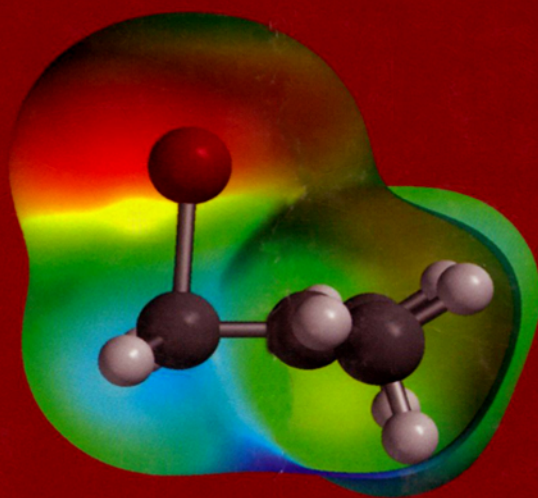


S E C O N D E D I T I O N

Perspectives on
Structure and
Mechanism
in Organic Chemistry



FELIX A. CARROLL

**PERSPECTIVES ON
STRUCTURE AND MECHANISM
IN ORGANIC CHEMISTRY**

PERSPECTIVES ON STRUCTURE AND MECHANISM IN ORGANIC CHEMISTRY

Second Edition

Felix A. Carroll
Davidson College



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Contents

Preface xi

Acknowledgments xiii

Introduction xv

Chapter 1 | Fundamental Concepts of Organic Chemistry 1

- 1.1 Atoms and Molecules 1**
 - Fundamental Concepts 1
 - Molecular Dimensions 5
- 1.2 Heats of Formation and Reaction 8**
 - Experimental Determination of Heats of Formation 8
 - Bond Increment Calculation of Heats of Formation 10
 - Group Increment Calculation of Heats of Formation 12
 - Homolytic and Heterolytic Bond Dissociation Energies 16
- 1.3 Bonding Models 19**
 - Electronegativity and Bond Polarity 21
 - Complementary Theoretical Models of Bonding 24
 - Pictorial Representations of Bonding Concepts 28
 - The sp^3 Hybridization Model for Methane 29
 - Are There sp^3 Hybrid Orbitals in Methane? 31
 - Valence Shell Electron Pair Repulsion Theory 35
 - Variable Hybridization and Molecular Geometry 37
- 1.4 Complementary Descriptions of the Double Bond 42**
 - The σ, π Description of Ethene 42
 - The Bent Bond Description of Ethene 42
 - Predictions of Physical Properties with the Two Models 43
- 1.5 Choosing Models in Organic Chemistry 48**
 - Problems 48

Chapter 2 | Stereochemistry 53

- 2.1 Introduction 53**
- 2.2 Stereoisomerism 56**
 - Isomerism 56
 - Symmetric, Asymmetric, Dissymmetric, and Nondissymmetric Molecules 58
 - Designation of Molecular Configuration 67
 - Fischer Projections 72
 - Additional Stereochemical Nomenclature 76
- 2.3 Manifestations of Stereoisomerism 86**
 - Optical Activity 86

Configuration and Optical Activity	90
Other Physical Properties of Stereoisomers	92
2.4 Stereotopicity	94
Stereochemical Relationships of Substituents	94
Chirotopicity and Stereogenicity	98
Problems	101
Chapter 3 Conformational Analysis and Molecular Mechanics	113
3.1 Molecular Conformation	113
3.2 Conformational Analysis	119
Torsional Strain	119
van der Waals Strain	120
Angle Strain and Baeyer Strain Theory	123
Application of Conformational Analysis to Cycloalkanes	124
Conformational Analysis of Substituted Cyclohexanes	128
3.3 Molecular Mechanics	135
3.4 Molecular Strain and Limits to Molecular Stability	155
Problems	169
Chapter 4 Applications of Molecular Orbital Theory and Valence Bond Theory	175
4.1 Introduction to Molecular Orbital Theory	175
Hückel Molecular Orbital Theory	175
Correlation of Physical Properties with Results of HMO Calculations	187
Other Parameters Generated Through HMO Theory	191
Properties of Odd Alternant Hydrocarbons	194
The Circle Mnemonic	198
4.2 Aromaticity	199
Benzene	201
Aromaticity in Small Ring Systems	211
Larger Annulenes	215
Dewar Resonance Energy and Absolute Hardness	218
4.3 Contemporary Computational Methods	220
Extended Hückel Theory	221
Perturbational Molecular Orbital Theory	226
Atoms in Molecules	232
Density Functional Theory	236
4.4 Valence Bond Theory	237
Resonance Structures and Resonance Energies	237
Choosing a Computational Model	245
Problems	246
Chapter 5 Reactive Intermediates	253
5.1 Reaction Coordinate Diagrams	253
5.2 Radicals	256
Early Evidence for the Existence of Radicals	257
Detection and Characterization of Radicals	258

Structure and Bonding of Radicals	264
Thermochemical Data for Radicals	267
Generation of Radicals	269
Reactions of Radicals	270
5.3 Carbenes 278	
Structure and Geometry of Carbenes	278
Generation of Carbenes	282
Reactions of Carbenes	284
5.4 Carbocations 289	
Carbonium Ions and Carbenium Ions	289
Structure and Geometry of Carbocations	290
The Norbornyl Cation	300
Rearrangements of Carbocations	302
Radical Cations	305
5.5 Carbanions 310	
Structure and Geometry of Carbanions	310
Generation of Carbanions	315
Stability of Carbanions	317
Reactions of Carbanions	318
5.6 Choosing Models of Reactive Intermediates 320	
Problems	321
Chapter 6 <i>Methods of Studying Organic Reactions</i>	327
6.1 Molecular Change and Reaction Mechanisms 327	
6.2 Methods to Determine Reaction Mechanisms 327	
Identification of Reaction Products	327
Determination of Intermediates	328
Crossover Experiments	333
Isotopic Labeling	335
Stereochemical Studies	337
Solvent Effects	337
Computational Studies	339
6.3 Applications of Kinetics in Studying Reaction Mechanisms 341	
6.4 Arrhenius Theory and Transition-State Theory 348	
6.5 Reaction Barriers and Potential Energy Surfaces 360	
6.6 Kinetic Isotope Effects 370	
Primary Kinetic Isotope Effects	371
Secondary Kinetic Isotope Effects	380
Solvent Isotope Effects	384
6.7 Substituent Effects 385	
6.8 Linear Free Energy Relationships 389	
Problems	404
Chapter 7 <i>Acid and Base Catalysis of Organic Reactions</i>	413
7.1 Acidity and Basicity of Organic Compounds 413	
Acid–Base Measurements in Solution	413
Acid–Base Reactions in the Gas Phase	422
Comparison of Gas Phase and Solution Acidities	426
Acidity Functions	430

- 7.2 Acid and Base Catalysis of Chemical Reactions 433**
 Specific Acid Catalysis 434
 General Acid Catalysis 435
 Brønsted Catalysis Law 437
- 7.3 Acid and Base Catalysis of Reactions of Carbonyl Compounds and Carboxylic Acid Derivatives 439**
 Addition to the Carbonyl Group 439
 Enolization of Carbonyl Compounds 442
 Hydrolysis of Acetals 447
 Acid-Catalyzed Hydrolysis of Esters 449
 Alkaline Hydrolysis of Esters 452
 Hydrolysis of Amides 460
Problems 464

Chapter 8 | Substitution Reactions

469

- 8.1 Introduction 469**
- 8.2 Nucleophilic Aliphatic Substitution 472**
 Introduction 472
 The S_N1 Reaction 473
 The S_N2 Reaction 494
 Brønsted Correlations 504
 Hard–Soft Acid–Base Theory and Nucleophilicity 505
 Edwards Equations 506
 Swain–Scott Equation 507
 Mayr Equations 508
 The α Effect 511
 Leaving Group Effects in S_N2 Reactions 512
 Aliphatic Substitution and Single Electron Transfer 513
- 8.3 Electrophilic Aromatic Substitution 518**
 The S_EAr Reaction 518
 Quantitative Measurement of S_EAr Rate Constants: Partial Rate Factors 521
 Lewis Structures as Models of Reactivity in S_EAr Reactions 524
- 8.4 Nucleophilic Aromatic and Vinylic Substitution 527**
 Nucleophilic Aromatic Substitution 527
 Nucleophilic Vinylic Substitution 532
 Nucleophilic Substitution Involving Benzyne Intermediates 535
 Radical-Nucleophilic Substitution 541
Problems 545

Chapter 9 | Addition Reactions

551

- 9.1 Introduction 551**
- 9.2 Addition of Halogens to Alkenes 553**
 Electrophilic Addition of Bromine to Alkenes 553
 Addition of Other Halogens to Alkenes 575
- 9.3 Other Addition Reactions 585**
 Addition of Hydrogen Halides to Alkenes 585
 Hydration of Alkenes 592
 Oxymercuration 595

Hydroboration	600
Epoxidation	605
Electrophilic Addition to Alkynes and Cumulenes	609
Nucleophilic Addition to Alkenes and Alkynes	618
Nucleophilic Addition to Carbonyl Compounds	622
Problems	627

Chapter 10 | Elimination Reactions **633**

10.1 Introduction	633
10.2 Dehydrohalogenation and Related 1,2-Elimination Reactions	638
Potential Energy Surfaces for 1,2-Elimination	638
Competition Between Substitution and Elimination	645
Stereochemistry of 1,2-Elimination Reactions	647
Regiochemistry of 1,2-Elimination Reactions	654
10.3 Other 1,2-Elimination Reactions	665
Dehalogenation of Vicinal Dihalides	665
Dehydration of Alcohols	669
Deamination of Amines	677
Pyrolytic Eliminations	681
Problems	688

Chapter 11 | Pericyclic Reactions **697**

11.1 Introduction	697
11.2 Electrocyclic Transformations	702
Definitions and Selection Rules	702
MO Correlation Diagrams	707
State Correlation Diagrams	711
11.3 Sigmatropic Reactions	715
Definitions and Examples	715
Selection Rules for Sigmatropic Reactions	717
Further Examples of Sigmatropic Reactions	725
11.4 Cycloaddition Reactions	731
Introduction	731
Ethene Dimerization	731
The Diels–Alder Reaction	734
Selection Rules for Cycloaddition Reactions	739
11.5 Other Concerted Reactions	747
Cheletropic Reactions	747
Atom Transfer Reactions	749
Ene Reactions	750
11.6 A General Selection Rule for Pericyclic Reactions	753
11.7 Alternative Conceptual Models for Concerted Reactions	756
Frontier Molecular Orbital Theory	756
Hückel and Möbius Aromaticity of Transition Structures	763
Synchronous and Nonsynchronous Concerted Reactions	770
The Role of Reaction Dynamics in Rearrangements	773
Problems	778

Chapter 12 | Photochemistry**787**

- 12.1 Photophysical Processes 787**
 - Energy and Electronic States 787
 - Designation of Spectroscopic Transitions 790
 - Photophysical Processes 792
 - Selection Rules for Radiative Transitions 795
 - Fluorescence and Phosphorescence 798
 - Energy Transfer and Electron Transfer 801
- 12.2 Fundamentals of Photochemical Kinetics 804**
 - Actinometry and Quantum Yield Determinations 804
 - Rate Constants for Unimolecular Processes 805
 - Transient Detection and Monitoring 807
 - Bimolecular Decay of Excited States: Stern–Volmer Kinetics 809
- 12.3 Physical Properties of Excited States 810**
 - Acidity and Basicity in Excited States 811
 - Bond Angles and Dipole Moments of Excited State Molecules 815
- 12.4 Representative Photochemical Reactions 818**
 - Photochemical Reactions of Alkenes and Dienes 818
 - Photochemical Reactions of Carbonyl Compounds 832
 - Photochemical Reactions of α,β -Unsaturated Carbonyl Compounds 840
 - Photochemical Reactions of Aromatic Compounds 843
 - Photosubstitution Reactions 845
 - σ Bond Photodissociation Reactions 846
 - Singlet Oxygen and Organic Photochemistry 851
- 12.5 Some Applications of Organic Photochemistry 853**
 - Problems 862

References for Selected Problems 871

Permissions 883

Author Index 895

Subject Index 927

Preface

This book is the result of my experience teaching physical organic chemistry at Davidson College. During this time I felt a need for a text that not only presents concepts that are central to the understanding and practice of physical organic chemistry but that also teaches students to think about organic chemistry in new ways, particularly in terms of complementary conceptual models. Because of this approach, the first edition of *Perspectives on Structure and Mechanism in Organic Chemistry* attracted attention beyond the chemistry community and was even quoted in a philosophy dissertation.¹

Soon after the first edition appeared, I received a telephone call from a student of the philosophy of science, who asked how I came to write a book with this emphasis. I did not have a ready answer, but as we talked I realized that this was primarily due to the influences of George Hammond and Jacob Bronowski. I was a graduate student with George Hammond. Although I cannot recall ever discussing conceptual models with him, his views were nonetheless imprinted on me—but in such a subtle way that I did not fully recognize it at the time. Jacob Bronowski's impact was more distinct because it resulted from a single event—the film *Knowledge or Certainty* in a series titled *The Ascent of Man*. That film offers a powerful commentary on both the limits of human knowledge and the nature of science as “a tribute to what we can know although we are fallible.”^{2a} Perhaps a hybridization of their influences led me to emphasize that familiar conceptual models are only beginning points for describing structures and reactions and that using complementary models can provide a deeper understanding of organic chemistry than can using any one model alone.

As with the first edition, the first five chapters of this book consider structure and bonding of stable molecules and reactive intermediates. There is a chapter on methods organic chemists use to study reaction mechanisms, and then acid–base reactions, substitution reactions, addition reactions, elimination reactions, pericyclic reactions, and photochemical reactions are considered in subsequent chapters. In each case I have updated the content to reflect developments since publication of the first edition.

It is essential for an advanced text to provide complete references. The literature citations in this edition range from 1851 to 2009. They direct interested readers to further information about all of the topics and also acknowledge the researchers whose efforts produced the information summarized here. A teaching text must also provide a set of problems of varying

¹ Weisberg, M. *When Less is More: Tradeoffs and Idealization in Model Building*; Ph.D. Dissertation, Stanford University, 2003. See also Weisberg, M. *Philos. Sci.* **2004**, *71*, 1071.

² The quotations are from the book with the same title as the film series: Bronowski, J. *The Ascent of Man*; Little, Brown and Company, Boston, 1973; (a) p. 374; (b) p. 353.

difficulty. The nearly 400 problems in this edition do more than just allow students to test their understanding of the facts and concepts presented in a chapter. They also encourage readers to actively engage the chemical literature and to develop and defend their own ideas. Some problems represent straightforward applications of the information in the text, but other problems can best be answered by consulting the literature for background information before attempting a solution. Still other problems are open-ended, with no one "correct" answer. I have prepared a solutions manual giving answers for problems in the first two categories as well as comments about the open-ended problems.

In *Knowledge or Certainty*, Bronowski shows many portraits of the same human face and observes that "we are aware that these pictures do not so much fix the face as explore it. . . and that each line that is added strengthens the picture but never makes it final."^{2b} So it is with this book. It is not a photograph but is, instead, a portrait of physical organic chemistry. As with the human face, it is not possible to fix a continually changing science—we can only explore it. I hope that the lines added in this edition will better enable readers to develop a deeper and more complete understanding of physical organic chemistry.

FELIX A. CARROLL

Davidson College

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F. A. C

Introduction

Every organic chemist instantly recognizes the drawing in Figure 1 as benzene, or at least one of the Kekulé structures of benzene. Yet, it is not benzene. It is a geometric figure consisting of a regular hexagon enclosing three extra lines, prepared by marking white paper with black ink. When we look at the drawing, however, we *see* benzene. That is, we visualize a colorless liquid, and we recall a pattern of physical properties and chemical reactivity associated with benzene and with the concept of aromaticity. The drawing in Figure 1 is therefore only a macroscopic representation of a presumed submicroscopic entity. Even more, the drawing symbolizes the *concept* of benzene, particularly its structural features and patterns of reactivity.¹

That all organic chemists instantly recognize the drawing in Figure 1 as benzene is confirmation that they have been initiated into the chemical fraternity. The tie that binds the members of this fraternity is more than a collective interest. It is also a common way of viewing problems and their solutions. The educational process that initiates members into this fraternity, like other initiations, can lead to considerable conformity of thinking and of behavior.² Such conformity facilitates communication among members of the group, but it can limit independent behavior and action.

This common way of looking at problems was explored by T. S. Kuhn in *The Structure of Scientific Revolutions*.³ Kuhn described processes fundamental to all of the sciences, and he discussed two related meanings of the term *paradigm*:

On the one hand, it stands for the entire constellation of beliefs, values, techniques, and so on shared by the members of a given community. On the other it denotes one sort of element in that constellation, the concrete puzzle solutions which, employed as models or examples, can replace explicit rules as a basis for the solution of the remaining puzzles of normal science.^{3a,4}

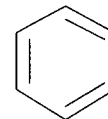


FIGURE 1.
A familiar drawing.

¹ For a discussion of "Representation in Chemistry," including the nature of drawings of benzene rings, see Hoffmann, R.; Laszlo, P. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1. For a discussion of the iconic nature of some chemical drawings, see Whitlock, H. W. *J. Org. Chem.* **1991**, *56*, 7297.

² Moreover, the interaction of these scientists with those who do not share their interests can be inhibited through what might be called a "sociological hydrophobic effect."

³ Kuhn, T. S. *The Structure of Scientific Revolutions*, 2nd ed.; The University of Chicago Press: Chicago, 1970; (a) p. 175; (b) p. 37.

⁴ The paradigm that we may think of chemistry only through paradigms may be an appropriate description of Western science only. For an interesting discussion of "Sushi Science and Hamburger Science," see Motokawa, T. *Perspect. Biol. Med.* **1989**, *32*, 489.

The parallel with a fraternity is more closely drawn by Kuhn's observation

...one of the things a scientific community acquires with a paradigm is a criterion for choosing problems that, while the paradigm is taken for granted, can be assumed to have solutions. To a great extent these are the only problems that the community will admit as scientific or encourage its members to undertake. Other problems... are rejected as metaphysical, as the concern of another discipline, or sometimes as just too problematic to be worth the time. A paradigm can, for that matter, even insulate the community from those socially important problems that are not reducible to the puzzle form, because they cannot be stated in terms of the conceptual and instrumental tools the paradigm supplies.^{3b,5,6}

The history of *phlogiston* illustrates how paradigms can dictate chemical thought. Phlogiston was said to be the "principle" of combustibility—a substance thought to be given off by burning matter.⁷ The phlogiston theory was widely accepted and was taught to students as established fact.⁸ As is the case with the ideas we accept, the phlogiston theory could rationalize observable phenomena (combustion) and could account for new observations (such as the death of animals confined in air-tight containers).⁹ As is also the case with contemporary theories, the phlogiston model could be modified to account for results that did not agree with its predictions. For example, experiments showed that some substances actually gained weight when they burned, rather than losing weight as might have been expected if a real substance had been lost by burning. Rather than abandoning the phlogiston theory, however, some of its advocates rationalized the results by proposing that phlogiston had negative weight.

As this example teaches us, once we have become accustomed to thinking about a problem in a certain way, it becomes quite difficult to think about it differently. Paradigms in science are therefore like the operating system of a computer: they dictate the input and output of information and control the operation of logical processes. Chamberlin stated the same idea with a human metaphor:

The moment one has offered an original explanation for a phenomenon which seems satisfactory, that moment affection for his intellectual child springs into existence. ... From an unduly favored child, it readily becomes master, and leads its author whithersoever it will.¹⁰

Recognizing that contemporary chemistry is based on widely (if perhaps not universally) accepted paradigms does not mean that we should resist using them. This point was made in 1929 in an address by Irving Langmuir, who was at that time president of the American Chemical Society.

⁵ See also the discussion of Sternberg, R. J. *Science* **1985**, 230, 1111.

⁶ The peer review process for grant proposals can be one way a scientific community limits the problems its members are allowed to undertake.

⁷ White, J. H. *The History of the Phlogiston Theory*; Edward Arnold & Co.: London, 1932.

⁸ Conant, J. B. *Science and Common Sense*; Yale University Press: New Haven, 1951; pp. 170–171.

⁹ Note the defense of phlogiston by Priestly cited by Pimentel, G. *Chem. Eng. News* **1989** (May 1), p. 53.

¹⁰ Chamberlin, T. C. *Science* **1965**, 148, 754; reprinted from *Science* (old series) **1890**, 15, 92. For further discussion of this view, see Bunnett, J. F. in Lewis, E. S., Ed. *Investigation of Rates and Mechanisms of Reactions*, 3rd ed., Part I; Wiley-Interscience: Hoboken, NJ, 1975; p. 478–479.

Skepticism in regard to an absolute meaning of words, concepts, models or mathematical theories should not prevent us from using all these abstractions in describing natural phenomena. The progress of physical chemistry was probably set back many years by the failure of the chemists to take full advantage of the atomic theory in describing the phenomena that they observed. The rejection of the atomic theory for this purpose was, I believe, based primarily upon a mistaken attempt to describe nature in some absolute manner. That is, it was thought that such concepts as energy, entropy, temperature, chemical potential, etc., represented something far more nearly absolute in character than the concept of atoms and molecules, so that nature should preferably be described in terms of the former rather than the latter. We must now recognize, however, that all of these concepts are human inventions and have no absolute independent existence in nature. Our choice, therefore, cannot lie between fact and hypothesis, but only between two concepts (or between two models) which enable us to give a better or worse description of natural phenomena.¹¹

Langmuir's conclusion is correct but, I think, incomplete. Saying that we often choose between two models does not mean that we must, from the time of that choice forward, use only the model that we accept. Instead, we must continually make selections, consciously or subconsciously, among many complementary models.¹² Our choice of models is usually shaped by the need to solve the problems at hand. For example, Lewis electron dot structures and resonance theory provide adequate descriptions of the structures and reactions of organic compounds for some purposes, but in other cases we need to use molecular orbital theory or valence bond theory. Frequently, therefore, we find ourselves alternating between these models. Furthermore, consciously using complementary models to think about organic chemistry reminds us that our models are only human constructs and are not windows into reality.

In each of the chapters of this text, we will explore the use of different models to explain and predict the structures and reactions of organic compounds. For example, we will consider alternative explanations for the hybridization of orbitals, the σ, π description of the carbon-carbon double bond, the effect of branching on the stability of alkanes, the electronic nature of substitution reactions, the acid-base properties of organic compounds, and the nature of concerted reactions. The complementary models presented in these discussions will give new perspectives on the structures and reactions of organic compounds.

¹¹ Langmuir, I. J. *Am. Chem. Soc.* **1929**, *51*, 2847.

¹² For other discussions of the role of models in chemistry, see (a) Hammond, G. S.; Osteryoung, J.; Crawford, T. H.; Gray, H. B. *Models in Chemical Science: An Introduction to General Chemistry*; W. A. Benjamin, Inc.: New York, 1971; pp. 2-7; (b) Sunko, D. E. *Pure Appl. Chem.* **1983**, *55*, 375; (c) Bent, H. A. *J. Chem. Educ.* **1984**, *61*, 774; (d) Goodfriend, P. L. *J. Chem. Educ.* **1976**, *53*, 74; (e) Morwick, J. J. *J. Chem. Educ.* **1978**, *55*, 662; (f) Matsen, F. A. *J. Chem. Educ.* **1985**, *62*, 365; (g) Dewar, M. J. S. *J. Phys. Chem.* **1985**, *89*, 2145.

Fundamental Concepts of Organic Chemistry

1.1 ATOMS AND MOLECULES

Fundamental Concepts

Organic chemists think of atoms and molecules as basic units of matter. We work with mental pictures of atoms and molecules, and we rotate, twist, disconnect, and reassemble physical models in our hands.^{1,2} Where do these mental images and physical models come from? It is useful to begin thinking about the fundamental concepts of organic chemistry by asking a simple question: What do we know about atoms and molecules, and how do we know it? As Kuhn pointed out,

Though many scientists talk easily and well about the particular individual hypotheses that underlie a concrete piece of current research, they are little better than laymen at characterizing the established bases of their field, its legitimate problems and methods.³

The majority of what we know in organic chemistry consists of what we have been taught. Underlying that teaching are observations that someone has made and someone has interpreted. The most fundamental observations are those that we can make directly with our senses. We note the physical state of a substance—solid, liquid, or gas. We see its color or lack of color. We observe whether it dissolves in a given solvent or whether it evaporates if exposed to the atmosphere. We might get some sense of its density by seeing it float or sink when added to an immiscible liquid. These are qualitative observations, but they provide an important foundation for further experimentation.

¹ For a detailed discussion of physical models in chemistry, see Walton, A. *Molecular and Crystal Structure Models*; Ellis Horwood: Chichester, England, 1978.

² For an interesting application of physical models to infer molecular properties, see Teets, D. E.; Andrews, D. H. *J. Chem. Phys.* **1935**, *3*, 175.

³ Kuhn, T. S. *The Structure of Scientific Revolutions*, 2nd ed.; The University of Chicago Press: Chicago, 1970; p. 47.

It is only a modest extension of direct observation to the use of some simple experimental apparatus for quantitative measurements. We use a heat source and a thermometer to determine melting and boiling ranges. We use other equipment to measure indices of refraction, densities, surface tensions, viscosities, and heats of reaction. Through classical elemental analysis, we determine what elements are present in a sample and what their mass ratios seem to be. Then we might determine a formula weight through melting point depression. In all of these experiments, *we use some equipment but still make the actual experimental observations by eye*. These limited experimental techniques can provide essential information nonetheless. For example, if we find that 159.8 grams of bromine will always be decolorized by 82.15 grams of cyclohexene, then we can observe the law of definite proportions. Such data are consistent with a model of matter in which submicroscopic particles combine with each other in characteristic patterns, just as the macroscopic samples before our eyes do. It is then only a matter of definition to call the submicroscopic particles atoms or molecules and to further study their properties. It is essential, however, to remember that our laboratory experiments are conducted with *materials*. While we may talk about the addition of bromine to cyclohexene in terms of individual molecules, we really can only infer that such a process occurs on the basis of experimental data collected with macroscopic samples of the reactants.

Modern instrumentation has opened the door to a variety of investigations, most unimaginable to early chemists, that expand the range of observations beyond those of the human senses. These instruments extend our eyes from seeing only a limited portion of the electromagnetic spectrum to practically the entire spectrum, from X-rays to radio waves, and they let us “see” light in other ways (e.g., in polarimetry). They allow us to use entirely new tools, such as electron or neutron beams, magnetic fields, and electrical potentials or current. They extend the range of conditions for studying matter from near atmospheric pressure to high vacuum and to high pressure. They effectively expand and compress the time scale of the observations, so we can study events that require eons or that occur in femtoseconds.^{4,5}

The unifying characteristic of modern instrumentation is that we no longer observe the chemical or physical change directly. Instead, we observe it only indirectly, such as through the change in illuminated pixels on a computer display. With such instruments, it is essential that we recognize the difficulty in freeing the observations from constraints imposed by our expectations. *To a layperson*, a UV–vis spectrum may not seem all that different from an upside-down infrared spectrum, and a capillary gas chromatogram of a complex mixture may appear to resemble a mass spectrum. But the chemist sees these traces not as lines on paper but as vibrating or rotating molecules, as electrons moving from one place to another, as substances separated from a mixture, or as fragments from molecular cleavage. Thus, implicit assumptions about the origins of experimental data both make the observations interpretable and influence the interpretation of the data.⁶

⁴ A femtosecond (fs) is 10^{-15} s. Rosker, M. J.; Dantus, M.; Zewail, A. H. *Science* **1988**, *241*, 1200 reported that the photodissociation of ICN to I and CN occurs in ca. 100 femtoseconds. See also Dantus, M.; Zewail, A. *Chem. Rev.* **2004**, *104*, 1717 and subsequent papers in this issue.

⁵ Baker, S.; Robinson, J. S.; Haworth, C. A.; Teng, H.; Smith, R. A.; Chirlă, C. C.; Lein, M.; Tisch, J. W. G.; Marangos, J. P. *Science* **2006**, *312*, 424; Osborne, I.; Yeston, J. *Science* **2007**, *317*, 765 and subsequent papers.

⁶ “Innocent, unbiased observation is a myth.”—P. Medawar, quoted in *Science* **1985**, *227*, 1188.

With that caveat, what do we know about molecules and how do we know it? We begin with the idea that organic compounds and all other substances are composed of atoms—indivisible particles which are the smallest units of that particular kind of matter that still retain all its properties. It is an idea whose origin can be traced to ancient Greek philosophers.⁷ Moreover, it is convenient to correlate our observation that substances combine only in certain proportions with the notion that these submicroscopic entities called atoms combine with each other only in certain ways.

Much of our fundamental information about molecules has been obtained from spectroscopy.⁸ For example, a 4000 V electron beam has a wavelength of 0.06 Å, so it is diffracted by objects larger than that size.⁹ Interaction of the electron beam with gaseous molecules produces characteristic circular patterns that can be interpreted in terms of molecular dimensions.¹⁰ We can also determine internuclear distance through infrared spectroscopy of diatomic molecules, and we can use X-ray or neutron scattering to calculate distances of atoms in crystals.

“Pictures” of atoms and molecules may be obtained through atomic force microscopy (AFM) and scanning tunneling microscopy (STM).^{11,12} For example, Custance and co-workers reported using atomic force microscopy to identify individual silicon, tin, and lead atoms on the surface of an alloy.¹³ Researchers using these techniques have reported the manipulation of individual molecules and atoms.¹⁴ There have been reports in which STM was used to dissociate an individual molecule and then examine the fragments,¹⁵ to observe the abstraction of a hydrogen atom from H₂S and from H₂O,¹⁶ and to reversibly break a single N–H bond.¹⁷ Such use of STM has been termed *angstromchemistry*.¹⁸ Moreover, it was proposed that scanning tunneling microscopy and atomic force microscopy could be used to image the lateral profiles of individual *sp*³ hybrid orbitals.¹⁹ Some investigators have

⁷ Asimov, I. *A Short History of Chemistry*; Anchor Books: Garden City, NY, 1965; pp. 8–14.

⁸ For a review of structure determination methods, see Gillespie, R. J.; Hargittai, I. *The VSEPR Model of Molecular Geometry*; Allyn and Bacon: Boston, 1991; pp. 25–39.

⁹ Moore, W. J. *Physical Chemistry*, 3rd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1962; p. 575 ff.

¹⁰ For discussions of structure determination with gas phase electron diffraction, see Karle, J. in Maksić, Z. B.; Eckert-Maksić, M., Eds. *Molecules in Natural Science and Medicine*; Ellis Horwood: Chichester, England, 1991; pp. 17–27; Hedberg, K. *ibid.*; pp. 29–42.

¹¹ Hou, J. G.; Wang, K. *Pure Appl. Chem.* **2006**, *78*, 905.

¹² See Ottensmeyer, F. P.; Schmidt, E. E.; Olbrecht, A. J. *Science* **1973**, *179*, 175 and references therein; Robinson, A. L. *Science* **1985**, *230*, 304; *Chem. Eng. News* **1986** (Sept. 1), *4*; Hansma, P. K.; Elings, V. B.; Marti, O.; Bracker, C. E. *Science* **1988**, *242*, 209; Parkinson, B. A. *J. Am. Chem. Soc.* **1990**, *112*, 1030; Frommer, J. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1298.

¹³ Sugimoto, Y.; Pou, P.; Abe, M.; Jelinek, P.; Perez, R.; Morita, S.; Custance, O. *Nature (London)* **2007**, *446*, 64.

¹⁴ Weisenhorn, A. L.; MacDougall, J. E.; Gould, S. A. C.; Cox, S. D.; Wise, W. S.; Massie, J.; Maivald, P.; Elings, V. B.; Stucky, G. D.; Hansma, P. K. *Science* **1990**, *247*, 1330; Whitman, L. J.; Stroschio, J. A.; Dragoset, R. A.; Celotta, R. J. *Science* **1991**, *251*, 1206; Leung, O. M.; Goh, M. C. *Science* **1992**, *255*, 64.

¹⁵ Dujardin, G.; Walkup, R. E.; Avouris, P. *Science* **1992**, *255*, 1232.

¹⁶ Lauhon, L. J.; Ho, W. J. *Phys. Chem. B*, **2001**, *105*, 3987.

¹⁷ Katano, S.; Kim, Y.; Hori, M.; Trenary, M.; Kawai, M. *Science* **2007**, *316*, 1883.

¹⁸ For a review of the application of scanning tunneling microscopy to manipulation of bonds, see Ho, W. *Acc. Chem. Res.* **1998**, *31*, 567.

¹⁹ Chen, J. C. *Nanotechnology* **2006**, *17*, S195.

reported imaging single organic molecules in motion with a very different technique, transmission electron microscopy,²⁰ and others have reported studying electron transfer to single polymer molecules with single-molecule spectroelectrochemistry.²¹

Even though “seeing is believing,” we must keep in mind that in all such experiments we do not really see molecules; we see only computer graphics. Two examples illustrate this point: STM features that had been associated with DNA molecules were later assigned to the surface used to support the DNA,²² and an STM image of benzene molecules was reinterpreted as possibly showing groups of acetylene molecules instead.²³

Organic chemists also reach conclusions about molecular structure on the basis of logic. For example, the fact that one and only one substance has been found to have the molecular formula CH_3Cl is consistent with a structure in which three hydrogen atoms and one chlorine atom are attached to a carbon atom in a tetrahedral arrangement. If methane were a trigonal pyramid, then two different compounds with the formula CH_3Cl might be possible—one with chlorine at the apex of the pyramid and another with chlorine in the base of the pyramid. The existence of only one isomer of CH_3Cl does not require a tetrahedral arrangement, however, since we might also expect only one isomer if the four substituents to the carbon atom were arranged in a square pyramid with a carbon atom at the apex or in a square planar structure with a carbon atom at the center. Since we also find one and only one CH_2Cl_2 molecule, however, we can also rule out the latter two geometries. Therefore we infer that the parent compound, methane, is also tetrahedral. This view is reinforced by the existence of two different structures (enantiomers) with the formula CHClBrF . Similarly, we infer the flat, aromatic structure for benzene by noting that there are three and only three isomers of dibromobenzene.²⁴

Organic chemists do not think of molecules only in terms of atoms, however. We often envision molecules as collections of nuclei and electrons, and we consider the electrons to be constrained to certain regions of space (orbitals) around the nuclei. Thus, we interpret UV–vis absorption, emission, or scattering spectroscopy in terms of movement of electrons from one of these orbitals to another. These concepts resulted from the development of quantum mechanics. The Bohr model of the atom, the Heisenberg uncertainty principle, and the Schrödinger equation laid the foundation for our current ways of thinking about chemistry. There may be some truth in the statement that

The why? and how? as related to chemical bonding were in principle answered in 1927; the details have been worked out since that time.²⁵

We will see, however, that there are still uncharted frontiers of those details to explore in organic chemistry.

²⁰ Koshino, M.; Tanaka, T.; Solin, N.; Suenaga, K.; Isobe, H.; Nakamura, E. *Science*, **2007**, *316*, 853.

²¹ Palacios, R. E.; Fan, F.-R. F.; Bard, A. J.; Barbara, P. F. *J. Am. Chem. Soc.* **2006**, *128*, 9028.

²² Clemmer, C. R.; Beebe, T. P., Jr. *Science* **1991**, *251*, 640.

²³ Moler, J. L.; McCoy, J. R. *Chem. Eng. News* **1988** (Oct 24), 2.

²⁴ These examples were discussed in an analysis of “topological thinking” in organic chemistry by Turro, N. J. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 882.

²⁵ Ballhausen, C. J. *J. Chem. Educ.* **1979**, *56*, 357.

TABLE 1.1 Bond Lengths and Bond Angles for Methyl Halides

Molecule	$r_{\text{C-H}}$ (Å)	$r_{\text{C-X}}$ (Å)	$\angle_{\text{H-C-H}}$	$\angle_{\text{H-C-X}}$
CH ₃ F	1.105	1.385	109°54'	109°2'
CH ₃ Cl	1.096	1.781	110°52'	108°0'
CH ₃ Br	1.10	1.939	111°38'	107°14'
CH ₃ I	1.096	2.139	111°50'	106°58'

Source: Reference 29.

Molecular Dimensions

Data from spectroscopy or from X-ray, electron, or neutron diffraction measurements allow us to determine the distance between atomic centers as well as to measure the angles between sets of atoms in covalently bonded molecules.²⁶ The most detailed information comes from microwave spectroscopy, although that technique is more useful for lower molecular weight than higher molecular weight molecules because the sample must be in the vapor phase.²⁷ Diffraction methods locate a center of electron density instead of a nucleus. The center of electron density is close to the nucleus for atoms that have electrons below the valence shell. For hydrogen, however, the electron density is shifted toward the atom to which it is bonded, and bonds to hydrogen are determined by diffraction methods to be shorter than are bond lengths determined with spectroscopy.²⁸ With solid samples, the possible effect of crystal packing forces must also be considered. Therefore, the various techniques give slightly different measures of molecular dimensions.

Table 1.1 shows data for the interatomic distances and angles of the methyl halides.²⁹ These distances and angles only provide geometric information about the location of nuclei (or local centers of electron density) as points in space. We infer that those points are connected by chemical bonds, so that the distance $r_{\text{C-H}}$ is the length of a C–H bond and the angle $\angle_{\text{H-C-H}}$ is the angle between two C–H bonds.

We may also define atomic dimensions, including the ionic radius (r_i), the covalent radius (r_c), and the van der Waals radius (r_{vdW}) of an atom.³⁰ The ionic radius is the apparent size of the electron cloud around an ion as deduced from the packing of ions into a crystal lattice.³¹ As might be expected, this value varies with the charge on the ion. The ionic radius for a C^{4+} ion is 0.15 Å, while that for a C^{4-} ion is 2.60 Å.³⁰ The van der Waals radius is the effective size of the atomic cloud around a covalently bonded atom as

²⁶ A tabulation of common bond length values was provided by Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. J. *Chem. Soc. Perkin Trans. 2* **1987**, S1.

²⁷ Wilson, E. B. *Chem. Soc. Rev.* **1972**, *1*, 293 and references therein; see also Harmony, M. D. *Acc. Chem. Res.* **1992**, *25*, 321.

²⁸ Clark, T. *A Handbook of Computational Chemistry*; John Wiley & Sons: New York, 1985; chapter 2.

²⁹ (a) Tabulations of bond length and bond angle measurements for specific molecules are available in *Tables of Interatomic Distances and Configuration in Molecules and Ions*; compiled by Bowen, H. J. M.; Donohue, J.; Jenkin, D. G.; Kennard, O.; Wheatley P. J.; Whiffen, D. H.; Special Publication No. 11, Chemical Society (London): Burlington House, W1, London, 1958. (b) See also the 1965 Supplement.

³⁰ Pauling, L. *Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

³¹ For an extensive discussion of ionic radii, see Marcus, Y. *Ion Properties*; Marcel Dekker: New York, 1997.

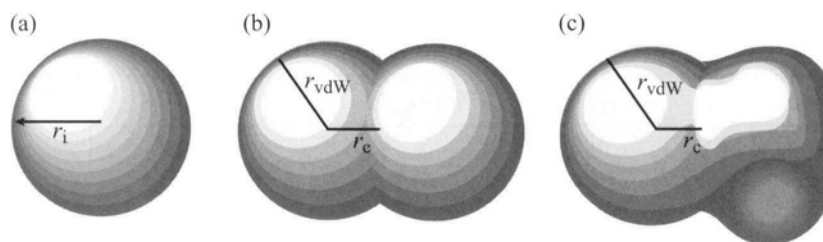


FIGURE 1.1
Radii values for chlorine.

perceived by another atom to which it is not bonded, and it also is determined from interatomic distances found in crystals. Note that the van der Waals radius is not the distance at which the repulsive interactions of the electrons on the two atoms outweigh the attractive forces between them, as is often assumed.^{32,33} Rather, it is a crystal packing measurement that gives a smaller value.^{32,33} The covalent radius of an atom indicates the size of an atom when it is part of a covalent bond, and this distance is much less than the van der Waals radius.³⁴ Figure 1.1 illustrates these radii for chlorine. The computer-drawn plots of electron density surfaces represent the following: (a) r_i for chloride ion; (b) r_c and r_{vdW} for chlorine in Cl_2 ; (c) r_c and r_{vdW} for chlorine in CH_3Cl .³⁵

Table 1.2 lists ionic and covalent radii values for several atoms. Note that the covalent radius for an atom depends on its bonding. A carbon atom with four single bonds has a covalent radius of 0.76 Å. The value is 0.73 Å for a carbon atom with one double bond, while the covalent radius for a triple-bonded carbon atom is 0.69 Å. The covalent radius of hydrogen varies considerably. The value of r_c for hydrogen is calculated to be 0.30 Å in H_2O and 0.32 Å in CH_4 .³⁰ We can also assign an r_{vdW} to a group of atoms. The value for a CH_3 or CH_2 group is 2.0 Å, while the van der Waals thickness of half the electron cloud in an aromatic ring is 1.85 Å.³⁰ Knowledge of van der Waals radii is important in calculations of molecular structure and reactivity, particularly with regard to proteins.³⁶

We may use the atomic radii to calculate the volume and the surface area of an atom. Then using the **principle of additivity** (meaning that the properties of a molecule can be predicted by summing the contributions of its component parts), we may calculate values for the volumes and surface areas of molecules. Such calculations were described by Bondi, and a selected set of atomic volume and surface areas is given in Table 1.3. For example, we estimate the molecular volume of propane by counting $2 \times 13.67 \text{ cm}^3/\text{mol}$ for the two methyl groups plus $10.23 \text{ cm}^3/\text{mol}$ for the methylene group, giving a total volume of $37.57 \text{ cm}^3/\text{mol}$. Similarly, we calculate that the volume of the atoms in hexane is $2 \times 13.67 \text{ cm}^3/\text{mol}$ for the two methyl groups plus $4 \times 10.23 \text{ cm}^3/\text{mol}$ for the four methylene groups, making a total volume of $68.26 \text{ cm}^3/\text{mol}$. The volume of one mole of liquid hexane at 20° is 130.5 mL,

³² Bondi, A. J. *Phys. Chem.* **1964**, *68*, 441.

³³ The difference is that distances between atoms in a crystal are determined by all of the forces acting on the molecules containing those atoms, not just the forces between those two atoms alone.

³⁴ Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832.

³⁵ The images were produced with a CAChe™ WorkSystem (CAChe Scientific).

³⁶ For example, see Proserpio, D. M.; Hoffmann, R.; Levine, R. D. *J. Am. Chem. Soc.* **1991**, *113*, 3217.

TABLE 1.2 Comparison of van der Waals, Ionic, and Covalent Radii for Selected Atoms (Å)

Atom	van der Waals Radius (r_{vdW}^a)	Ionic Radius		Covalent Radii (r_c)		
		Ion	r_i	Single Bonded ^b	Double Bonded	Triple Bonded
H	1.11 Å	H ⁻	2.08 Å	0.31 Å		
C	1.68	C ⁴⁻	2.60	0.76	0.73 ^b	0.69 ^b
N	1.53	N ³⁻	1.71	0.71		
O	1.50	O ²⁻	1.40	0.66		
F	1.51	F ⁻	1.36	0.57		
Cl	1.84	Cl ⁻	1.81	1.02	0.89	
Br	1.96	Br ⁻	1.95	1.20	1.04	
I	2.13	I ⁻	2.16	1.39	1.23	
P	1.85	P ³⁻	2.12	1.07	1.00	0.93
S	1.82	S ²⁻	1.64	1.05	0.94	0.87
Si	2.04	Si ⁴⁻	2.71	1.11	1.07	1.00

Source: Reference 30.

^aReference 37.

^bReference 34.

TABLE 1.3 Group Contributions to van der Waals Atomic Volume (V_W) and Surface Area (A_W)

Group	V_W (cm ³ / mole)	A_W (cm ² / mole $\times 10^9$)
Alkane, C bonded to four other carbon atoms	3.33	0
Alkane, CH bonded to three other carbon atoms	6.78	0.57
Alkane, CH ₂ bonded to two other carbon atoms	10.23	1.35
Alkane, CH ₃ bonded to one other carbon atom	13.67	2.12
CH ₄	17.12	2.90
F, bonded to a 1° carbon atom	5.72	1.10
F, bonded to a 2° or 3° carbon atom	6.20	1.18
Cl, bonded to a 1° carbon atom	11.62	1.80
Cl, bonded to a 2° or 3° carbon atom	12.24	1.82
Br, bonded to a 1° carbon atom	14.40	2.08
Br, bonded to a 2° or 3° carbon atom	14.60	2.09
I, bonded to a 1° carbon atom	19.18	2.48
I, bonded to a 2° or 3° carbon atom	20.35	2.54

Source: Reference 32.

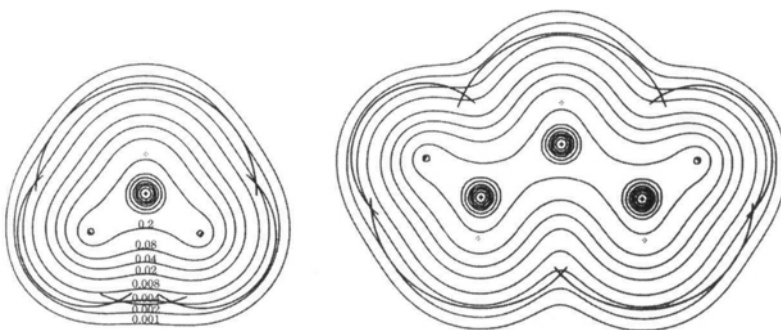
which means that nearly half of the volume occupied by liquid hexane corresponds to space that is outside the boundaries of the carbon and hydrogen atoms as defined above.

Increasingly, values for atomic and molecular volume are available from theoretical calculations. The calculated values vary somewhat, depending on

³⁷ Many sets of van der Waals radii are available in the literature. The data shown are values reported by Chauvin, R. *J. Phys. Chem.* **1992**, 96, 9194. These values correlate well with—but are sometimes slightly different from—values given by Pauling (reference 30), Bondi (reference 32), and O'Keefe, M.; Brese, N. E. *J. Am. Chem. Soc.* **1991**, 113, 3226. A set of van der Waals radii of atoms found in proteins was reported by Li, A.-J.; Nussinov, R. *Proteins* **1998**, 32, 111.

FIGURE 1.2

Contour maps and van der Waals radii arcs for methane (left) and propane (right). (Reproduced from reference 38.)

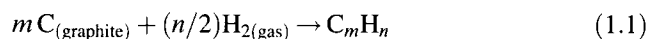


the definition of the surface of the atom or molecule. Usually the boundary of an atom is defined as a certain minimum value of electron density in units of au ($1.00 \text{ au} = 6.748 \text{ e}/\text{\AA}^3$). Bader and co-workers determined that the 0.001 au volumes of methane and ethane are 25.53 and 39.54 cm^3/mol , respectively, while the corresponding 0.002 au volumes are 19.58 and 31.10 cm^3/mol .³⁸ Thus, it appears that the 0.002 au values are closer to, but still somewhat larger than, those calculated empirically using the values in Table 1.3. The relationships between atomic volumes and van der Waals radii are illustrated for cross sections through methane and propane in Figure 1.2. The contour lines represent the electron density contours, and the intersecting arcs represent the van der Waals radii of the atoms.

1.2 HEATS OF FORMATION AND REACTION

Experimental Determination of Heats of Formation

Thermochemical measurements provide valuable insights into organic structures and reactions. The **heat of formation** (ΔH_f°) of a compound is defined as the difference in enthalpy between the compound and the starting elements in their standard states.³⁹ For a hydrocarbon with molecular formula (C_mH_n), we define ΔH_f° as the heat of reaction (ΔH_r°) for the reaction

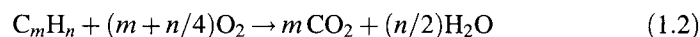


We usually determine the heat of formation of an organic compound indirectly by determining the heat of reaction of the compound to form other substances for which the heats of formation are known, and the heat of combustion ($\Delta H_{\text{combustion}}^\circ$) of a substance is often used for this purpose. Consider the combustion of a compound with the formula C_mH_n . The

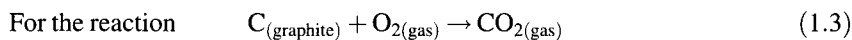
³⁸ Bader, R. F. W.; Carroll, M. T.; Cheeseman, J. R.; Chang, C. J. *Am. Chem. Soc.* **1987**, *109*, 7968. See the discussion of the theory of atoms in molecules in Chapter 4.

³⁹ Mortimer, C. T. *Reaction Heats and Bond Strengths*; Pergamon Press: New York, 1962; Clark, T.; McKervey, M. A. in Stoddart, J. F., Ed. *Comprehensive Organic Chemistry*, Vol. 1; Pergamon Press: Oxford, England, 1979; p. 66 ff. For a discussion of the experimental techniques involved in calorimetry experiments, see (a) Wiberg, K. in Liebman, J. F.; Greenberg, A., Eds. *Molecular Structure and Energetics*, Vol. 2; VCH Publishers: New York, 1987; p. 151; (b) Sturtevant, J. M. in Weissberger, A.; Rossiter, B. W., Eds. *Physical Methods of Chemistry*, Vol. I, Part V; Wiley-Interscience: New York, 1971; p. 347.

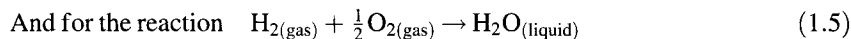
balanced chemical equation is



We know the heats of formation of CO₂ and H₂O:



$$\Delta H_r^\circ = \Delta H_f^\circ(CO_2) \quad (1.4)$$



$$\Delta H_r^\circ = \Delta H_f^\circ(H_2O) \quad (1.6)$$

Combining the above equations, we obtain

$$\Delta H_f^\circ(C_mH_n) = m \Delta H_f^\circ(CO_2) + (n/2)\Delta H_f^\circ(H_2O) - \Delta H_{\text{combustion}}^\circ(C_mH_n) \quad (1.7)$$

As an example, the heat of combustion of 1,3-cyclohexanedione was found to be -735.9 kcal/mol.^{40,41} Taking -94.05 kcal/mol and -68.32 kcal/mol as the standard heats of formation of CO₂ and H₂O, respectively, gives a standard heat of formation for crystalline 1,3-cyclohexanedione of $6(-94.05) + 4(-68.32) - (-735.9) = -101.68$ kcal/mol. It is sometimes necessary to correct heats of reaction for the heats associated with phase changes in the reactants or products. To convert from a condensed phase to the gas phase (e.g., for comparison with values calculated theoretically) the relevant terms are the heat of vaporization (ΔH_v°) of a liquid or heat of sublimation (ΔH_s°) of a solid.⁴²⁻⁴⁴ Correcting for the standard heat of sublimation of 1,3-cyclohexanedione, $+21.46$ kcal/mol, gives its standard heat of formation in the gas phase of -80.22 kcal/mol.

If we are interested only in the difference between the heats of formation of two compounds, we may be able to measure their relative enthalpies more accurately by measuring the heat of a less exothermic reaction. That is, we measure very accurately the ΔH of a reaction in which the two different reactants combine with identical reagents to give the same product(s). Figure 1.3 illustrates how the difference in enthalpy of reactants A and B can be calculated in this manner. If the reaction of A and C to give D has a ΔH_r of $-X$ kcal/mol, and if the reaction of B and C to give D has a ΔH_r of $-Y$ kcal/mol, then the difference in energy between A and B must be $(X - Y)$ kcal/mol. For example, Wiberg and Hao determined that ΔH_r values for the reaction of trifluoroacetic acid with 2-methyl-1-butene and with 2-methyl-2-butene were

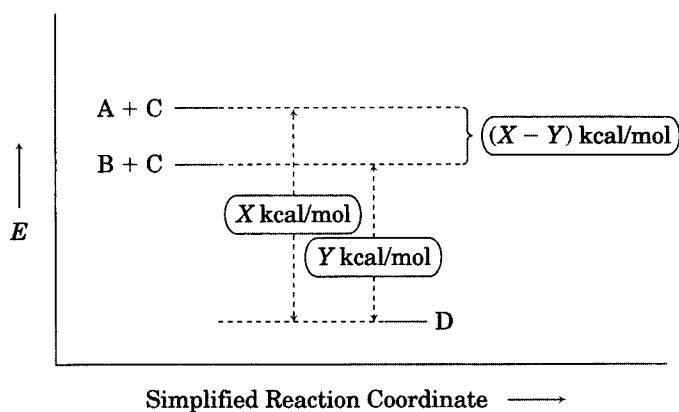
⁴⁰ Pilcher, G.; Parchment, O. G.; Hillier, I. H.; Heatley, F.; Fletcher, D.; Ribeiro da Silva, M. A. V.; Ferrão, M. L. C. C. H.; Monte, M. J. S.; Jiye, F. J. *Phys. Chem.* **1993**, *97*, 243.

⁴¹ The reported value (converted from kJ/mol) was -735.9 ± 0.2 kcal/mol. Experimental uncertainties will not be carried through this discussion because the emphasis is on the calculation procedure and not the precision of the experimental method.

⁴² Determination of heats of sublimation was discussed by Chickos, J. S. in Liebman, J. F.; Greenberg, A., Eds. *Molecular Structure and Energetics*, Vol. 2; VCH Publishers: New York, 1987; p. 67.

⁴³ The enthalpy associated with transformation of a solid to a liquid is the **heat of fusion**. For a discussion, see Chickos, J. S.; Braton, C. M.; Hesse, D. G.; Liebman, J. F. *J. Org. Chem.* **1991**, *56*, 927.

⁴⁴ Data for heat capacity can be used to correct ΔH values measured at one temperature to another temperature. See Orchin, M.; Kaplan, F.; Macomber, R. S.; Wilson, R. M.; Zimmer, H. *The Vocabulary of Organic Chemistry*; Wiley-Interscience: New York, 1980; pp. 255-256.

**FIGURE 1.3**

Calculation of the enthalpy difference of isomers.

−10.93 kcal/mol and −9.11 kcal/mol, respectively.⁴⁵ Therefore, the 2-alkene was judged to be 1.82 kcal/mol lower in energy than the 1-alkene. Heats of hydrogenation are also used to determine the difference in heats of formation of alkenes even though heats of combustion may be measured much more *precisely* than heats of hydrogenation. Because heats of hydrogenation are smaller in magnitude than are heats of combustion, small enthalpy differences between isomers may be determined more *accurately* by hydrogenation.⁴⁶

Bond Increment Calculation of Heats of Formation

Table 1.4 shows experimental ΔH_f° values for some linear alkanes.⁴⁷ There is a general trend in the data: each homolog higher than ethane has a ΔH_f° value about 5 kcal/mol more negative than the previous alkane. This observation suggests that it should be possible to use the principle of additivity (page 6) to predict the heat of formation of an organic compound by summing the contribution each component makes to ΔH_f° .⁴⁸ Extensive work in this area was done by Benson, who published tables of **bond increment contributions** to heats of formation and other thermodynamic properties.^{48–53} A portion of one such table is reproduced as Table 1.5.

The heats of formation of some linear alkanes calculated by the bond increment method are shown in Table 1.4. As an example of such calculations, let us determine the ΔH_f° values for methane and ethane. For methane, there

⁴⁵ Wiberg, K. B.; Hao, S. *J. Org. Chem.* **1991**, *56*, 5108.

⁴⁶ Davis, H. E.; Allinger, N. L.; Rogers, D. W. *J. Org. Chem.* **1985**, *50*, 3601.

⁴⁷ Experimental data for ΔH_f° at 298 K are from tabulations in Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Thermodynamics of Organic Compounds*; John Wiley & Sons: New York, 1969; pp. 243–245.

⁴⁸ Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976; p. 24.

⁴⁹ Benson, S. W.; Buss, J. H. *J. Chem. Phys.* **1959**, *29*, 546.

⁵⁰ Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279.

⁵¹ For a discussion of the development of bond increment and group increment calculations, see Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377.

⁵² Calculation of group increments to heats of formation of linear hydrocarbons was reported by Pitzer, K. S. *J. Chem. Phys.* **1940**, *8*, 711 and to nonlinear hydrocarbons by Franklin, J. L. *Ind. Eng. Chem.* **1949**, *41*, 1070.

⁵³ Cohen, N.; Benson, S. W. *Chem. Rev.* **1993**, *93*, 2419.