlaxoSmithKline 445
- 11 Miriam Quintal, Managing Principal, Lewis-Burke Associates LLC 502
- **12 LaShonda T. Cureton,** Lead Chemist, U.S. Food and Drug Administration 547
- 13 Sathish Kumar Lageshetty, Senior Scientist, CHASM Advanced Materials, Inc. 568
- 14 RaiAnna Arscott Hopson, Scientist, AMVAC Chemical Corp 620
- 15 Kevin Meraz, Senior Scientist, PDD Inc. 643
- **16 Weijun Niu, Research Associate, Corning** 664
- 17 James Mack, Professor of Chemistry, University of Cincinnati 741
- 18 Shelbie Shelder, Family Medicine Doctor and Resident Physician, Seattle Indian Health Board and Swedish First Hill Hospital 791
- 19 Rami Abu-Aita, Chief Medical Physicist, SSM Health for the South Central Wisconsin region 849
- 20 Paul Cunningham, Small Animal Emergency Veterinarian Animal Emergency Centre Pty Ltd. 923
- 21 Chinenyeze Nwankwoala, Senior Chemist, Ascend Performance Materials 969

- xxviii
- **22 Goupu Touthang,** Research Chemist, MECS Sulfuric Acid and Environmental Technologies 1028
- 23 Brent Dial, Research Scientist: Organic Chemist, Oak Ridge National Laboratory 1075
- **24 Arnie R. de Leon,** Senior Process Development Group Leader, Nitto Denko Avecia Inc. 1132
- 25 Luis Ernesto Miramontes Cárdenas, Chemist 1180
- **26** Percy Lavon Julian, Director, Julian Laboratories 1214

Preface

Learning Through Understanding

The best way to master organic chemistry is to first develop an intuitive understanding of basic principles, and then understand how to apply those principles to new and increasingly complex situations.

The learning of organic chemistry is analogous to putting together a complex jigsaw puzzle—and at least two distinct approaches can be imagined. The first approach, unfortunately, reflects the way many students approach their first organic chemistry class: by memorizing each new piece of the puzzle individually, with no context, and then trying to blindly guess where it is to be placed by trial and error. We can all agree that a much better approach to finishing a jigsaw puzzle (as well as learning organic chemistry) is to keep the overall picture of the completed puzzle in one's mind and then evaluate each new piece being considered in the context of where it might fit into the emerging image. This book has been written in alignment with the far more effective second approach to learning by providing a strong foundation of basic concepts at the beginning, and then consistently emphasizing a"big picture" understanding as each new concept and functional group is presented in context. To accomplish this, the Ninth Edition uses two key innovations from previous editions that teach students how to learn two of the most important elements of organic chemistry: mechanisms and synthesis.

- Mechanisms We present a revolutionary paradigm for learning organic chemistry
 mechanisms. Students are introduced to a small set of individual mechanism elements, and importantly, when each of these mechanism elements is to be used.
 The four most important of these elements are:
 - Make a bond between a nucleophile and an electrophile
 - Break a bond to create stable molecules or ions
 - Add a proton
 - Take a proton away

Reaction mechanisms throughout the book are written in stepwise fashion and described as logical combinations of the individual mechanism elements. This new approach not only simplifies the learning of mechanisms for students but also makes it easier for them to recognize similarities and differences between related reactions. Most important, this approach makes the prediction of reaction mechanisms a straightforward, multiple-choice situation in which the correct mechanism



element for a given step of each new reaction mechanism is systematically chosen from a small menu of options.

Synthesis We present another important innovation in organic chemistry learning that we refer to as the "Organic Chemistry Reaction Roadmap." It is a graphical representation of the different organic reactions taught in the context of the important functional groups. The functional groups of an organic chemistry roadmap are analogous to cities on a real roadmap, and the reactions are like the roads between those cities. Arrows are used to represent known routes between functional groups, and the reagents required to bring about each reaction are written next to the corresponding arrow. Multistep synthesis questions are often very challenging for organic chemistry students, even though synthesis is at the core of organic chemistry as a discipline. The power of the Organic Chemistry Reaction Roadmap is that it helps students visualize the reactions that are appropriate to interconvert key functional groups in multistep synthesis problems. The construction and use of Organic Chemistry Reaction Roadmaps are introduced in the end-of-chapter problems beginning in Chapter 6 and presented in complete form in the Appendix section of this book, which students can tear out and use.

What's New in the Ninth Edition?

Each new feature is intended to enhance student engagement and learning.

New Section Overview: Each section begins with a bulleted summary of the content, providing highlights, "crib notes," and key reactions.

New Examples with Step-by-Step Solutions: All Solutions to the Examples have been rewritten in a stepwise fashion so that students learn how to master complicated problems. Students are first reminded of relevant, important concepts, then walked through a systematic approach to arriving at the correct solution.

New Think–Pair–Share: Think–Pair–Share activities pose a question to students, who first consider it independently, and then discuss with one or two other students before settling on a final answer. This is a great way to motivate students and promote higher-level thinking. Sometimes this group discussion "sharing" is followed up with a larger classroom discussion. Some Think–Pair–Share activities are short "quick-response Think–Pair–Shares," and sometimes the activities may be a longer and more involved "extended Think–Pair–Share."

4.37 Think-Pair-Share

HI and NaOCH, react in an acid-base reaction.

- (a) Write out a reaction equation for these two reagents.
- **(b)** Identify which covalent bonds are formed and which covalent bonds are broken in the reaction.
- **(c)** Use curved arrow notation to show electron pair movement to go from reactants to products.
- **(d)** Draw the transition state for the reaction.

New Things You Should Know: Key Principles: There are important transitions between distinct topics in the sequence of the book that are good checkpoints to stop, reflect, and take stock of important concepts or ideas that will be needed

going forward. "Things You Should Know" appropriately emphasize key principles from the chapters, while preserving reading fluency. When students read and fully digest these primers, they will be better prepared to approach critical topics in following sections. Things You Should Know recap the most important lessons and principles from quantum mechanics and other essential pieces of information that the students must use to understand many different aspects of molecular structure, properties, reactions, and mechanisms. Such overarching principles include "Delocalization of charge over a larger area is stabilizing," and "Delocalization of π electron density over a larger area is stabilizing."

▶ Things You Should Know

Key Principle

There are two possible arrangements of four different groups around a tetrahedral atom.

The two different arrangements are mirror images of each other, a property referred to as chirality and often use of extensive memorization. The key principle above each other, a property referred to as chirality and often compared to handedness.

not memorize, the material presented in your organic chemistry course. Thoroughly understanding key principles presented throughout this text will allow you to develop an intuitive feel for organic chemistry that

has a basis in symmetry operations, and should be used as a foundation for building your understanding Very important: Your goal should be to understand, throughout the course. As appropriate, these principles will be mentioned in the margins of various future chapters as a reminder of just how extensively we fall back on these notions to explain organic chemistry.

New Careers in Chemistry: These profiles of diverse individuals showcase various career paths that students can take after studying organic chemistry. By showing a diverse, inclusive, and equitable chemical community, all students know that they have a future in chemistry-related jobs.



Careers in Chemistry Dana L. Broughton, PhD, Esq. is a patent attorney with GlaxoSmithKline (GSK).

New and Revised Exercises: About 140 new and over 250 revised exercises were added to the book and online course to keep the content current.

New to the Online OWL Course

New Targeted Feedback: Over 30 percent of the problems in OWLv2 now have targeted feedback on common errors that students make. The targeted feedback explains why the student's answer is incorrect and guides them toward a correct solution.

New Laddered Assessments: Conceptual mastery modules have been combined with more traditional homework questions into one structured learning path, organized by topic at the chapter level.

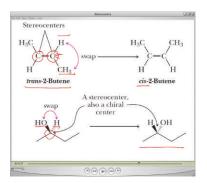
Content Audit: All online exercises and randomizations were reviewed for accuracy and to ensure that they align with the textbook so that students are tested on content that they have learned.

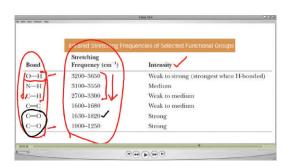
Drawing Tool Enhancements: The drawing tool now allows multiple structures to be drawn in one canvas, and new curved arrows for mechanisms were added.

OWLv2 Help: Resources have been streamlined and improved to make it easier for instructors and students to master OWL.

Major Features of *Organic Chemistry*, Ninth Edition

Videos: The leading authors, Eric Anslyn and Brent Iverson, created over 90 short videos for the eBook and online course. The videos provide students with an ondemand resource that provides insight into the most difficult and important material. Icons in the margin of the text indicate to students when a video is available to walk them through problems and key figures in the text. These videos have been thoroughly student tested and approved.





Margin Bullets: A series of bullet points emphasizing key foundational ideas that recur throughout the book guide the discussions of topics in future chapters. Their objective is to reiterate that the same fundamental principles are used throughout the text to explain patterns of molecular structure, properties, and reactivity.

Delocalization of charge over a larger area is stabilizing.

Survival Skills: Mastering organic chemistry requires the development of certain intellectual skills. To this end, 15 "How To" boxes highlight "survival skills" for organic chemistry students. These include the following:

- How to Quickly Figure Out Formal Charge
- How to Quickly Recognize the Hybridization and Geometry of Atoms

- How to Quickly Draw and Recognize Enantiomers and Diastereomers
- How to Retrosynthetically Dissect an Amine into the Proper Starting Materials for a Reductive Amination
- How to Recognize Aromatic Compounds: Criteria and Caveats

MCAT Preparation: A significant number of students taking organic chemistry will take standardized tests such as the MCAT, DAT, or PCAT. Organic chemistry content on the MCAT, or similar exams, is generally in the form of passages followed by a series of multiple-choice questions. Learning to answer questions based on passages requires students to develop increased reading comprehension and analytical skills. Our textbook is the first to aid students in developing these skills by introducing an extensive series of passages followed by several thought-provoking, multiple-choice questions in almost every chapter (MCAT Practice: Passage and Questions). The passages cover interesting applications of organic chemistry principles as well as biological and chemical topics. These passages add considerable enrichment to the material being presented.

Unique Chapter Sequence: Carbonyl chemistry (Chapters 16–19) is placed earlier than in most texts so that instructors have time to teach this material to their students who have selected a life science degree and/or career in the health professions. Carbonyl chemistry is fundamental to the chemistry of living systems; therefore, the connections between carbonyl chemistry and the chemistry of carbohydrates are highlighted earlier in the book. This latter change mirrors the increasing importance of carbohydrate chemistry as well as other biological molecules on the MCAT.

Applications to Synthesis: Organic chemistry enables the synthesis of useful molecules. Synthetic applications of the reactions covered in this text are emphasized throughout, partly through the challenging end-of-chapter synthesis problems. The goal is to demonstrate to students how synthetic organic chemistry is used in pharmaceutical research and in the production of useful pharmaceuticals. The text provides applications of the reactions to the synthesis of important molecules, such as Valium, fluoxetine (Prozac), meperidine (Demerol), albuterol (Proventil), tamoxifen, and sildenafil (Viagra). Multistep synthesis problems challenge students to develop their own multistep synthetic plan for converting a relatively simple starting material into a more complex target molecule. Multistep synthesis is supported by the Organic Chemistry Reaction Roadmaps as well as an expanded description of retrosynthetic analysis in multiple chapters. We include tips on recognizing when to use certain reactions, such as those involving enolates in the construction of complex structures.

Applications to Biology: The application of organic chemistry principles to important biological molecules is integrated where appropriate to establish a bridge with biochemistry courses. In particular, "Connections to Biological Chemistry" gives special attention to those aspects of organic chemistry that are essential to understanding the chemistry of living systems. For example, the organic chemistry of amino acids is highlighted beginning in Section 3.8, along with the importance of alkene geometry to both membrane fluidity and nutrition. How hydrogen bonding is involved with drug-receptor interactions (Section 10.2) is discussed. It is important to note that these Connections to Biological Chemistry features have been added throughout the book, not just at the end, because not all instructors make it through the biological chemistry chapters at the end of the text.

Chemical Connections: Relevance to practical application is also emphasized in an expanded array of essays titled "Chemical Connections." Topics include

medicines such as penicillin and cephalosporins (MCAT Practice: Section 18.8), food supplements such as antioxidants (Section 8.7), and materials science concepts such as spider silk (Chemical Connections: Section 27.6). These sections provide a bridge between the theory of organic chemistry and well-known, current, practical applications.

Instructor and Student Resources

Additional instructor and student resources are available online. Instructor assets include the following:

- Instructor Manual
- Guide to Teaching Online
- Transition Guide from the Eighth Edition to the Ninth Edition
- Educator's Guide
- Lecture Notes PowerPoint® slides
- Image Library PowerPoint® slides
- Solution and Answer Guide
- Organic Chemistry Reaction Roadmaps
- Test Bank

Acknowledgments

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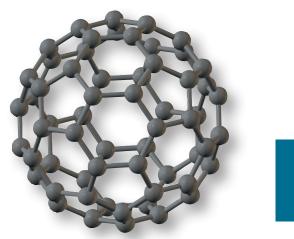
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Covalent Bonding and Shapes of Molecules

Outline

- 1.1 Electronic Structure of Atoms
- 1.2 Lewis Model of Bonding HOW TO: Quickly Figure Out Formal Charge HOW TO: Draw Lewis Structures from Condensed Structural Formulas
- **1.3** Functional Groups
- **1.4** Bond Angles and Shapes of Molecules
- 1.5 Polar and Nonpolar Molecules
- 1.6 Quantum or Wave Mechanics
- 1.7 A Combined Valence Bond and Molecular Orbital Theory Approach to Covalent Bonding HOW TO: Quickly Recognize the Hybridization and Geometry of Atoms
- 1.8 Resonance
 - HOW TO: Draw Curved Arrows and Push Electrons in Creating Contributing Structures
- **1.9** Molecular Orbitals for Delocalized Systems
- **1.10** Bond Lengths and Bond Strengths in Alkanes, Alkenes, and Alkynes

A model of the structure of diamond, one form of pure carbon. Each carbon is bonded to four other carbons at the corners of a tetrahedron. **Above:** a model of fullerene (C_{60}). See "MCAT Practice: Fullerenes." © Cengage Learning/Charles D. Winters

According to the simplest definition, **organic chemistry** is the study of the compounds of carbon. Remarkably most organic compounds consist of carbon and only a few other elements—chiefly, hydrogen, oxygen, and nitrogen. Organic compounds are all around us—in our foods, flavors, and fragrances; in our medicines, toiletries, and cosmetics; in our plastics, films, fibers, and resins; in our paints and varnishes; in our glues and adhesives; in our fuels and lubricants; and, of course, in our bodies and the bodies of all living things. Let us review how the elements of C, H, O, and N combine by sharing electron pairs to form bonds, and ultimately molecules.



Electronic Structure of Atoms

>> SECTION OVERVIEW Atoms consist of a small, dense nucleus and electrons distributed about the nucleus in regions of space called shells.

- Each shell can contain as many as $2n^2$ electrons, where n is the number of
- Each principal energy level is subdivided into regions of space called orbitals. The **valence shell** is the outermost occupied shell, and it contains the **valence** electrons. Valence electrons are important because they take part in chemical
- The Lewis dot structure of an atom shows the symbol of the atom surrounded by a number of dots equal to the number of electrons in the valence shell of the atom.

FIGURE 1.1 A schematic view of an atom. Most of the mass of an atom is concentrated in its small, dense nucleus.

Nucleus containing

neutrons and protons

Extranuclear

space containing electrons

Shell

⊱10⁻¹⁰ m→

A region of space around a nucleus that can be occupied by electrons, corresponding to a principal quantum number.

Quantized

Having discrete values for energy and momentum.

Delocalization

The spreading of electron density over a larger volume of space.

An atom contains a small, dense nucleus made of neutrons and positively charged protons. Most of the mass of an atom is contained in its nucleus. The nucleus is surrounded by an extranuclear space containing negatively charged electrons. The nucleus of an atom has a diameter of 10^{-14} to 10^{-15} meters (m). The electrons occupy a much larger volume with a diameter of approximately 10^{-10} m (Figure 1.1).

Shells define the probability of finding an electron in various regions of space relative to the nucleus. The energy of electrons in the shells is quantized. Quantization means that only specific values of energy are possible, rather than a continuum of values. These shells occur only at quantized energies in which three important effects balance each other. The first is the electrostatic attraction that draws the electrons toward the nucleus; the second is the electrostatic repulsion between the electrons; and the third is the wavelike nature of an electron that prefers to be delocalized, thereby spreading the electron density away from the nuclei. Delocalization describes the spreading of electron density over a larger volume of space.

Electron shells are identified by the principal quantum numbers 1, 2, 3, and so forth. Each shell can contain up to $2n^2$ electrons, where n is the number of the shell. Thus, the first shell can contain 2 electrons; the second, 8 electrons; the third, 18 electrons; the fourth, 32 electrons; and so on (Table 1.1). Electrons in the first shell are nearest to the positively charged nucleus and are held most strongly by it; these electrons are lowest in energy. Electrons in highernumbered shells are farther from the positively charged nucleus and are held less strongly.

Table 1.1	Distribution of Electrons in Shells						
Shell		Number of Electrons Shell Can Hold	Relative Energies of Electrons in Shells				
4		32	higher				
3		18					
2		8					
1		2	lower				

Table 1.2	Distribution of Orbitals in Shells				
Shell	Orbitals Contained in Shell				
3	$3s$, $3p_x$, $3p_y$, $3p_z$, plus five $3d$ orbitals				
2	$2s, 2p_x, 2p_y, 2p_z$				
1	1s				

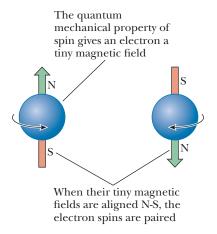
Shells are divided into subshells designated by the letters s, p, d, and f, and within these subshells, electrons are grouped in orbitals (Table 1.2). An **orbital** is a region of space that can hold two electrons and has a specific quantized energy. The first shell contains a single orbital called a 1s orbital. The second shell contains one s orbital and three p orbitals. The three 2p orbitals reflect orthogonal angular momentum states in three-dimensional space. **Orthogonal** in this context results in 90° angles between the orbitals, but in all cases, orthogonal also means that the orbitals have no net overlap. As a point of reference, to discuss the 2p orthogonal orbitals, consider them to be directed along the x-, y-, and z-axes and give them designations, $2p_x$, $2p_y$, and $2p_z$. The shapes of s and p orbitals are shown in Figures 1.8 and 1.9 and are described in more detail in Section 1.6B.

A. Electron Configuration of Atoms

The electron configuration of an atom is a description of the orbitals its electrons occupy. At this stage, we are concerned primarily with the **ground-state electron configuration**—the electron configuration of lowest energy. Determine the ground-state electron configuration of an atom by using the following three rules.

Rule 1: The Aufbau ("Build-Up") Principle. According to the **Aufbau principle**, orbitals fill in order of increasing energy, from lowest to highest. In this course, you will be concerned primarily with the elements of the first, second, and third periods of the Periodic Table. Orbitals fill in the order 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, and so on.

Rule 2: The Pauli Exclusion Principle. The **Pauli exclusion principle** requires that only two electrons can occupy an orbital and that their spins must be paired. To understand what it means to have paired spins, recall from general chemistry that just as the Earth has a spin, electrons have a quantum mechanical property referred to as spin. And just as the Earth has magnetic north (N) and south (S) poles, so do electrons. As described by quantum mechanics, a given electron can exist in only two different spin states. Two electrons with opposite spins are said to have **paired spins**.



Orbital

A region of space that can hold two electrons.

Orthogonal

Having no net overlap.

Ground-state electron configuration

The lowest-energy electron configuration for an atom or a molecule.

Aufbau principle

Orbitals fill in order of increasing energy, from lowest to highest.

Pauli exclusion principle

No more than two electrons may be present in an orbital. If two electrons are present, their spins must be paired.

Hund's rule

When orbitals of equal energy are available, but there are not enough electrons to fill all of them completely, one electron is put in each before a second electron is added to any.

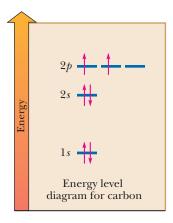
When filling orbitals with electrons, place no more than two in an orbital. For example, with four electrons, the 1s and 2s orbitals are filled and are written $1s^2$ $2s^2$. With an additional six electrons, the set of three 2p orbitals is filled and is written $2p_x^2$ $2p_y^2$ $2p_z^2$. Alternatively, a filled set of three 2p orbitals may be written $2p^6$.

Rule 3: Hund's Rule. Hund's rule has two parts. The first part states that when orbitals of equal energy (called degenerate) are available, but there are not enough electrons to fill all of them completely, then one electron is added to each orbital before a second electron is added to any one of them. The second part of Hund's rule states that the spins of the single electrons in the degenerate orbitals should be aligned. Recall that electrons have a negative charge; partially filling orbitals as much as possible minimizes electrostatic repulsion between electrons. After the 1s and 2s orbitals are filled with four electrons, a fifth electron is added to the $2p_x$ orbital, a sixth to the $2p_y$ orbital, and a seventh to the $2p_z$ orbital. Only after each 2p orbital contains one electron is a second electron added to the $2p_x$ orbital. Carbon, for example, has six electrons, and its ground-state electron configuration is $1s^2 2s^2 2p_x^{-1} 2p_y^{-1} 2p_z^{-0}$. Alternatively, it may be simplified to $1s^2 2s^2 2p^2$. Table 1.3 shows ground-state electron configurations of the first 18 elements of the Periodic Table.

Chemists routinely write **energy-level diagrams** that pictorially designate where electrons are placed in an electron configuration. For example, the energy-level diagram for the electron configuration of carbon, $1s^2$, $2s^2$, $2p^2$, shows three energy levels, one each for the 1s, 2s, and 2p orbitals. Moving up in the diagram on the next page means higher energy. Electrons in these diagrams are drawn as arrows. The Aufbau principle says to place the first four electrons in the 1s and 2s orbitals, and the Pauli exclusion principle says to pair the two electrons in each orbital (shown as arrows with opposing directions). The remaining two electrons are left to go into the 2p level, and because there are three such orbitals, Hund's rule says to place these electrons in different orbitals with their spins aligned (shown as arrows pointing in the same direction).

Table 1.3	Ground-State Electron Configurations for Elements 1–18					
First Period*	Second Period	Third Period				
H 1 $1s^1$	Li 3 [He] 2s ¹	Na 11 [Ne] 3s ¹				
He 2 $1s^2$	Be 4 [He] 2s ²	Mg 12 [Ne] $3s^2$				
	B 5 [He] $2s^2 2p^1$	Al 13 [Ne] $3s^2 3p^1$				
	C 6 [He] $2s^2 2p^2$	Si 14 [Ne] $3s^2 3p^2$				
	N 7 [He] $2s^2 2p^3$	P 15 [Ne] $3s^2 3p^3$				
	O 8 [He] $2s^2 2p^4$	S 16 [Ne] $3s^2 3p^4$				
	F 9 [He] 2s ² 2p ⁵	Cl 17 [Ne] $3s^2 3p^5$				
	Ne 10 [He] $2s^2 2p^6$	Ar 18 [Ne] $3s^2 3p^6$				

^{*}Elements are listed by symbol, atomic number, and simplified ground-state electron configuration.



Example 1.1 Electron Configurations

Write the ground-state electron configuration for each element showing the occupancy of each p orbital. For (c), write the energy-level diagram.

(a) Lithium

(b) Oxygen

(c) Chlorine

Solution

STEP 1 Determine the atomic number of the element from the Periodic Table. This is the number of electrons in the ground state.

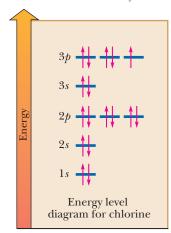
STEP 2 Fill the orbitals from the lowest energy to the highest energy using Table 1.2 as a guide. Remember to place 2 electrons in the lowest energy first shell, up to 8 electrons in the second shell, and up to 18 electrons in the third shell until all of the electrons are placed in an orbital.

NOTE The group number for each element gives the number of electrons in the outermost (valence) shell.

(a) Lithium (atomic number 3): $1s^2 2s^1$

(b) Oxygen (atomic number 8): $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$

(c) Chlorine (atomic number 17): $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^2 3p_x^2 3p_y^2 3p_z^2$



Problem 1.1

Write and compare the ground-state electron configurations for each pair of elements.

- (a) Carbon and silicon
- **(b)** Oxygen and sulfur
- **(c)** Nitrogen and phosphorus



Energy

The ability to do work.

Potential energy

The energy that can be released if given an opportunity.

Ground state

The lowest energy state of a system.

Excited state

A state of a system at higher energy than the ground state.

Ionization potential

The energy needed to remove an electron from an atom or a molecule.

Valence electrons

Electrons in the valence (outermost) shell of an atom.

Valence shell

The outermost occupied electron shell of an atom.

Lewis dot structure

The symbol of an element surrounded by the number of dots equal to the number of electrons in the valence shell of the atom.

B. The Concept of Energy

In the discussion of energy-level diagrams, the lines were drawn on the diagram to depict relative energy. In the energy-level diagram for carbon, the 1s level is the reference, and the 2s and 2p levels are placed higher on the diagram relative to it. But you may be asking, "How is energy defined?"

Energy is the ability to do work. The higher in energy an entity is, the more work it can perform. If you hold an object above the ground, it is unstable relative to when it is lying on the ground. You expend energy lifting the object, and this energy is stored in the object as potential energy. The **potential energy** can be released when the object is released. The higher you hold the object, the more energy the object stores, and the greater the impact the object has when it hits the ground.

The force that restores the object to its resting state on the ground is the gravitational attraction of the object to the Earth. Interestingly, the farther the object is from the Earth, the easier it is to take the object even farther from the Earth. As an extreme example, thousands of miles above the Earth the object has incredibly large potential energy and could wreak serious damage to a building if dropped. But at that distance, it is relatively easy to remove the object farther from the Earth because the gravitational attraction is weak.

You can generalize this example to chemical structures. Unstable structures possess energy waiting to be released. When a structure is higher in energy, the more energy it has stored. When that energy is released, work can be done. In chemistry, released energy is very often harnessed to do work, such as the burning of gasoline to drive the pistons in an internal combustion engine.

Let's return to the energy-level diagram of carbon. In the **ground state** of carbon, the electrons are placed in accordance with the quantum chemistry principles (such as Aufbau principle, Pauli exclusion principle, and Hund's rule) that dictate the lowest energy form of carbon. If you place the electrons in a different manner (as an example, only one electron in 2s and three electrons in 2p), you would have a higher energy state of carbon, referred to as an **excited state**. All of nature seeks its lowest energy state; when the electrons are rearranged back to the ground state, energy is released.

Note that the electrons in the lowest energy orbital, 1s, are held tightest to the nucleus. It would take the largest amount of energy to remove these electrons relative to the others. The energy it takes to remove an electron from an atom or a molecule is called the **ionization potential**. The 1s electrons, therefore, have the highest ionization potential; however, the electrons in the 2p levels of carbon are the farthest from the nucleus and are held the weakest. They are the easiest to remove from the atom, and therefore have the lowest ionization potential. This is analogous to it being easier to remove an object from the Earth the farther it is from the surface.

C. Lewis Dot Structures

Chemists often focus on the electrons in the outermost shell of the atom because these electrons are involved in the formation of chemical bonds and in chemical reactions. Carbon, for example, with the ground-state electron configuration $1s^2 2s^2 2p^2$, has four outer-shell electrons. Outer-shell electrons are called **valence electrons**, and the energy level in which they are found is called the **valence shell**. To illustrate the outermost electrons of an atom, chemists commonly use a representation called a **Lewis dot structure**, named after the American chemist Gilbert N. Lewis (1875–1946), who devised it. A Lewis dot structure shows the symbol of the element surrounded by the number of dots equal to the number of electrons in the outer shell of an atom of that element. In Lewis dot structures, the atomic symbol represents the core (that is, the nucleus and all inner shell

Table 1.4		Lewis Dot Structures for Elements 1–18*					
1A	2A	3 A	4A	5A	6A	7A	8A
н•							Не
Li•	Be:	В:	· C :	· N :	: O:	F :	Ne:
Na•	Mg:	Al	·Si	• P :	·s:	: Cl :	Ar

*These dots represent electrons from the valence shell. They are arranged as pairs or single electrons in accordance with Hund's rule.

electrons). Table 1.4 shows Lewis dot structures for the first 18 elements of the Periodic Table.

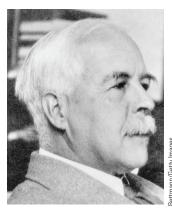
The noble gases helium and neon have filled valence shells. The valence shell of helium is filled with two electrons; that of neon is filled with eight electrons. Neon and argon have in common an electron configuration in which the s and p orbitals of their valence shells are filled with eight electrons. The valence shells of all other elements shown in Table 1.4 contain fewer than eight electrons.

For C, N, O, and F in period 2 of the Periodic Table, the valence electrons belong to the second shell. With eight electrons as with Ne, this shell is completely filled. For Si, P, S, and Cl in period 3 of the Periodic Table, the valence electrons belong to the third shell. This shell is only partially filled with eight electrons; the 3s and 3p orbitals are fully occupied, but the five 3d orbitals can accommodate an additional ten electrons.

1.2 Lewis Model of Bonding

>>> SECTION OVERVIEW According to the Lewis model of covalent bonding, atoms bond together in such a way that each atom participating in a chemical bond acquires a completed valence-shell electron configuration resembling that of the noble gas nearest it in atomic number.

- Anions and cations attract each other but do not form bonds with defined directionality.
- A covalent bond is a chemical bond formed by the sharing of electron pairs between adjacent atoms.
- The tendency of main-group elements (Groups 1A–7A) to achieve an outer shell
 of eight valence electrons is called the octet rule.
- **Electronegativity** is a measure of the force of attraction by an atom for electrons it shares in a chemical bond with another atom. In the context of the Periodic Table, the electronegativity of elements increases from left to right with a period (increasing positive charge of the nucleus) and decreases from the top to bottom within a group (increasing distance of electrons from the nucleus).
- A nonpolar covalent bond is a covalent bond in which the difference in electronegativity of the bonded atoms is less than 0.5.
- A **polar covalent bond** is a covalent bond in which the difference in electronegativity of the bonded atoms is between 0.5 and 1.9.
- In a polar covalent bond, the more electronegative atom bears a partial negative charge (δ-) and the less electronegative atom bears a partial positive charge (δ+).
- A polar bond has a bond dipole moment equal to the product of the absolute value of the partial charge times the distance between the dipolar charges (the bond length).



Gilbert N. Lewis (1875–1946) introduced the theory of the electron pair that extended our understanding of covalent bonding and of the concept of acids and bases. It is in his honor that we often refer to an "electron dot" structure as a Lewis structure.

- An acceptable Lewis structure for a molecule or an ion must show (1) the correct connectivity of atoms, (2) the correct number of valence electrons, (3) no more than two electrons in the outer shell of hydrogen and no more than eight electrons in the outer shell of any second-period element, and (4) all formal charges.
- There are some apparent exceptions to the octet rule: neutral compounds of boron and aluminum can have only six valence electrons.

In 1916, Lewis pointed out that the chemical inertness of the noble gases indicates a high degree of stability of the electron configurations of these elements: helium with a valence shell of two electrons ($1s^2$), neon with a valence shell of eight electrons ($2s^2 2p^6$), and argon with a valence shell of eight electrons ($3s^2 3p^6$). The tendency of atoms to react in ways that achieve an outer shell of eight valence electrons is particularly common among second-row elements of Groups 1A–7A (the main-group elements) and is given the name **octet rule**.

Octet rule

Group 1A–7A elements react to achieve an outer shell of eight valence electrons.

Example 1.2 The Octet Rule

Show how the loss of an electron from a sodium atom leads to a stable octet.

Solution

RECALL The octet rule states that a high degree of stability is achieved when an element has a filled outermost (valence) shell with 8 electrons.

STEP 1 Determine the ground-state electron configuration for each atom as shown in the previous example.

STEP 2 Add an electron to the configuration for each negative charge and take away an electron for each positive charge of the ion. The most stable ions have a filled octet in the valence shell.

The ground-state electron configurations for Na and Na⁺ are:

Na (11 electrons): $1s^2 2s^2 2p^6 3s^1$ Na⁺ (10 electrons): $1s^2 2s^2 2p^6$

Thus, Na⁺ has a complete octet of electrons in its outermost (valence) shell and has the same electron configuration as neon, the noble gas nearest it in atomic number.

Problem 1.2

Show how each chemical change leads to a stable octet.

(a) Sulfur forms S^{2-} . (b) Magnesium forms Mg^{2+} .

A. Formation of Chemical Bonds

According to Lewis's model, atoms interact in such a way that each participating atom acquires a completed outer-shell electron configuration resembling that of the noble gas nearest to it in atomic number. Atoms acquire completed valence shells in two ways.

1. An atom may become ionic (that is, lose or gain enough electrons to acquire a completely filled valence shell). An atom that gains electrons becomes an

anion (a negatively charged ion), and an atom that loses electrons becomes a cation (a positively charged ion). A positively charged ion and a negatively charged ion attract each other. When atoms are held together primarily by attraction of oppositely charged ions, it is said that an ionic bond exists between them.

- 2. An atom may share electrons with one or more other atoms to complete its valence shell. A chemical bond formed by sharing electrons is called a covalent bond.
- 3. Bonds may be partially ionic and partially covalent; these bonds are called **polar** covalent bonds.

B. Electronegativity and Chemical Bonds

How do you estimate the degree of ionic or covalent character in a chemical bond? One way is to compare the electronegativities of the atoms involved. **Electronegativity** is a measure of an atom's attraction for electrons that it shares in a chemical bond with another atom. The most widely used scale of electronegativities (Table 1.5) was devised by Linus Pauling in the 1930s.

Table 1.5 Electronegativity Values for Some Atoms (Pauling Scale) 2A2.1 4 A 5 A 6 A 7 A 1 A 3 A Li Be В C F N 0 2.5 1.0 1.5 2.0 3.0 3.5 4.0 Mg Na Si Р C1 8B A1 0.9 1.2 5B 1.5 1.8 2.1 2.5 3.0 3B 4B **6B** 7 B 1 B 2 B K Ca Sc Ti V Cr Mn Fe Co Ni Zn Ge Cu Ga As Se Br 0.8 1.3 1.6 1.9 1.0 1.5 1.6 1.5 1.8 1.8 1.8 1.6 1.6 1.8 2.0 2.4 2.8 Y Rb Sr Zr Nb Mo Tc Ru Rh Pd Cd In Sn 1.9 0.8 1.2 1.9 1.0 1.4 1.6 1.8 2.2. 2.2 2.2 1.7 1.7 1.8 1.9 2.1 2.5 Cs W Po Ba Hf Ta Re Os Hg Tl Pb Bi La Ir Au At 0.7 0.9 1.7 1.9 2.2 1.9 1.1 1.3 1.5 2.2 1.8 1.8 1.9 2.0 <1.0 1.5-1.9 2.5-2.9 1.0-1.4 2.0 - 2.43.0-4.0

On the Pauling scale, fluorine, the most electronegative element, is assigned an electronegativity of 4.0, and all other elements are assigned values in relation to fluorine. As you study the electronegativity values in this table, note that they generally increase from left to right within a period of the Periodic Table and generally decrease from top to bottom within a group. Values increase from left to right because the increasing positive charge on the nucleus results in a greater force of attraction for the atom's valence electrons. Electronegativity decreases from top to bottom because the increasing distance of the valence electrons from the nucleus results in a lower attraction between the nucleus and these electrons.

Let's further analyze the trends in the Periodic Table we just discussed. As you proceed from left to right in a row of the Periodic Table, the atoms get smaller. This contraction occurs because as you go across a row, the electrons are placed in the same shell, but the charge on the nuclei is increasing, thereby pulling the electrons in closer. This means that the orbitals get lower in energy as you move from left to right in the table, while the atoms hold their electrons tighter. It therefore takes more energy to remove the electrons from atoms as you move toward the right in the Periodic Table (with some exceptions), meaning that these atoms have a higher ionization potential.

Anion

An atom or a group of atoms bearing a negative charge.

Cation

An atom or a group of atoms bearing a positive charge.

lonic bond

Attraction between oppositely charged ions.

Covalent bond

A chemical bond formed between two atoms by sharing one or more pairs of electrons.

Electronegativity

A measure of the force of an atom's attraction for electrons.



Linus Pauling (1901-1994) was the first person to receive two unshared Nobel prizes. He received the 1954 Nobel Prize in Chemistry for his contributions to our understanding of chemical bonding. He received the 1962 Nobel Peace Prize for his efforts on behalf of international control of nuclear weapons testing.

Electron affinity

Energy added or released when an electron is added to an atom or a molecule.

In contrast, consider adding—rather than removing—an electron to the atoms. For example, when an electron is added to the halogens (Group 7A), energy is released because these atoms achieve a noble gas configuration. The energy released upon addition of an electron is called the **electron affinity**, which becomes more favorable as you move from left to right in a row of the Periodic Table. In contrast, as you proceed down a column in the Periodic Table, the principal quantum levels increase, and the outermost electrons are farther from the nuclei, are held less tightly, and have lower ionization potentials. The atoms also have decreasing electron affinities. Because the electronegativity of an atom reflects its tendency to hold onto and to acquire electrons, the phenomenon arises from a combination of ionization potentials and electron affinities.

Example 1.3 Electronegativity

Judging from their relative positions in the Periodic Table, which element in each set is more electronegative?

(a) Lithium or carbon

(b) Nitrogen or oxygen

(c) Carbon or oxygen

Solution

RECALL Electronegativity is the tendency to hold onto or acquire electrons. The Pauling scale defines fluorine as the most electronegative element with an assigned value of 4.0. All other elements are assigned a value relative to fluorine as shown in Table 1.5.

Electronegativity generally increases from left to right within a row (period) of the Periodic Table because the atoms get smaller increasing the charge on the nucleus, pulling the electrons more strongly.

Electronegativity decreases from top to bottom within a group. The atoms get larger, and the increased distance from the nucleus to the valence electrons reduces the attraction, and the electrons are held less tightly.

STEP 1 Locate the elements in the periodic table. Combine the trends above and determine which is more electronegative from their relative positions on the Periodic Table.

All of the elements in these sets are in the second period of the Periodic Table. Electronegativity in this period increases from left to right.

(a) C > Li

(b) O > N

(c) O > C

Problem 1.3

Judging from their relative positions in the Periodic Table, which element in each set is more electronegative?

(a) Lithium or potassium (b) Nitrogen or phosphorus (c) Carbon or silicon

Formation of lons

Ions are formed by the transfer of electrons from the valence shell of an atom of lower electronegativity to the valence shell of an atom of higher electronegativity. As a rough guideline, ions form if the difference in electronegativity between interacting atoms is 1.9 or greater. As an example, ions are formed from sodium (electronegativity 0.9) and fluorine (electronegativity 4.0). In the following equation, use a single-headed (barbed) curved arrow to show the transfer of one electron from sodium to fluorine.

$$Na + F : \longrightarrow Na^+ : F$$

As a result of this transfer of one electron, both sodium and fluorine form ions that have the same electron configuration as neon, the noble gas nearest each in atomic number. The attraction between ions is what permits ionic salts such as sodium fluoride to form a strong crystal lattice and gives them a high melting point.

Covalent Bonds

A covalent bond is formed between atoms that share one or more pairs of electrons to give a noble gas configuration to each atom. The simplest example occurs in the hydrogen molecule. When two hydrogen atoms bond, the single electrons from each combine to form an electron pair. This shared pair completes the valence shell of each hydrogen. According to the Lewis model, a pair of electrons in a covalent bond functions in two ways simultaneously: it is shared by two atoms and at the same time fills the outer (valence) shell of each. Use a line between the two hydrogens to symbolize the covalent bond formed by the sharing of a pair of electrons.

$$H \cdot + \cdot H \longrightarrow H:H$$
 Symbolized H—H
 $\Delta H^0 = -435 \text{ kJ } (-104 \text{ kcal})/\text{mol}$

In this pairing, a large amount of energy is released, meaning that two hydrogen atoms are unstable relative to \mathbf{H}_2 . The same amount of energy, called the **bond dissociation enthalpy** (BDE, also known as the bond dissociation energy) would have to be absorbed to break the bond. Later in the chapter, you will see that electrons have both wave and particle character (Section 1.6). When bonds are formed by the sharing of two electrons between adjacent atoms, the system becomes more stable because the wave character of the electrons is stabilized relative to two separate atoms.

The distance between nuclei participating in a chemical bond is called the **bond length**. Every covalent bond has a characteristic bond length. In H—H, it is 74 pm (picometer; 1 pm = 10^{-12} m). We use SI units of picometers in this book; many chemists still use Å (Ångstroms); 1 Å = 100 pm.

Because each bond requires two electrons, a maximum of four bonds can form with second-row atoms. For each unshared pair of electrons on an atom (called a **lone pair**), one fewer bond is possible.

In many situations, filled valence shells can be satisfied only when bonded atoms share more than two electrons. In these cases, multiple covalent bonds form between the same two atoms. For example, four electrons shared between two atoms form a double bond. Six shared electrons form a triple bond.

Polar Covalent Bonds

Although all covalent bonds involve the sharing of electrons, they differ widely in the degree of sharing. Homonuclear diatomics such as H_2 , N_2 , O_2 , and F_2 share the electrons equally between the two atoms and are said to have nonpolar covalent bonds. Many compounds such as HCl and H_2O share the electrons in the bond unequally and are said to contain polar covalent bonds. The polarity in the bond increases with increasing difference in electronegativity between the bonded atoms (Table 1.6).

A covalent bond between carbon and hydrogen, for example, is classified as **nonpolar covalent** because the difference in electronegativity between these two atoms is relatively small, that is, 2.5 - 2.1 = 0.4.

An example of a **polar covalent bond** is that of H—C1. The difference in electronegativity between chlorine and hydrogen is 3.0 - 2.1 = 0.9. An important consequence of the unequal sharing of electrons in a polar covalent bond is that the more electronegative atom gains a greater fraction of the shared

Bond length

The distance between nuclei in a covalent bond in picometers (pm; 1 pm = 10^{-12} m) or Å (1 Å = 10^{-10} m).

Nonpolar covalent bond

A covalent bond between atoms whose difference in electronegativity is less than approximately 0.5.

Polar covalent bond

A covalent bond between atoms whose difference in electronegativity is between approximately 0.5 and 1.9.



Careers in Chemistry

Dahlia Haynes, PhD, MPD is an innovation portfolio manager and RDE technical leader at SC Johnson. There, she is responsible for managing innovation-based Portfolio Strategies for the Air Care— Glade and Home Storage— Ziploc categories. Dr. Haynes acts as the key interface between leadership across the company and leads strategic communication to stakeholders to deliver fast-paced and cohesive initiatives to reach customers through multiple communication channels.

Dr. Haynes obtained her BS in chemistry at Claflin University, an HBCU in Orangeburg, SC. She received her PhD in organic polymer chemistry from Clemson University in Clemson, SC. She obtained her MS in product development and product design at Northwestern University while already working at SC Johnson. Dr. Haynes completed a post-doctoral stint in the Chemistry Department at Carnegie Mellon University.

Dr. Haynes went on to work on the research, development, and engineering team at SC Johnson. Moving to this career path was a natural next step for her. Dr. Haynes knew that she liked solving technical challenges and learning new things, but her natural strengths as a leader and a manager led her to a career in management. While her chemistry background allows her to interface between the researchers and other teams at SC Johnson, the more general skills she learned in her stint in academia—especially problemsolving technical challenges also make her successful at her current job.

Table 1.6 Classification of Chemical Bonds

Difference in Electronegativity Between Bonded Atoms	Type of Bond
Less than 0.5	Nonpolar covalent
0.5 to 1.9	Polar covalent
Greater than 1.9	Ions formed

electrons and acquires a partial negative charge, indicated by the symbol $\delta-$. The less electronegative atom has a smaller fraction of the shared electrons and acquires a partial positive charge, indicated by the symbol $\delta+$. Alternatively, show the direction of bond polarity using an arrow with the arrowhead pointing toward the negative end and a plus sign on the tail of the arrow at the positive end.

$$\begin{array}{ccc}
\delta^{+} & \delta^{-} & & \longleftrightarrow \\
H - Cl & H - Cl
\end{array}$$

Example 1.4 Types of Bonds

Classify each bond as nonpolar covalent or polar covalent or state that ions are formed.

Solution

- **STEP 1** Determine the electronegativity of each atom in the bond from Table 1.5.
- **STEP 2** Calculate the difference in electronegativities.
- **STEP 3** Refer to Table 1.6 to classify the bond type between the two atoms.

NOTE Electronegativity can vary depending on the chemical environment and oxidation state of an atom. Therefore, these rules are only guidelines.

Based on differences in electronegativity between the bonded atoms, three of these bonds are polar covalent, and one involves the formation of ions.

Bond	Difference in Electronegativity	Type of Interaction
(a) O—H	3.5 - 2.1 = 1.4	Polar covalent
(b) N—H	3.0 - 2.1 = 0.9	Polar covalent
(c) K—Br	2.8 - 0.8 = 2.0	Ions formed
(d) C—Mg	2.5 - 1.2 = 1.3	Polar covalent

Problem 1.4

Classify each bond as nonpolar covalent or polar covalent or state that ions are formed.

Example 1.5 Bond Polarity

Using the symbols δ – and δ +, indicate the direction of polarity in each polar covalent bond.

(a) C—O

- (b) N—H
- (c) C—Mg

Solution

STEP 1 Assign the electronegativity value given for each atom from Table 1.5.

STEP 2 Assign the atom with the greater electronegativity the partial negative charge $(\delta-)$ and the atom with the lesser electronegativity the partial positive charge $(\delta+)$.

- (a) $C \longrightarrow O$
- **(b)** N H
- (c) C Mg
- 2.5 3.5
- 3.0 2.1
- 2.5 1.2

Problem 1.5

Using the symbols $\delta-$ and $\delta+$, indicate the direction of polarity in each polar covalent bond.

(a) C—N

- (b) N—O
- (c) C—C1

The polarity of a covalent bond is measured by a vector quantity called a **bond dipole moment** and is given the symbol μ (Greek mu). Bond dipole moment is defined as the product of the charge, e (either the $\delta+$ or $\delta-$ because each is the same in absolute magnitude), on one of its atoms times the distance, d, separating the two atoms. Note that the dipole moment (μ) is not simply the difference between the electronegativities of the atoms, as students sometimes mistakenly believe. The SI unit for a dipole moment is the coulomb · meter, but they are commonly reported instead in a derived unit called the debye (D: 1 D = 3.34×10^{-30} C · m). Table 1.7 lists bond dipole moments for the types of covalent bonds you will deal with most frequently in this course.

Bond dipole moment (μ)

A measure of the polarity of a covalent bond. It is the product of the charge on either atom of a polar covalent bond times the distance between the nuclei.

Table 1.7	Average Bond Dipole Moments of Selected Covalent Bonds
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Bond	Bond Dipole (D)	Bond	Bond Dipole (D)	Bond	Bond Dipole (D)
\mapsto		\leftrightarrow		↔	
Н—С	0.3	С—Г	1.4	с—о	0.7
H—N	1.3	C—Cl	1.5	C=O	2.3
Н—О	1.5	C—Br	1.4	C—N	0.2
H—S	0.7	C—I	1.2	C≡N	3.5